PHOTOCHEMICAL STUDIES EMPLOYING MICELLAR SYSTEMS

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CONTENTS

Page

Page

LIST OF TABLES

Page

DIAGRAMS

Page

Page

Page

LIST OF SCHEMES

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PUBLICATIONS

Some of the work contained in this thesis has been published as outlined below:-

1. The application of ultrasound to the N-alkylation of amines using phase transfer catalysts.

   R.S. Davidson, A.M. Patel, A. Safdar and D. Thornthwaite, Tetrahedron Letters, 24, 5907 (1983).

2. N-Alkylation of aromatic amines and related compounds using polyethylene glycol methyl ether as phase transfer catalyst.

   R.S. Davidson, A.M. Patel and A. Safdar, J. Chem. Research (S), 88 (1984).

ABSTRACT

The chemistry of micelles and other organised systems is an area of major activity. The study of the physicochemical properties of these systems e.g. their kinetics and thermodynamics has been aided by luminescent probes. The literature survey given in this thesis discusses the current trends in the application of photoluminescent techniques in micellar systems.

Since fluorescence is very rapid (typically 10^{-9} - 10^{-6} seconds c.f. phosphorescence 10 - 10^{-6} seconds), it is ideally suited to the detection of fast changes in the physico-chemical environment. Different methods for the determination of critical micellar concentration (CMC) are described.

The synthesis of some 3-alkyl indoles was carried out according to the method of W.C. Anthony. This was found to give a higher yield than the method of Jackson and Smith. Various methods for the N-alkylation of these indoles including the use of phase transfer catalysts and the application of ultrasound to the N-alkylation of heterocyclic compounds were also investigated.

The CMC of the synthesised 1,3-dialkyl indolic surfactants were determined by plotting a graph of their fluorescence wavelength maxima against concentration. The effect of the chain length of the alkyl chain, at both the 1 and 3 positions of the indole, on the CMC was also investigated. Because by varying the hydrocarbon chain length it should be possible to alter the depth at which such fluorescent groups 'sit' in a micelle and therefore make a depth profile of the micelle. The possibility of determining the CMCs of the host surfactants (e.g. CTAB, SDS) using these indole chromophores was also investigated.

Investigations were also carried out to determine whether anionic and nonionic indolic surfactants can be used as fluorescent probes.

A variety of indolic acids and indolic alcohols have been synthesised. It was found that the indolic acid salts and indolic alcohols, which were employed as fluorescent probes for the determination of CMC of host surfactants, did not behave in the same way as the corresponding trimethyl ammonium bromide derivatives.

Different methods were investigated for the synthesis of 1,2-dialkyl benzimidazolyl bromides and their trimethyl ammonium bromide salts. The purification of the products proved to be very difficult since these surfactants are hygroscopic.

CHAPTER ONE

INTRODUCTION

INTRODUCTION

1.1 General Discussion on Photophysics:

Photochemistry is concerned with reactions which are initiated by electronically excited molecules and photophysics with processes which lead to deactivation to give back the initially excited molecule in its ground state. The excited molecules are produced by the absorption of suitable radiation in the visible or the ultraviolet region.[1-5]

1.1.1 State Energy Diagram:

After absorption of a photon, an atom or a molecule, if not consumed by photochemical reaction, can return to the ground state by a number of photophysical pathways. The photophysical processes may be defined as transitions which interconvert excited states with each other or with the ground state. The important photophysical processes in turn are classified as radiative and radiationless processes. The commonly encountered radiative/radiationless processes are shown in a modified Jablonski diagram (Figure 1).

The radiative processes are:

(1) "Allowed" or singlet-singlet absorption ($S_o + h\nu \longrightarrow S_1$) characterised experimentally by an extinction coefficient $\varepsilon(S_o \longrightarrow S_1)$.

(2) "Forbidden" or singlet-triplet absorption ($S_o + h\nu \longrightarrow T_1$), characterised experimentally by an extinction coefficient $\varepsilon(S_o \longrightarrow T_1)$.

(3) "Allowed" or singlet-singlet emission, called fluorescence ($S_1 \longrightarrow S_o + h\nu$), characterised by a radiative rate constant K_f.

(4) "Forbidden" or triplet-singlet emission called phosphorescence ($T_1 \longrightarrow So + h\nu$), characterised by radiative rate constant K_p.

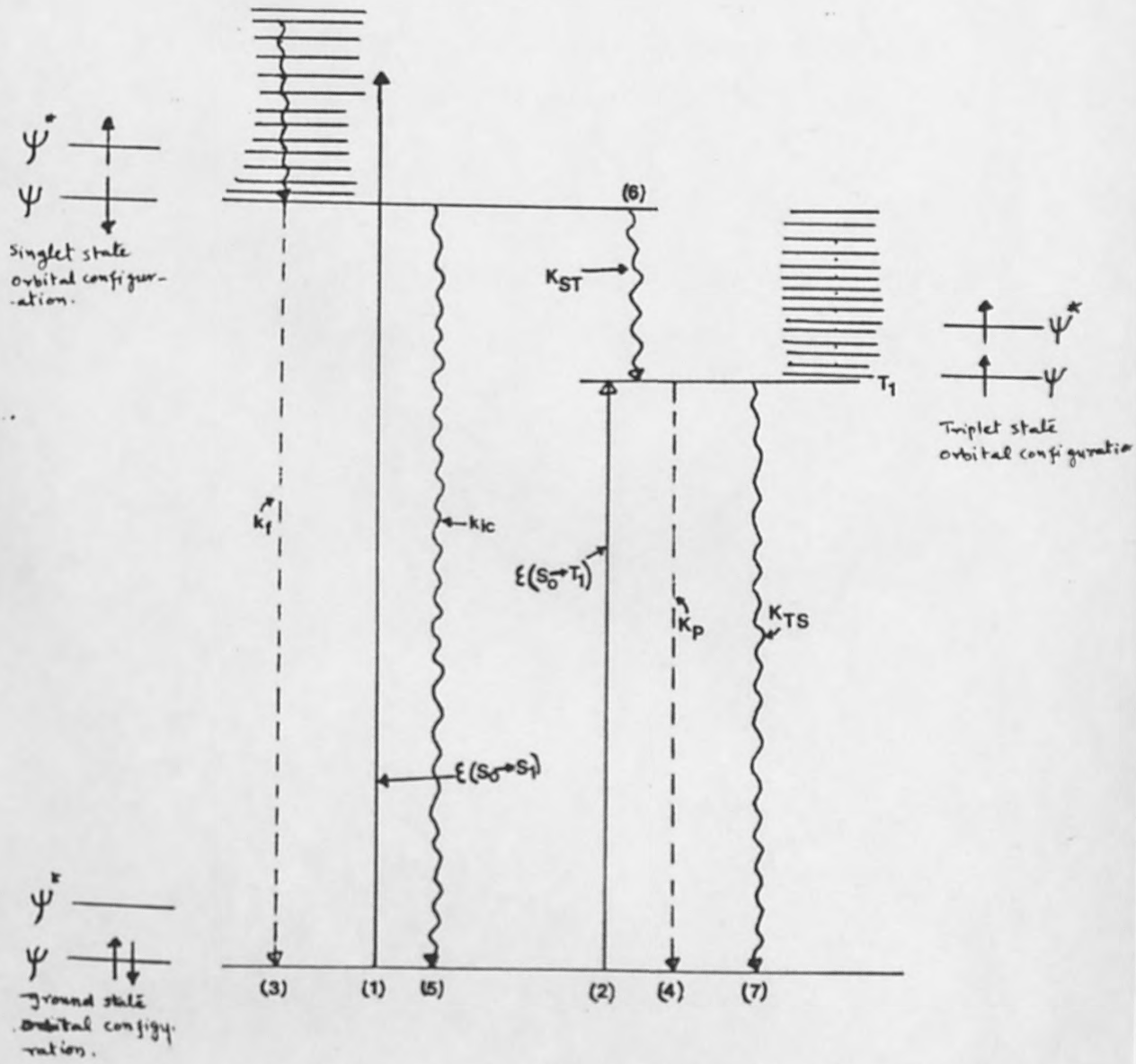


Figure 1: Jablonski Diagram.

The commonly encountered photophysical radiationless processes are:

(5) "Allowed" transitions between states of the same spin called internal conversion (e.g. $S_1 \longrightarrow S_o$ + heat) characterised by a rate constant K_{ic}.

(6) "Forbidden" transitions between excited states of different spin, called intersystem crossing (e.g. $S_1 \longrightarrow T_1$ + heat), characterised by a rate constant K_{ST} or K_{isc}.

(7) "Forbidden" transitions between triplet states and the ground state - also called intersystem crossing (e.g. $T_1 \longrightarrow S_o$ + heat) and characterised by a rate constant K_{TS}.

In radiationless or non radiative transitions, electronic-energy is dissipated as small vibrational quanta in which the environment acts as the heat sink.

1.1.2 Franck-Condon Principle:

Franck-Condon principle which states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.

If a diatomic molecule undergoes a transition into an upper electronic state in which the excited molecule is stable with respect to dissociation into its atoms, then we can represent the upper state by a Morse curve similar in outline to that of the ground electronic state.[4] Figure (2) shows the upper electronic state having the same initial internuclear distance as the lower.

According to the Franck-Condon principle, the internuclear distance in the molecule does not change while electronic transition takes place, and so if we consider the molecule to be initially in the ground state both electronically (ε'') and vibrationally ($\nu'' = 0$), then the most probable transition is that indicated by the vertical line in Fig. (2). Thus the strongest spectral line of the $\nu'' = 0$ progression will be the $(0,4)$.

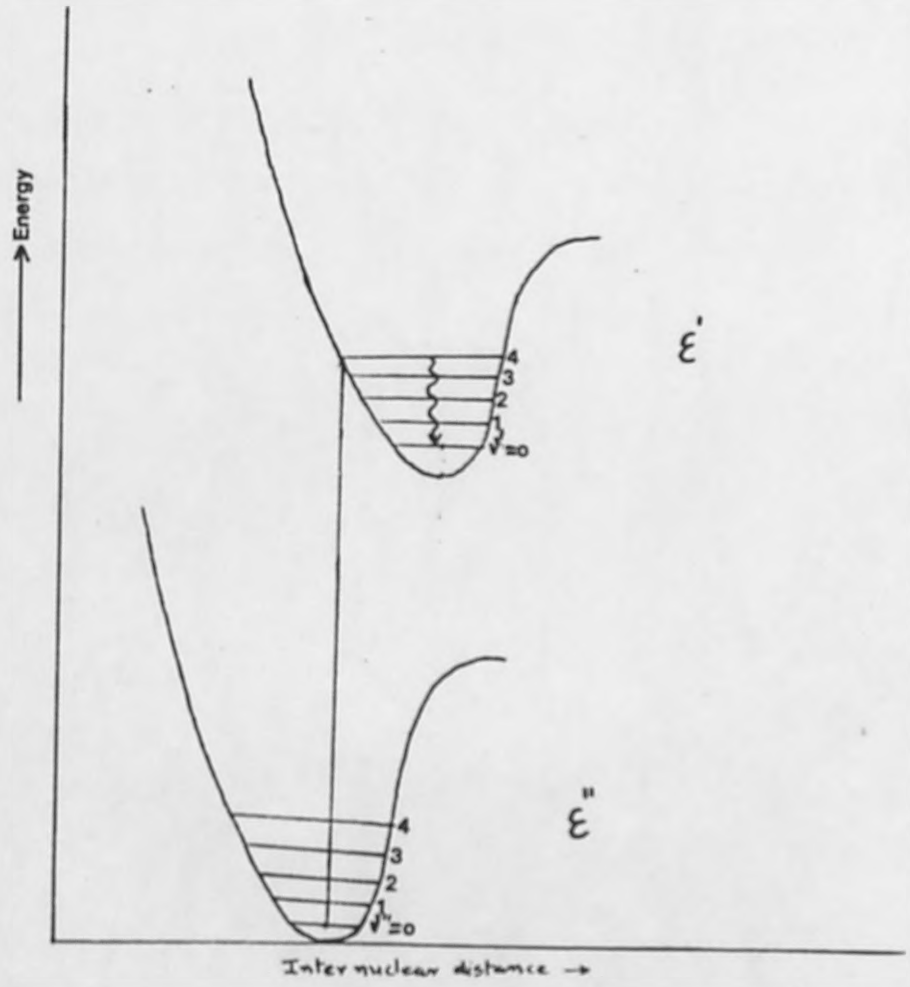


Figure 2: Morse curve diagram representing Franck Condon principle for internuclear distances equal in upper and lower states.

1.1.3 Quantum Yield:

The quantum yield (ϕ) is a useful parameter in quantitative photochemistry. This is a measure of the efficiency of photon usage, and quantum yield is defined as follows:

$$\phi_{product} = \frac{\text{number of moles (molecules) of product formed}}{\text{number of photons of radiation absorbed}}$$

$$= \frac{\text{rate of formation of product}}{\text{intensity of absorbed radiation.}}$$

This definition can be modified to give expressions for the quantum yield of light emission or for the quantum yield of disappearance of starting material.

1.1.4 Quantum Yield of Fluorescence (ϕ_F):

Quantum yield of the fluorescence can be defined as the ratio of photons emitted by the singlet state to the ratio of photons absorbed by the ground state.

$$\phi_F = \frac{\text{rate of emission by singlet state}}{\text{rate of absorption of photons by ground state}} .$$

If we consider the general kinetic scheme set forth in Fig. (3), where I is the rate of absorption of photons and K_f and K_p are the rate constants for fluorescence and phosphorescence respectively.

The steady state approximation is applicable to excited states, and it follows that the rates of formation and destruction of S_1 are equal.

$$\therefore \quad I = [S_1]\ \Sigma^1K \quad (\text{where } \Sigma^1K = K_{ic} + K_f + {}^1K_{isc}) \qquad \text{(i)}$$

The quantum yield of fluorescence is given by

$$\phi_F = \frac{\text{rate of emission by } S_1}{\text{rate of absorption of photons by } S_o} = \frac{K_f[S_1]}{I} = \frac{K_f}{\Sigma {}^1K}.$$

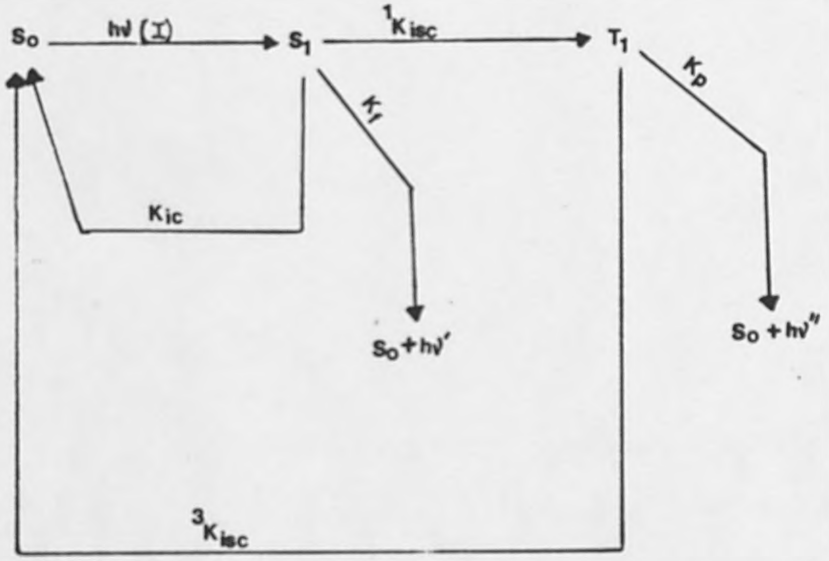


Figure 3: General kinetic scheme for fluorescence and phosphorescence.

1.1.5 Lifetime of Fluorescence (τ_f):

Lifetime of the fluorescence (τ_f) is defined as the time taken for the population of electronically excited singlet state to diminish to $1/e$ of its initial concentration value.

A situation such as that depicted in Fig. (4), where an excited species A* is subject to several first order or pseudo first order deactivating processes.

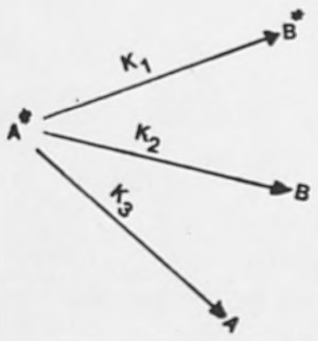


Figure 4:

It follows that $\frac{d[A^*]}{dt} = -[A^*]\ (K_1 + K_2 + K_3) = -\ \Sigma K[A^*]$

hence $[A^*] = [A^*_o]\ e^{-\Sigma K t}$.

The concentration of A* falls exponentially with a rate constant given by ΣK, and if the lifetime (τ) of A* is defined as the time taken for $[A^*]$ to fall to $^1/e$ of its initial value, then

$$\tau = \frac{1}{\Sigma K} \ .$$

Thus the fluorescence life (τ_f) for the system depicted in Fig. (3) will be defined as,

$$\tau_f = \frac{1}{\Sigma^1 K}$$

Hence, $K_f = \frac{\phi_f}{\tau_f}$ $\quad \left[\because \phi_f = \frac{K_f}{\Sigma^1 K}\right]$ as described earlier.

$$\therefore \quad \phi_f = K_f \cdot \tau_f$$

1.1.6 Quantum Yield of Phosphorescence:

Phosphorescence quantum yield can be defined as the ratio of photons emitted by the triplet excited state to the ratio of photons absorbed by the ground state. Therefore,

$$\phi_p = \frac{\text{rate of emission by excited triplet state}}{\text{rate of absorption of photons by ground state}}$$

for the system shown in Fig. (3).

If we apply steady state approximation to the triplet state (T_1) - it gives,

$$^1K_{isc}\,[S_1] = \Sigma^3K[T_1] \qquad \text{(ii)}$$

(where $\Sigma^3K = K_p + {}^3K_{isc}$)

The quantum yield of phosphorescence is:

$$\phi_p = \frac{K_p[T_1]}{I} = \frac{K_p}{I} \cdot \frac{^1K_{isc}[S_1]}{\Sigma^3K} \qquad \text{(from eq. (ii))}$$

$$= \frac{K_p}{\Sigma^3K} \cdot \frac{^1K_{isc}}{\Sigma^1K} \qquad \text{(from eq. (i) } I = [S_1]\,\Sigma^1K)$$

Hence, $\phi_p = \Theta_p \cdot \Theta_{isc}$.

where Θ_p and Θ_{isc} are the quantum efficiencies of phosphorescence and intersystem crossing respectively. Quantum efficiency is the ratio of the rate of a process involving an excited state to the rate of production of that state. Quantum efficiency is to be distinguished from quantum yield.

1.1.7 Lifetime of Phosphorescence:

The phosphorescence lifetime (τ_p) is defined as the time taken for the population of an electronically excited triplet state to diminish

to $^{1}/_{e}$ of its initial value.

Hence, the phosphorescence lifetime (τ_p) for the system shown in Fig. (3) will be defined as,

$$\tau_p = \frac{1}{\Sigma^3 K} \qquad (\text{where } \Sigma^3 K = K_p + {}^3K_{isc})$$

1.1.8 Flash Photolysis:

The technique of flash photolysis has been applied to the study of excited state and transient intermediates whose lifetimes are exceedingly short (10^{-11} or 10^{-12} sec).[6] The idea of flash spectroscopy is to "very quickly" introduce an intense pulse of light into an absorbing system and then "very quickly" analyse the time evolution of the system by absorption or emission spectroscopy. The high intensity pulse of radiation produces a large number of photons, which in turn can produce a large number of electronically excited molecules or intermediates. If these intermediates are produced in sufficiently large concentrations they may be monitored spectroscopically and the decay of concentration with time (decay kinetics) may be measured. The intense pulses (10^{16}-10^{18} photons) may be delivered in time periods as short as 10^{-12} sec. (a picosecond !).

A basic flash system in diagrammatic form is shown in Figure (5). The conventional flash sources can be derived from gas discharge lamps (flash durations down to 1 μs), spark discharge sources (flashes down to a few μs), or exploding wire sources (flashes down to a few hundred μs). Detection techniques vary according to the

nature of the system and the information required, but in all cases the time resolution of the method is limited by the duration of the initial flash. The emission spectrum of an intermediate can be photographed using a spectrograph, or the visible absorption spectrum can be similarly recorded if an analytical beam passing through the reaction cell is triggered to flash at a predetermined time interval after the initial flash. Alternatively, the process can be followed kinetically by monitoring the emission or absorption at a particular wavelength and coupling to an oscilloscope with a time based sweep. These methods give some indication from the spectrum obtained as to the nature of the species generated and they allow direct estimation of the lifetime of an intermediate. However, the difficulty of the interpretation of spectra can arise if more than one emitting or absorbing species are present. Flash techniques have developed rapidly over the past few years with the introduction of laser sources.

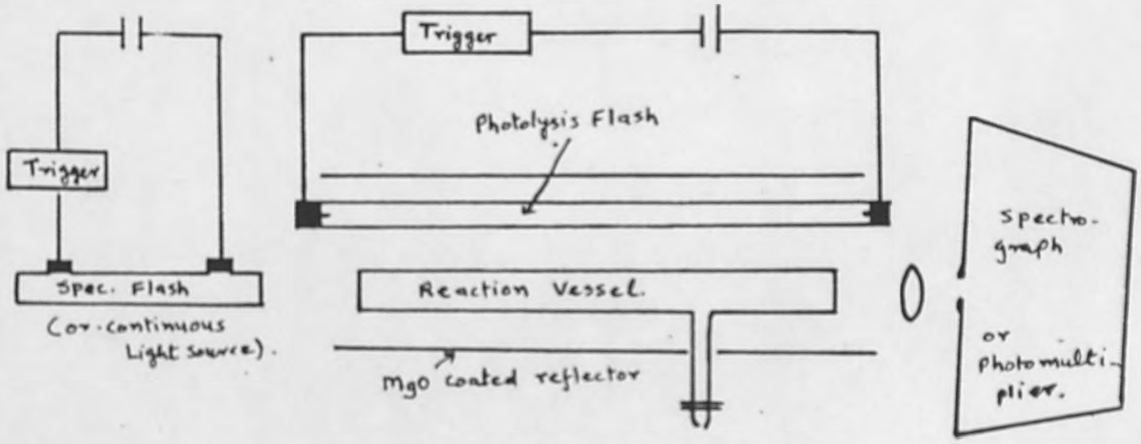


Figure 5: Basic flash photolysis arrangement.

1.1.9 Laser Flash Photolysis:

The polychromatic nature of the radiation from conventional gas discharge lamps is a disadvantage which has been eliminated largely by the introduction of lasers for flash photolysis, because the radiation from laser sources is unique in its monochromatic nature. The most commonly used lasers are solid-state lasers employing rods of such material as ruby or neodymium glass. It is possible to build up a picture of the decay of an intermediate by recording a series of spectra at different predetermined time-intervals after the excitation flash or to build up a complete spectrum of the intermediate, point by point, by changing the setting of the monitoring monochromator in a series of readings at a fixed time interval after the initial flash. Laser flash photolysis has been used widely to study the excited triplet states of aromatic hydrocarbons in solution.[7]

The flash photolysis technique can be adapted to measure a lifetime in the presence of excited state quencher, and this gives a direct measure of the rate constant for the quenching process. The excited lifetimes (τ) can also be measured by following absorption or emission decay using flash photolysis. This technique also enables us to study $T_1 \longrightarrow T_n$ absorption described as follows.

1.1.10 Triplet-Triplet Absorption:

A state diagram in Fig. (6) shows the pathway leading to triplet-triplet (T-T) absorption. Absorption (a) is followed by inter-system crossing (b) to populate triplet (T_1). The latter is

capable of absorbing photons and undergoing $T_1 \longrightarrow T_2$ and $T_1 \longrightarrow T_3$ transitions.

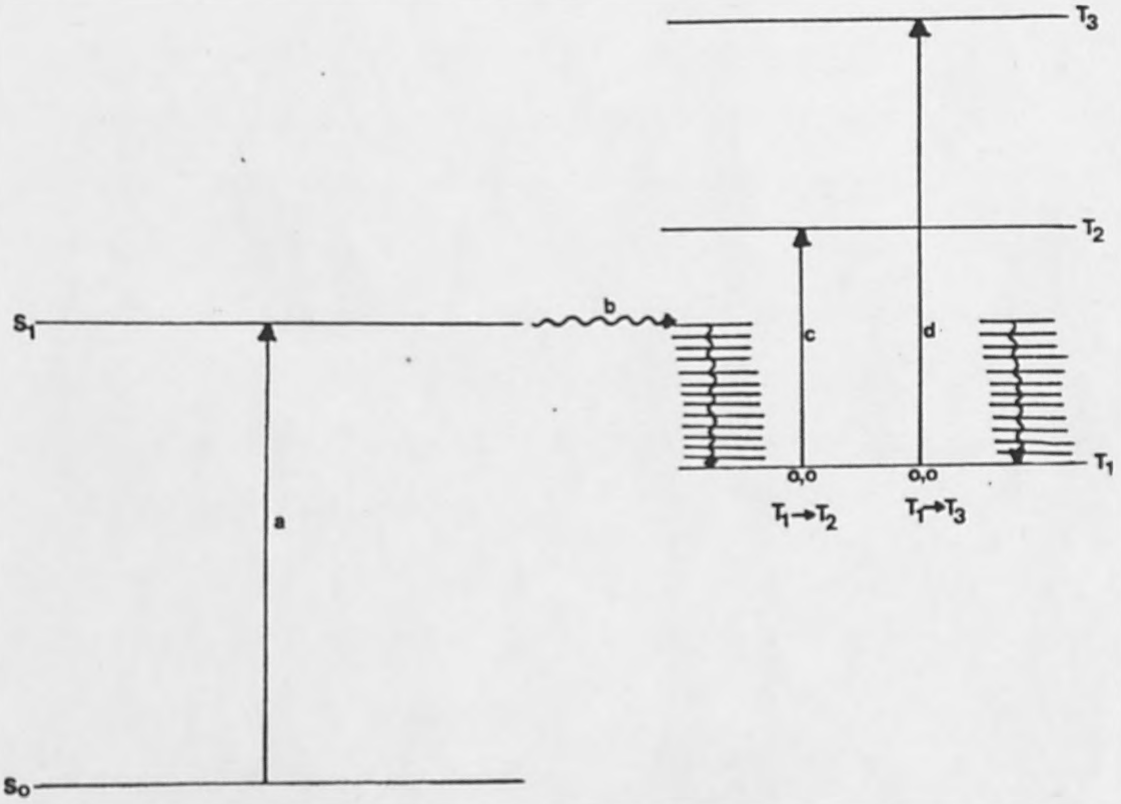


Figure 6: State diagram showing the pathway leading to T-T absorption.

Triplet-triplet absorptions can be studied by flash spectroscopy.[8-11] The relatively long lifetime of triplets allows the build up of substantial concentrations of T_1. If the $T_1 \longrightarrow T_n$ transition is moderately or strongly allowed ($\varepsilon \sim 10{,}000 - 1000{,}000$), it is generally possible to detect T_1 by the measurement of its absorption

spectrum. Once the absorption spectrum is established, the decay kinetics of T_1 may be measured. $T_1 \longrightarrow T_n$ is feasible in vapours, liquids and solids. An experimental example of a triplet-triplet absorption has been shown for naphthalene by Turro.[1]

1.1.11 Polarization of absorption and emission spectra:

The absorption and emission can be polarized along particular molecular axis. This is controlled by the symmetry properties of the participating orbitals and predictable by group theory.[2] (A system which remains unchanged by symmetry operation (e.g. rotation or reflection) is said to be symmetric with respect to that operation. Conversely, a system changed into its inverse by the symmetry operation is called antisymmetric).

The transition moment (T.M.) of the electronic states of a molecule is defined by the following equation.

$$\text{T.M.} = \int \Theta_i \Theta_f d\tau N \quad \int S_i S_f d\tau s \quad \int \psi_i \mu \psi_f d\tau e$$

where the first term is the overlap integral of the wave functions for nuclear vibrations the second term is spin overlap integral and the third term is called electronic transition movement and its value depends on the symmetries and amount of overlap of the initial and final spatial orbitals. In the above equation the terms Θ_i and Θ_f = initial and final nuclear (vibrational) wave functions respectively. S_i and S_f refers to initial and final spin orbitals respectively. ψ_i and ψ_f refers to initial and final space orbitals. μ = the dipole moment operator. N = Nuclei, S = Spin orbital and e = electrons.

The E.T.M. is intimately related to the symmetries of orbitals.

E.T.M. total = $E.T.M._x + E.T.M._y + E.T.M._z$.
Where E.T.M. = Electronic Transition Movement.

Unless the integral is totally symmetric the transition is forbidden. If the integrand of just one of the components of the E.T.M. (e.g. $E.T.M._x$) is totally symmetric, the transition will be polarized along the x-axis. In such a case, illuminating an oriented assembly of molecules (crystal or thin layer) with plane polarized light (the electronic vector of which oscillates in a particular plane), maximum absorption will occur when the plane of polarization of the incident light is parallel to the molecular x-axis. Rotation of the crystal will cause a decrease in absorption which falls to zero when the plane of polarization and the x-axis are perpendicular.

In a similar way, emission is frequently polarized along a particular molecular axis. Polarization measurements can give important information about the electronic transitions responsible for particular absorption bands.[3]

The methods of obtaining polarization data and their applications are shown as follows.

With single crystals of known and appropriate structure the orientation of the plane polarization with respect to the crystal axis and hence the molecular axis may be determined. This gives the absolute polarization of absorption and emission. It is easier and more useful to determine the relative polarization of absorption

bands, This information is given by polarization spectra in which the polarization is plotted against the wavelength of the exciting light. Such spectra may be obtained by inserting polarization devices (P_1 and P_2) into the incident and emitted light beams in the spectrofluorimeter or spectrophosphorimeter as shown in Fig. (7):

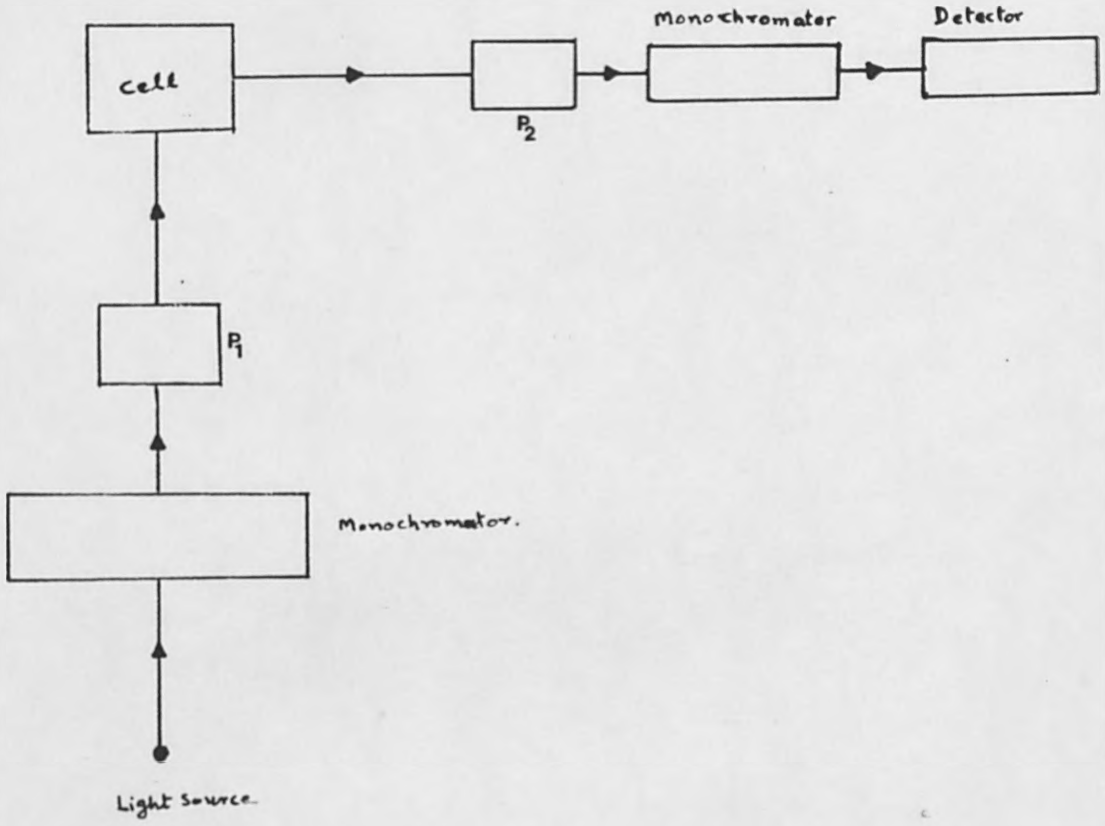


Figure 7: Schematic diagram of apparatus for determining polarization spectra.

With P_1 fixed for each exciting frequency the intensity of the emitted light is measured with the plane of polarization defined by P_2 parallel or perpendicular to that of P_1. This gives the degree of polarization (P) defined by

$$P = \frac{I_{11} - I_{\perp}}{I_{11} + I_{\perp}}$$

where I_{11} and $I_{\perp}$ are the intensities of the parallel and perpendicular components of the emitted light, respectively.

For randomly oriented molecules in a highly viscous solvent, which inhibits rotation in the time interval between absorption and emission, it can be shown that

$$P = \frac{3\cos^2\alpha - 1}{\cos^2\alpha + 3}$$

where α is the angle between the directions of polarization of absorption and emission of the substrate. Generally, emission polarization spectroscopy gives a value for α and if the absorption (or emission) can be identified with a particular transition the transition associated with the emission (or absorption) can often be assigned. The interpretation of phosphorescence polarization data depends upon a knowledge of the mixing of singlet and triplet states induced by spin-orbit coupling.

1.1.12 Rotational Depolarization of Fluorescence:

A beam of radiation is said to be depolarized if the electric vectors are oriented in all directions in space (Fig. 27a). In a partially polarized beam the majority of waves will vibrate with electric-vector in one plane (Fig. 27b). In a completely polarized beam all the vibrations are unidirectional with respect to a defined co-ordinate system (Fig. 27c).

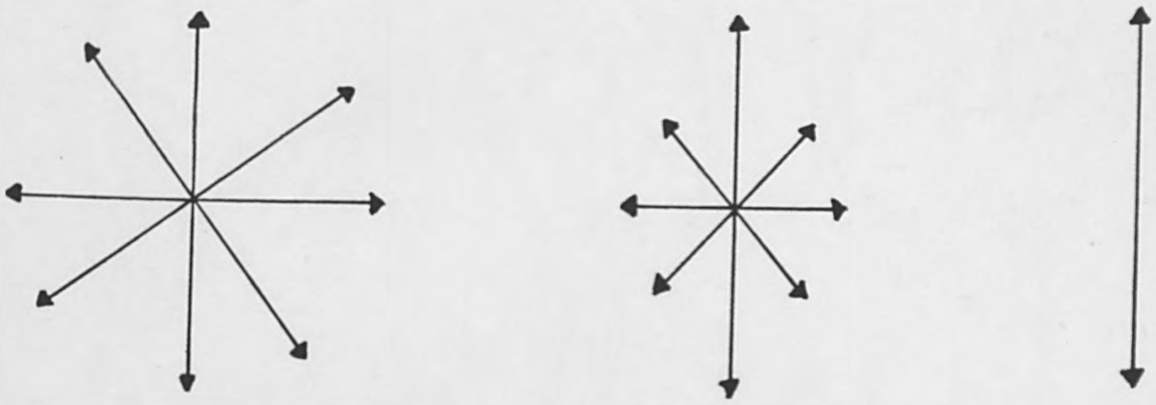
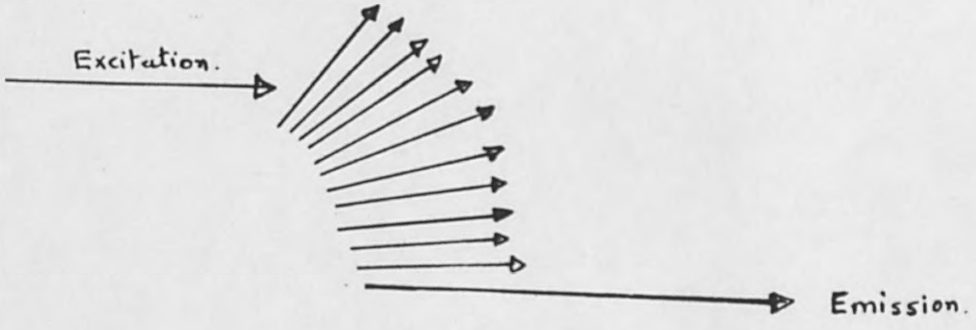


Figure 27: (a) Depolarized, (b) Partially polarized (c) Plane polarized beam of radiation.

The electric vector of emitted radiation will be parallel to the transition moment of emission oscillator. If the excited molecules do not rotate within their lifetimes the angular relationship between absorption oscillator and emission oscillator will be maintained. This situation may occur in infinitely viscous mediums. However, if the less viscous media is used this condition will no longer hold. The translational component of thermal agitation will have no effect on the degree of polarization of emitted radiation. But the rotational component will change the relative orientation of the transition moment during emission from that at the instant of absorption.

The frequency of rotation in a medium of low viscosity is of an order of 10^{11} sec^{-1}, whereas the lifetime of the excited state molecule is of the order of 10^{-8} sec.[5] Thus, in such a medium each excited molecule, on average, can rotate about 1000 times before it fluoresces. As a result the fluorescence is depolarised completely and spherically distributed in space. But, if rotation is hindered by using a viscous media like glycerol or sugar solutions, the emitted radiation

may not be completely depolarised unless the period of rotation is less than the lifetime of the excited state. The greater the viscosity η of the solvent the greater will be the degree of polarization for a given lifetime τ. The degree of polarization will be small for long-lived (τ-large) excited states. Therefore, the degree of polarization depends on the average period of rotation and the radiative lifetime of the molecule.



Rotational depolarization.

According to the theory developed by Smoluchowski and by Einstein, if a spherical particle of radius r rotates in a liquid of viscosity η, in a short time Δt, by an angle of $\Delta\alpha$, then the mean value of angular rotation $\overline{\Delta\alpha}^2$ is given by the Brownian equation for rotational motion

$$\overline{\Delta\alpha}^2 = \frac{KT}{4\pi r^3 \eta} \Delta t$$

$$= \frac{RT}{3\eta V} \Delta t = \frac{\Delta t}{\rho}$$

where $V = {}^4/_3 \pi r^3 N$ is the molar volume and $\rho = 3\eta V/RT$ is the average period of rotation or the rotational relaxation time. By inserting sufficiently short lifetime τ for Δt in the above equation the observed degree of polarization P, which results from rotation of all the individual oscillators around statistically oriented axes, has been obtained by Perrin, for vertically exciting light, as

$$\frac{1}{P} = \frac{1}{P_o} + \left(\frac{1}{P_o} - \frac{1}{3}\right) \frac{RT}{\eta V} \tau.$$

this equation gives a linear relationship between $^1/P$ and fluidity of the solvent medium.

1.1.13 Concentration depolarization:

The concentration depolarization is observed at a concentration $\sim 10^{-3}$ M where molecules are apart by an average distance of 7 nm or more.[5] This effect is caused by dipole-dipole interaction between the neighbouring molecules whereby electronic excitation energy is transferred from initially excited molecule to its neighbour at fairly large distances. If the acceptor molecule has a

different orientation than the donor molecule the emitted radiation will be depolarized. Such long-range energy transfer by dipole-dipole mechanisms can lead to energy wandering from molecule to molecule until it is finally emitted (Fig. 28) thereby completely losing its initial polarization direction. The concentration depolarization is independent of viscosity of the medium, liquid and solid solutions behave alike.

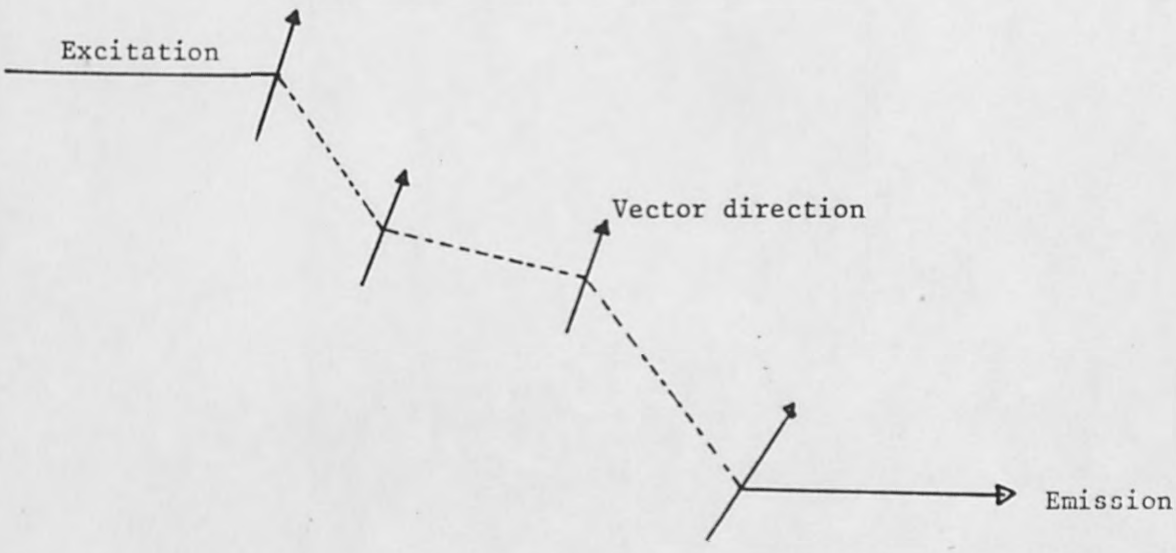


Figure 28: Concentration depolarization.

1.1.14 Method for the determination of fluorescence quantum yield (ϕ_F):

In order to obtain the quantum yield of fluorescence one has, in principle, to measure the ratio of the number of photons emitted to those absorbed. However, in practice, some grave difficulties do

occur while determining the quantum yield of fluorescence. These difficulties arise from (i) the difference in spatial distribution of the exciting and emitted light, (ii) the polychromatic character of the emitted light and (iii) the variation of the sensitivity of the detector with wavelength. The last two problems can be greatly simplified by directing the incident light and fluorescent emission successively onto a 'quantum counter' (a solution of a substance such as Rhodamine B, which, within a certain range of wavelengths, converts all absorbed light at constant quantum yield into its own fluorescent emission). The detector then receives signals of constant spectral distribution from both incident and emitted light beams.

Provided that the spectral response of the light detector is known, the most rapid and accurate way of determining emission efficiency is to measure the unknown quantum yield relative to that of some substance whose absolute emission quantum yield has already been accurately measured. It will be necessary to determine, under identical conditions of cell geometry, incident light intensity and temperature the fluorescence spectra of dilute solutions of the unknown and of the standard. The solutions should have the same optical density at the wavelength of the exciting light so that they both capture the same number of photons. The quantum yield of the unknown relative to that of the standard is the ratio of integrated band areas under the two fluorescence spectra (plotted on a frequency scale) after they have been corrected for the detector response factor. Multiplying by the known quantum yield of the standard then gives the absolute quantum yield of the unknown, e.g.

Absolute quantum yield ϕ_{FA} of compound A =

$$\frac{\text{Integrated band area of the fluorescence of A}}{\text{Integrated band area of the fluorescence of standard S}} \times \phi_{FS}$$

$$\phi_{FA} = \frac{A}{S} \times \phi_{FS}$$

1.1.15 Fluorescence spectra:

The fluorescence spectra can be recorded using an instrument called a spectrofluorimeter as shown in Fig. (8).

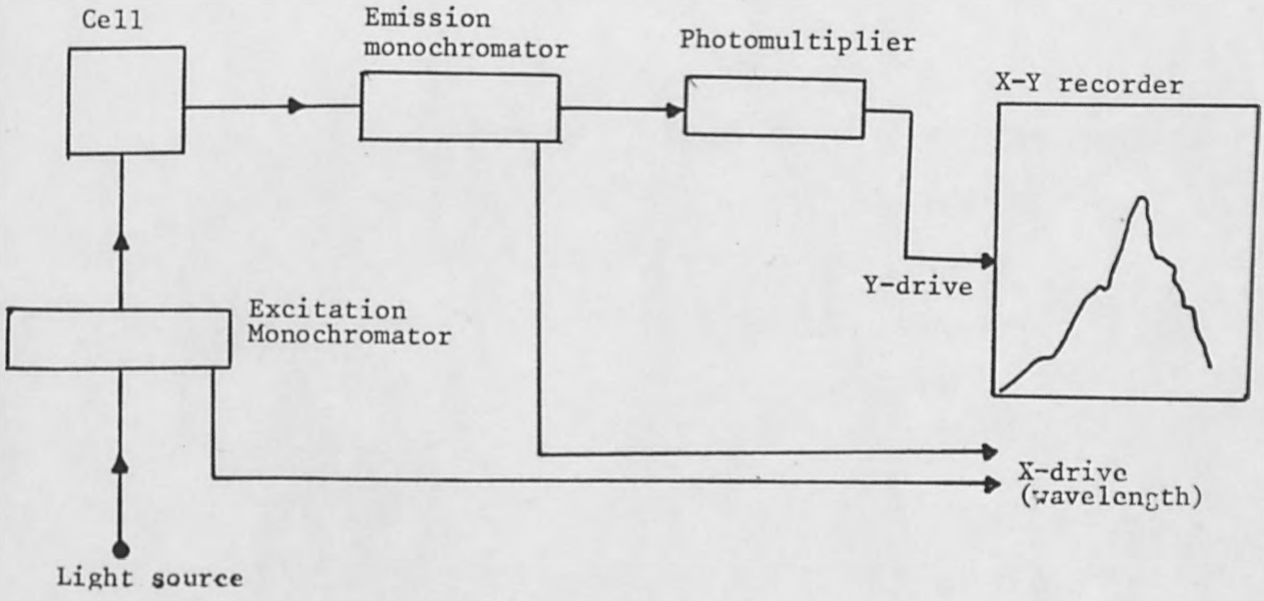


Figure 8: Schematic diagram of a spectrofluorimeter.

A beam of monochromatic light excites the specimen in the cell and the emission is observed and analysed at right angles to the incident beam. The output is the emission spectrum plotted by the XY recorder. The system will record just the fluorescence spectrum and since either the excitation or the emission monochromator may be coupled to the XY recorder, it follows that two sorts of spectra may be obtained.

(i) The excitation monochromator can be set to a particular wavelength which is absorbed by the sample and the emitted light is scanned with the emission monochromator. This gives the fluorescence emission spectrum.

(ii) Alternatively, the emission monochromator can be set to a particular wavelength in the fluorescent output and the exciting wavelengths are scanned with the exciting monochromator. This gives rise to the fluorescence excitation spectrum, which normally resembles closely the absorption spectrum in sufficiently dilute solutions.

1.1.16 Method for the determination of lifetime of fluorescence τ_F: Pulse fluorimetry is the most direct method for the determination of fluorescence lifetime (τ_F). In this method a recurrent light pulse of very short duration ($\sim$ 1 ns) is used to excite the sample. The emission is monitored (after each pulse) with a fast photomultiplier and the output, as a function of time, is displayed on an

oscilloscope screen. The decay curve of the emitting species is obtained after the decay function of the exciting flash is corrected. If this is a simple exponential function it is merely necessary to determine the time taken for the fluorescence to decay to $^1/_e$ of some arbitrary intensity.

An extension of the above technique is the photon sampling technique. It depends on counting individual photons and it can be used on extremely weakly luminescent substances. Measurement of lifetimes in the range of 10^{-6}-10^{-10} sec. can be carried out using this technique.

Fluorescence lifetimes can also be determined by the employment of a suitable 'quencher' which interacts with the excited state in an energy transfer process whose rate constant is known. This is shown for the system (Fig. (9)) in which a single chemical product (B) is formed in a unimolecular reaction from the first formed excited state (A*) of the starting material, and in which A* can be quenched by an added species (Q).

A	$\xrightarrow{h\nu}$	A*	rate I (= intensity)
A*	$\longrightarrow$	A	K_{-1} [A*]
A*	$\longrightarrow$	B	K_r [A*]
A* + Q	$\longrightarrow$	A + Q*	K_q [A*] [Q]

Figure (9)

K_{-1} is a composite first order rate constant which takes into account radiative and radiationless deactivation of A*. Using

the steady state approximation the quantum yield for product formation in the absence of quencher (ϕ_B^o) can be expressed as:

$$\phi_B^o = \frac{K_r}{K_r + K_{-1}}$$ and the quantum yield with added

quencher $$\phi_B = \frac{K_r}{K_r + K_{-1} + K_q [Q]}$$

Hence, $$\frac{\phi_B^o}{\phi_B} = 1 + \frac{K_q [Q]}{K_r + K_{-1}} = 1 + K_q \tau_o [Q]$$

Where τ_o is the lifetime of the excited state in absence of quencher. This expression is linear in $[Q]$ and is the form of the normal 'Stern-Volmer' quenching plot (Fig. 10) often obtained in photochemical studies.

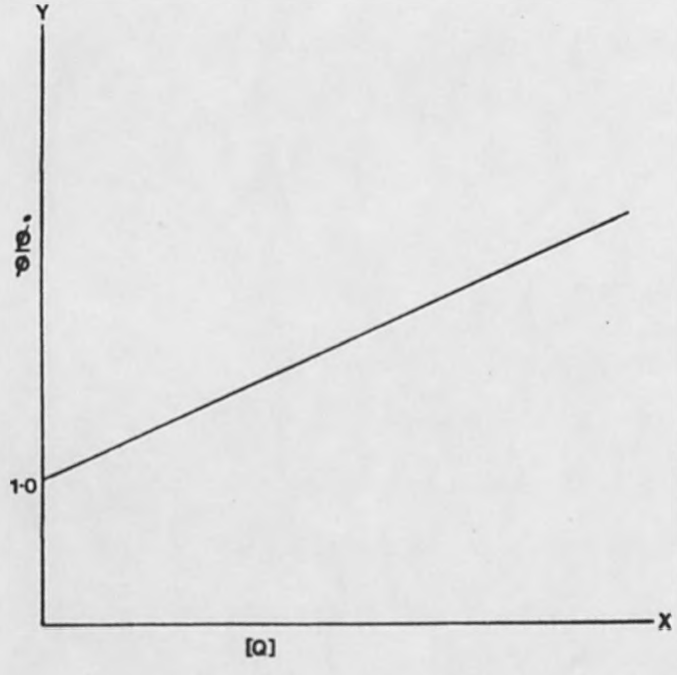


Figure 10: Stern Volmer quenching plot.

From the above equation the lifetime (τ_o) of the excited state can be calculated.

1.1.17 Single photon counting technique

This technique could be used for the measurements of fluorescence decay times in the nanosecond region using a low light intensity. The great advantage is that the method eliminates disturbance due to noise and stray light. The technique measures the time of emission of individual fluorescene photons, the reference zero time being the initial rise of the flash lamp light or an electrical pulse related in time to the flash lamp discharge. The time coordinate of arrival of each recorded photon with reference to a fixed time zero is converted into an amplitude of the resultant pulse in a time-to-amplitude converter (TAC) circuit. Each time the lamp flashes a synchronization pulse is sent to TAC and starts the time-sweep. If a stop pulse is received from the photomultiplier during the time sweep a TAC pulse is generated with amplitude proportional to the time ($t_{stop}-t_{start}$) (Fig. (26)).

The TAC output in the form of pulse height information is fed to the multi-channel pulse height analyser (MCPHA). The analyzer channels now represent increments in time, and the counts in each channel are proportional to the probability for fluorescence emission from the sample between t and t + Δt, where t is measured from an arbitrary but fixed point each flash. The contents of MCPHA memory can be read onto a punched tape or onto XY recorder or typewriter. The signal analysers simply consist of counters which store standard pulses of specific heights and then output numbers which represent the

number of pulses accumulated in a specified measurement time. The free running lamp is used for single photon counting. Decay curves can be obtained by plotting counts/channel against channel number.

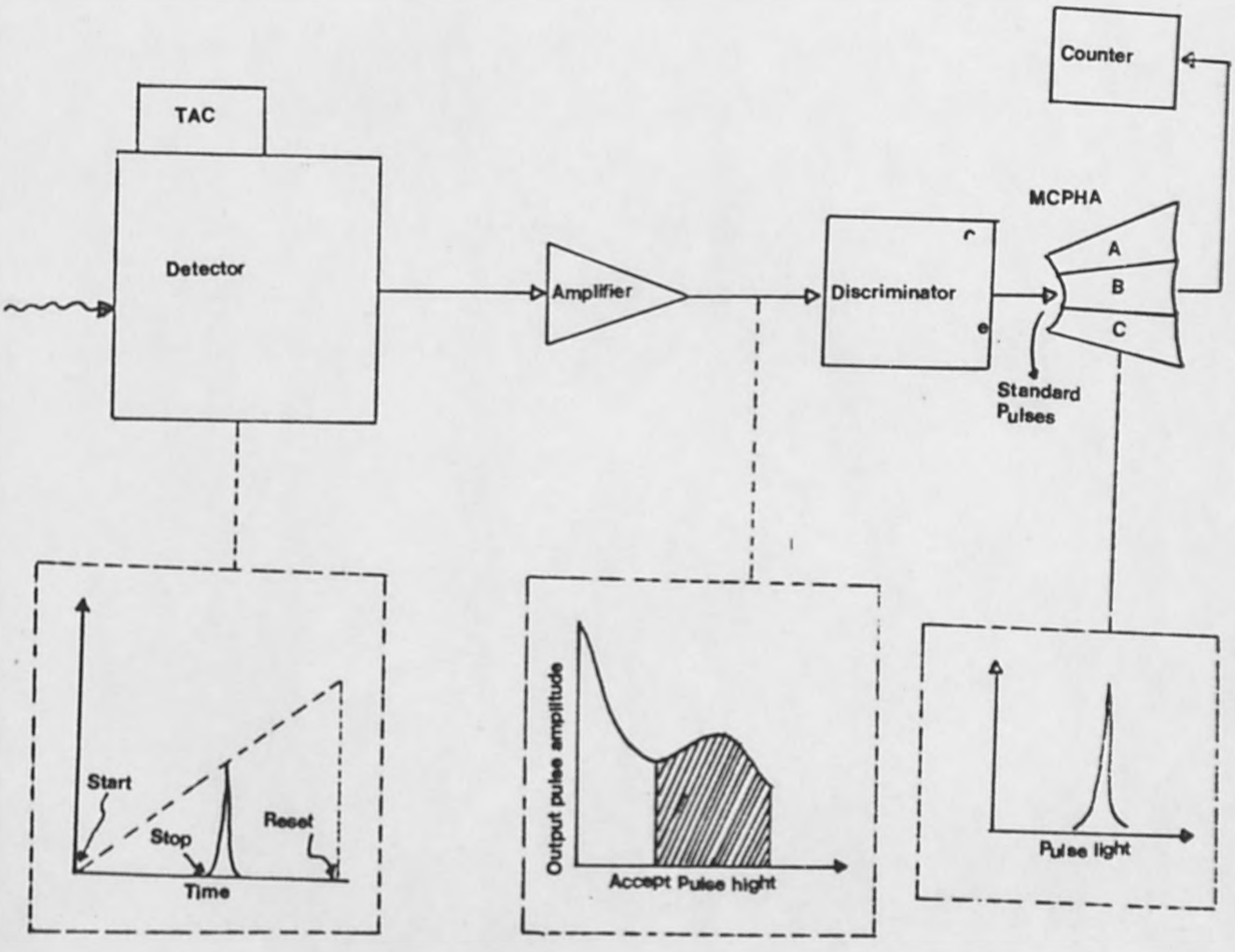


Figure 26: Single photon counting technique.

1.1.18 Phosphorescence spectra:

The phosphorescence spectra are recorded with spectro-phosphorimeters which differ from spectrofluorimeters only in the incorporation of a mechanical or optical shutter which repetitively chops the exciting and emitted light beams in such a manner that excitation occurs when the detector is cut off and emission is not observed until a definite period after excitation has ceased. This delay between excitation and observation permits fluorescence ($\tau_f < 10^{-6}$ sec) to decay to zero before the longer lived phosphorescent emission is recorded. The phosphorescence is most easily observed in rigid matrices which inhibit the quenching collisions between adventitious impurities and the excited triplets. Hence the sample is usually investigated in mixed organic solvents which set to form rigid glasses when cooled in liquid nitrogen.

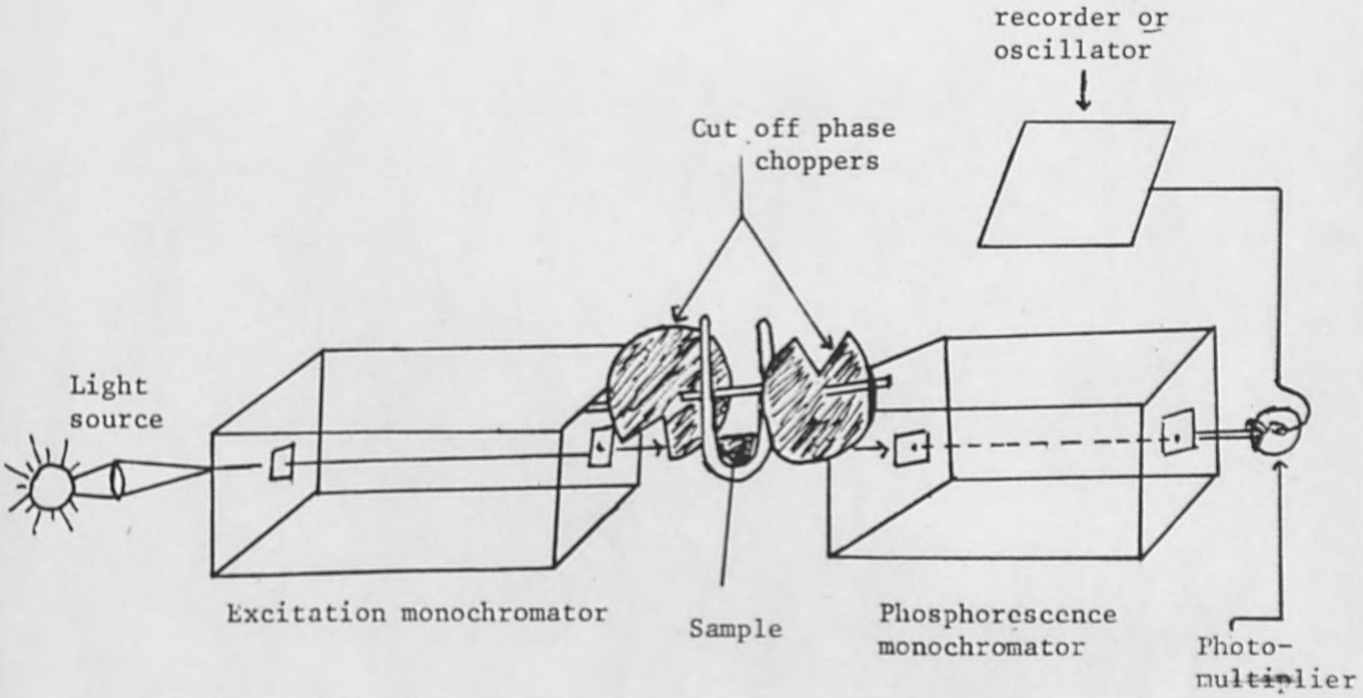


Figure 24: Spectrophosphorimeter.

1.1.19 Method for the measurement of quantum yield of phosphorescence (ϕ_p):

Phosphorescence quantum yield can also be measured in the same way as the fluorescence quantum yield are measured, but require choppers for eliminating fluorescence, as shown in Fig. (24).

Provided that the spectral response of the light detector is known the unknown quantum yield, relative to that of some substance (whose absolute emission ϕ_p has already been accurately measured) can be determined. It will be necessary to determine, under identical conditions of cell geometry, incident light intensity and temperature, the phosphorescence spectra of dilute solutions of the unknown and of the standard.

1.1.20 Method for the measurement of lifetime of phosphorescence (τ_p):

The actual lifetimes of phosphorescence can be measured by pulse phosphorimetry in which a recurrent light pulse of very short duration ($\sim$ 1 ns) is used to excite the sample. The decay curve of the emitting species is obtained as was described for fluorimetry in the measurement of the lifetime of fluorescence (Section: 1.1.16). The chopped light source is used for the excitation of the sample.

1.1.21 Becquerel phosphoroscope:

This apparatus was constructed by Becquerel for the measurement of phosphorescence and consists of a pair of rotating sectors mounted on a common shaft (Fig. (24). The openings in the sectors are so arranged that the sample is alternatively illuminated and viewed

during cut-off periods. For solutions and for 90° illumination a modification is made, the sample is placed within a rotating cylinder with cut-out slots (Fig.(25)).

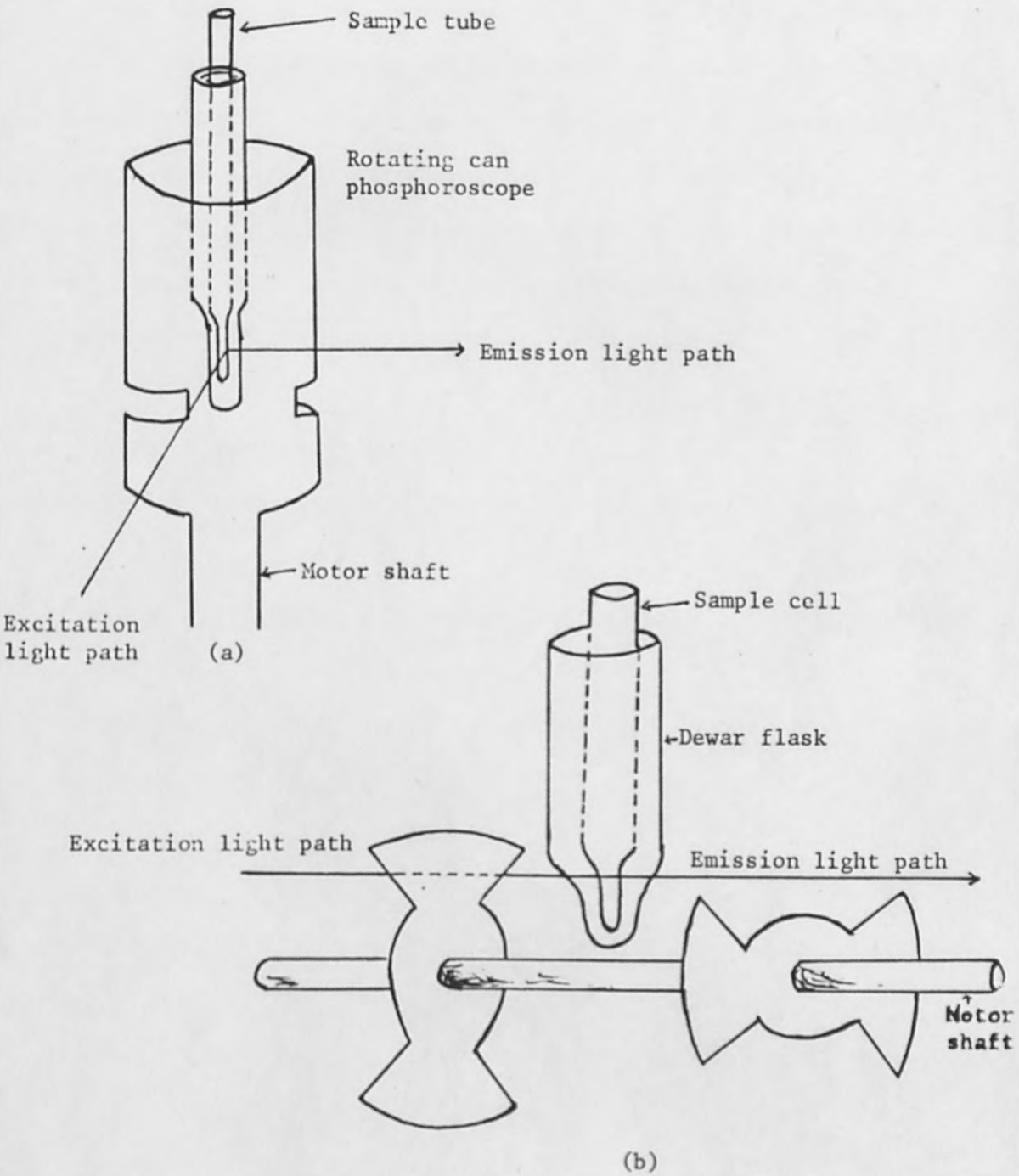


Figure 25: Bacquerel phosphoroscope with (a) co-axial cylinders, (b) a pair of rotating sectors mounted on a common shaft.

During the course of rotation of the cylinder when the window faces the light source the sample is excited and when it faces the detector the emission from the sample is recorded. The detector output may either be fed to an ammeter or to an oscilloscope. The time between excitation and detection can be varied by changing the speed of rotation, thus the complete decay curve can be plotted. If an oscilloscope is used, the signal is applied to the y-axis of the oscilloscope and the phosphoroscope is synchronized with oscilloscope sweep. The oscilloscope then displays the exponential decay curve of phosphorescence which can be photographed. The shortest time measured by this type of phosphoroscope is only 10^{-4} s.

1.1.22 Solvent effects:

When absorption spectra are measured in solvents of increasing polarity it is found that for some systems λ_{max} moves to longer wavelengths (red shift) and for others an inverse blue shift is encountered. These shifts provide information on the nature of the transition and can afford estimates of the dipole moments of the excited states.

The solvent effect also plays an important role on the wavelength maximum of the fluorescence spectra due to solute-solvent interaction.

Molecular electronic interactions occur in a time interval of about 10^{-15} seconds during which, according to the Franck-Condon principle,[12] no changes in bonding length can occur. Hence the absorption process produces a transitory excited state possessing an altered electron distribution but with ground state geometry. This transitory

excited state is called a Franck-Condon excited state. Since no significant transitional motion of solvent molecules can occur in 10^{-15} seconds,[13] the Franck-Condon excited state is therefore surrounded by the equilibrium ground state solvent cage. The molecule relaxes to a structure which approaches an 'equilibrium' excited state geometry within a shorter time than it takes for singlet state radiative decay to occur. At the same time the solvent cage relaxes to a new configuration consistent with the changed electron distribution and geometry of the molecule. The resulting excited state is much lower in energy than the Franck-Condon excited state and is often termed as an "equilibrium" excited state. Generally in solution, fluorescence originates from the relaxed equilibrium excited state and not from the spectroscopic Franck-Condon excited state.

Fluorescence is likewise subject to Franck-Condon restrictions and hence the emission results in the formation of a transitory Franck-Condon ground state, which subsequently undergoes structural and solvent re-orientation to yield the equilibrium ground state. Thus absorption by a diatomic molecule (A-B) may be represented as:

$$h\nu + (A\text{-}B)_{eq} \quad m \longrightarrow (A\text{-}B)^{*}_{F.C.}$$

while solution fluorescence can be depicted as:

$$(A\text{———}B)^{*}_{eq} \quad m \longrightarrow (A\text{———}B)_{F.C.} + h\nu'$$

This is shown in Fig. (11) for a simple diatomic molecule, A-B, which shows changes in bond length and electronic configuration. (It is thus apparent that the excited and ground states in

absorption and fluorescence are "different", and hence no precise correlation between absorption and fluorescence can be drawn).

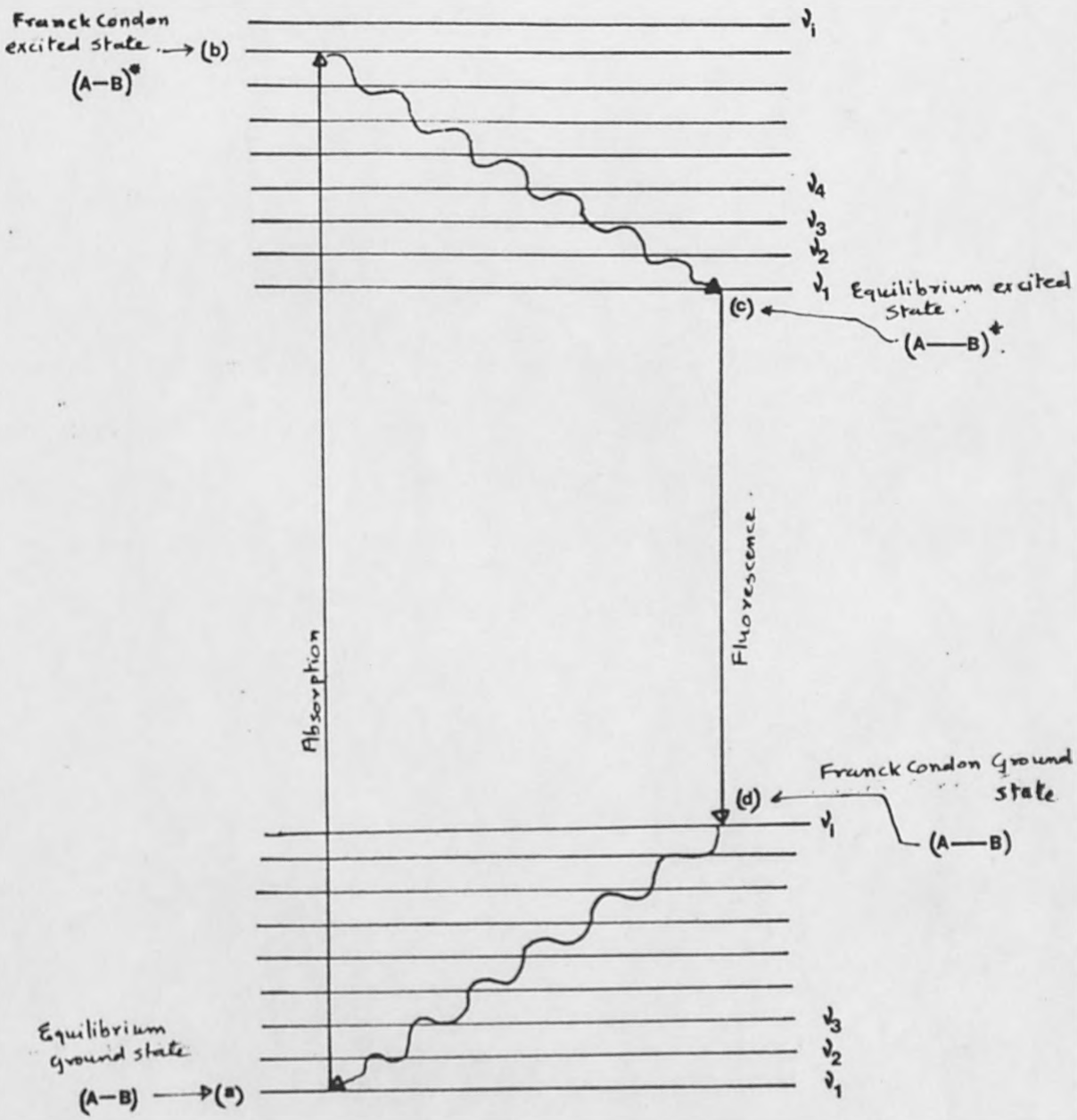


Figure 11: Diagramatic representation of equilibrium and Franck Condon electronic states.

In the case where both solvent and solute have permanent dipole moments, dipole-dipole interactions will be the predominant factor in determining magnitudes of emission maxima shifts (as well as absorption shift). In many cases where both solute and solvent are highly polar the magnitude of spectral shift produced by electrostatic interactions is small compared with more specific local perturbations, particularly hydrogen bonding.

In most polar aromatic molecules whose lowest singlet states are ($\pi\pi^*$), the excited state is more polar than the ground state. Thus any increase in polarity of the solvent will produce a greater stabilization of the excited than the ground state.[14,15] Therefore, the absorption and fluorescence spectra will both shift to lower energies as the solvent polarity is increased, Fig. (12).

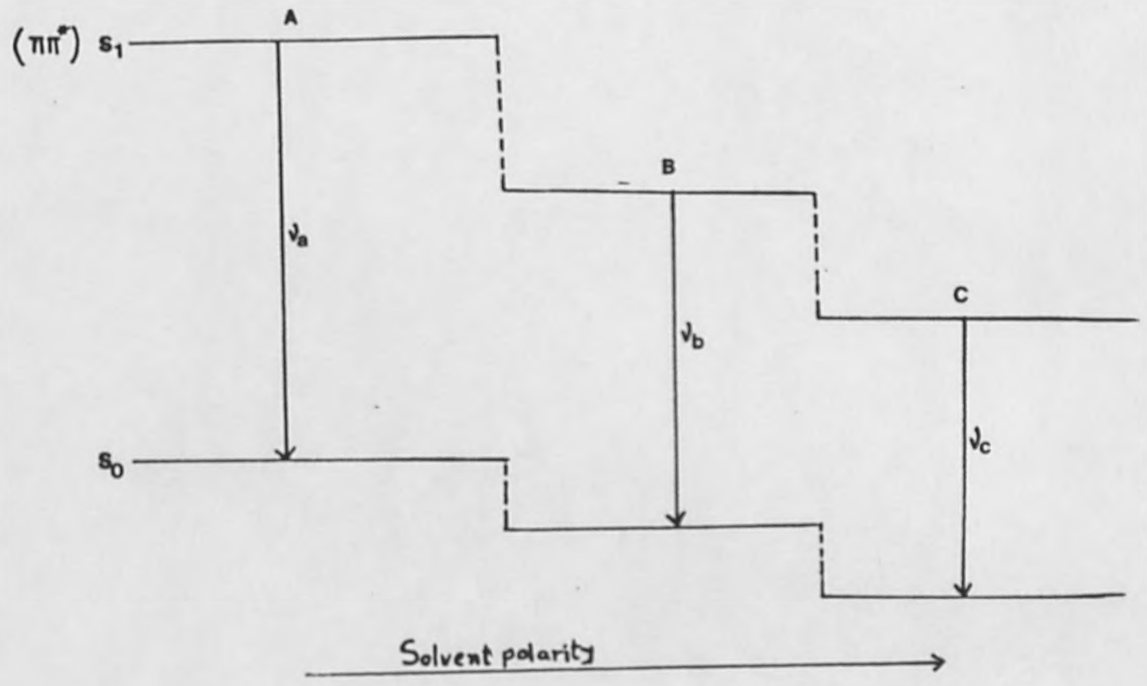
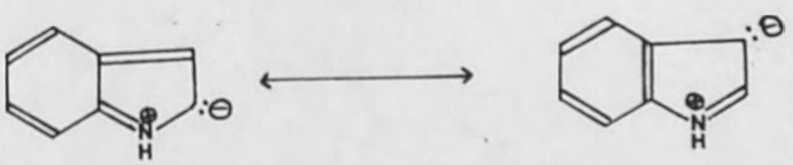


Figure 12: Schematic representation of the "red shift" in $\pi - \pi^*$ fluorescence spectra as the polarity of the solvent is increased.

In the case of solute-solvent pairs in which neither the solvent or solute is appreciably polar, a red shift (compared to the vapour spectrum) is still observed. The main reason for that shift is a dispersive interaction resulting from the fact that electronic transitions produce changes in the electron densities of solute molecules.

1.1.23 Wavelength maximum shift in indole:

The ultraviolet absorption and fluorescence excitation spectra of indole remain unchanged with the change of solvents (non-polar to polar solvent). However, a red shift occurs in the fluorescence emission spectra of indoles as the solvent polarity is increased. This fact indicates that there is an interaction between solvent and the excited indole molecule, which is greater than that between the solvent and the ground-state of the indole molecule. Thus it seems probable that polar contributing mesomeric states of indole molecules such as (I) and (II) make a larger contribution in the excited indole molecule than in the ground state.



(I) (II)

Contributions of structures such as (I) and (II) to the excited state would account for these states having a much higher dipole moment than the ground state, and would be more sensitive to the

dielectric constant of the surrounding solvent. This would cause a much greater stabilisation due to solute-solvent interaction in the excited state.[16] However, the question arises as to whether the solvent stabilization is a bulk solvent effect, e.g. as determined by dielectric constant,or whether it is covered by localized interaction of the excited species with a few specially oriented solvent molecules. It is possible that such a stabilization process may involve a particular number of solvent molecules. Evidence in favour of the stabilization via specific solute-solvent molecular interactions comes from the finding that when the fluorescence emission is observed in an ethanol-cyclohexane solution of indole, a maximum shift is observed at alcohol concentrations so low as to have a negligible effect on the solvent dielectric constant.[14] This argument leaves out the probability that the concentration of ethanol in the solvent shell of indole is much greater than would be calculated from the solvent proportions.[17]

Hydrogen bonding has been implicated as a red shift mechanism.[18] Hydrogen bonding can stabilize the excited state leading to a lower energy fluorescence emission and thus a longer wavelength maximum results. However, the observation that 1,2-dimethyl indole[14] and 1-methyltryptophan[19] have practically the same polar solvent shift as the unsubstituted molecules seems to indicate that hydrogen bonding is not necessary for the red shift.

Walker, Bednar and Lumry[20] suggested that an excited state solute-solvent complex (exciplex) has been responsible for a large red shift and loss of vibrational structure in the fluorescence spectra

of some indoles in polar solvents. Emission spectra of indole and 1-methyl indole in a variety of non-polar solvents were measured and the above suggestion has been confirmed.[20,21] Apart from indoles there are other compounds, such as arylamino naphthalenes[22-24] (e.g. 1-anilino-8-naphthalene sulphonate (ANS), N-phenyl naphthyl amine (NPN)) and aromatic aldehydes[25] (e.g. pyrene-3-carboxaldehyde), which exhibit solvent-induced red shifts of their fluorescence wavelength maximum, variations in their fluorescence lifetimes and quantum yields with change in solvent polarity.

1.1.24 Quenching of excited states:

A substance which accelerates the decay of an electronically excited state to the ground state or to lower electronically excited states is described as a quencher and is said to quench that state. If the original excited state is luminescent quenching will reduce the intensity (quantum yield) of light emission. The process can be represented as:

$$M^* \xrightarrow{Q} M'$$

where M' is the ground state or another excited state of M and Q is the quencher. The quenching process occurs by many different mechanisms and is induced by many different substances. Of these, oxygen is considered to be the most efficient excited state quencher. For this reason it is essential in all quantitative work to reduce the concentration of oxygen to the smallest possible value, either by bubbling oxygen-free nitrogen through the solution or, even better by degassing with several 'freeze-pump-thaw' cycles. The solvent should be non-fluorescent and substrates should be purified by chromatography until the lifetime of their luminescence is constant.

In principle quenching can occur in either encounter complexes, excimer/exciplexes or both. The quenching process can occur by the routes indicated in Fig. (13). These routes or modes of relaxation can be followed through the excimer or exciplex.

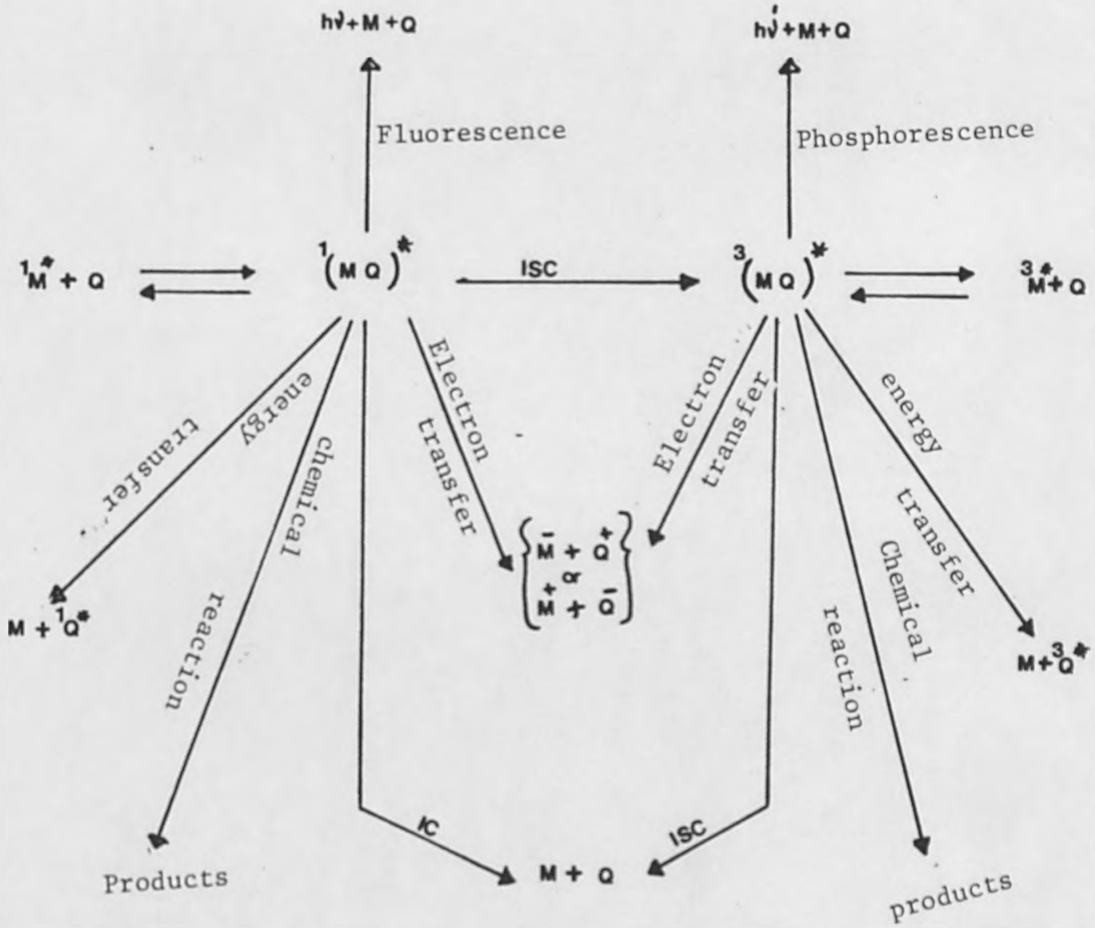


Figure 13: Relaxation pathways in exciplexes.

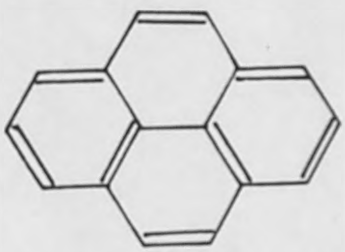
1.1.25 Concentration quenching and excimer formation:

The terms exciplex and excimer are defined as follows:

Exciplex: An exciplex is an excited complex which is formed by the association of two different species, one excited and the other in its ground state (e.g. $(MQ)^*$).

Excimer: An excimer is an excited dimer, i.e. an exciplex involving the ground and excited states of the same species, e.g. $((MM)^*)$.

Concentration quenching: An increase in the concentration of a solute is accompanied by a decrease in the intensity (quantum yield) of its fluorescence. This phenomenon is called concentration quenching and is commonly observed. It has been found that such quenching is often accompanied by the appearance of a new emission at longer wavelengths, the intensity of which increases with concentration. For example, the violet fluorescence of pyrene in dilute solutions is gradually replaced by a blue fluorescence with



Pyrene

increasing pyrene concentration.[26] These phenomena could be explained by the formation and fluorescence of a pyrene excimer (Fig. 14),

$$M \underset{\text{monomer fluorescence}}{\overset{h\nu}{\rightleftharpoons}} {}^1M^* \overset{M}{\rightleftharpoons} {}^1(MM)^* \xrightarrow[\text{excimer}]{\text{excimer fluorescence}} M + M + h\nu'$$

Figure (14)

Such complexes exist only in the excited state, therefore they are undetectable in the ground state. The emission from an excimer will be structureless and will occur at longer wavelengths than that of its components. These points are illustrated in Fig. (15).

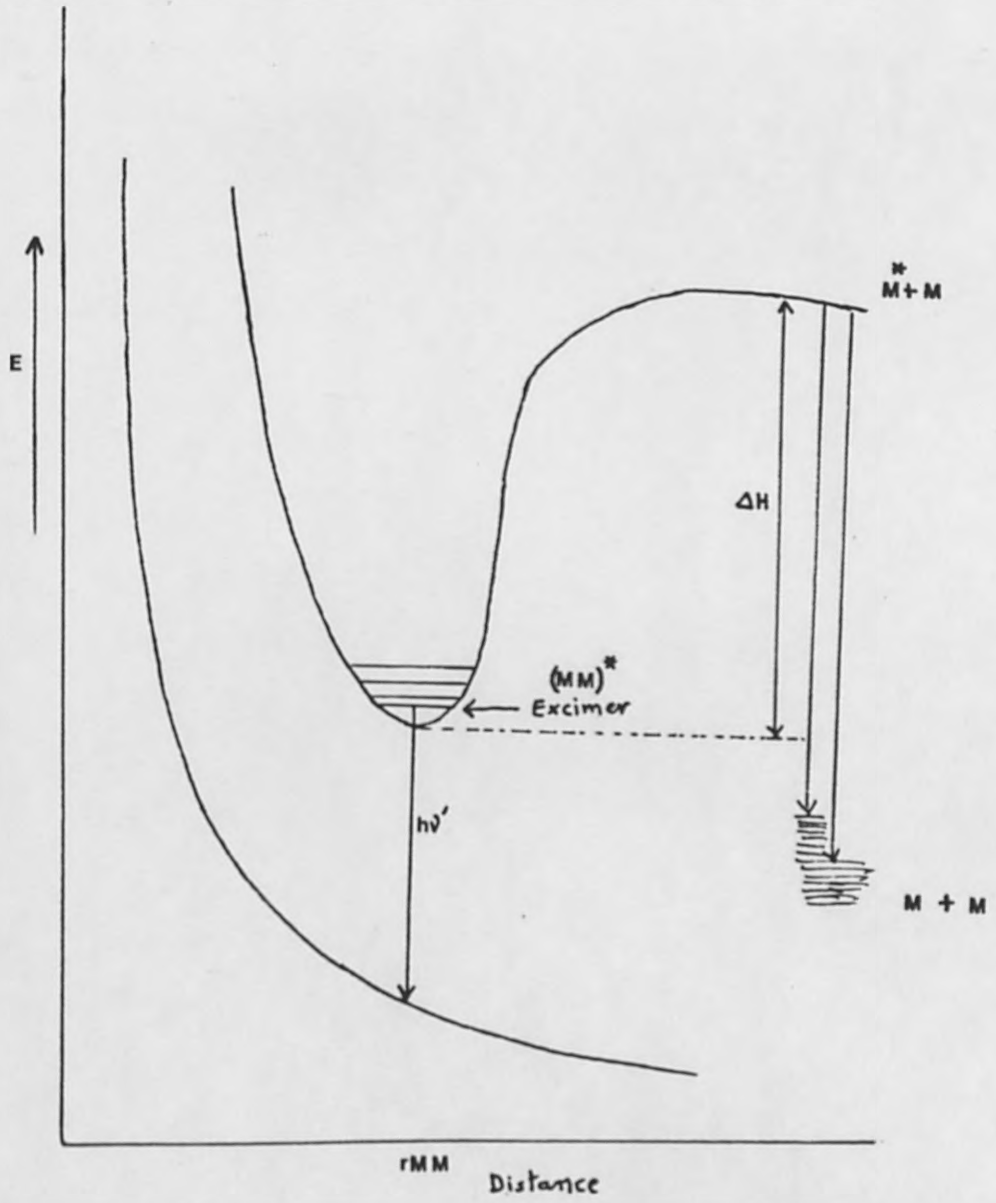


Figure 15: Schematic energy surfaces showing excimer formation and emission. The emission to the non-quantized ground state is structureless.

Excimers derived from aromatic hydrocarbons seem to adopt a sandwich structure. Excimers have zero dipole moments.

1.1.26 Exciplex formation:

This phenomenon is observed in solutions of mixed solutes. For example,[27] addition of diethyl aniline to a solution of anthracene in toluene quenches the fluorescence of the latter and replaces it by a new structureless emission at longer wavelengths. This is found to be due to the formation of an exciplex (excited complex) ^{1}(anthracence-diethylanilene)*. The exciplex formation can be depicted as follows:

$$M \xrightarrow{h\nu} M^* \xrightarrow{Q} \underset{\text{exciplex}}{(MQ)^*}$$

Exciplexes are polar entities. Weller explained this property by a simple molecular orbital treatment.[27] In an exciplex, an electron is transferred from one component D (donor), to another A (acceptor). Figure (16) and (17) illustrate the situation where the donor and the acceptor respectively are excited.

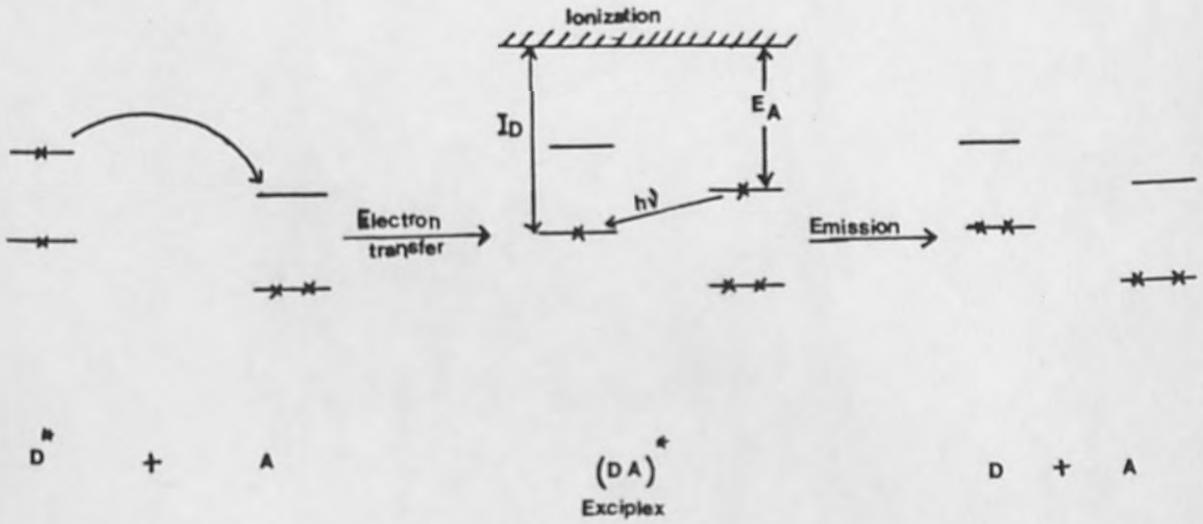


Figure 16: Molecular orbital treatment of exciplex formation and emission (donor excited).

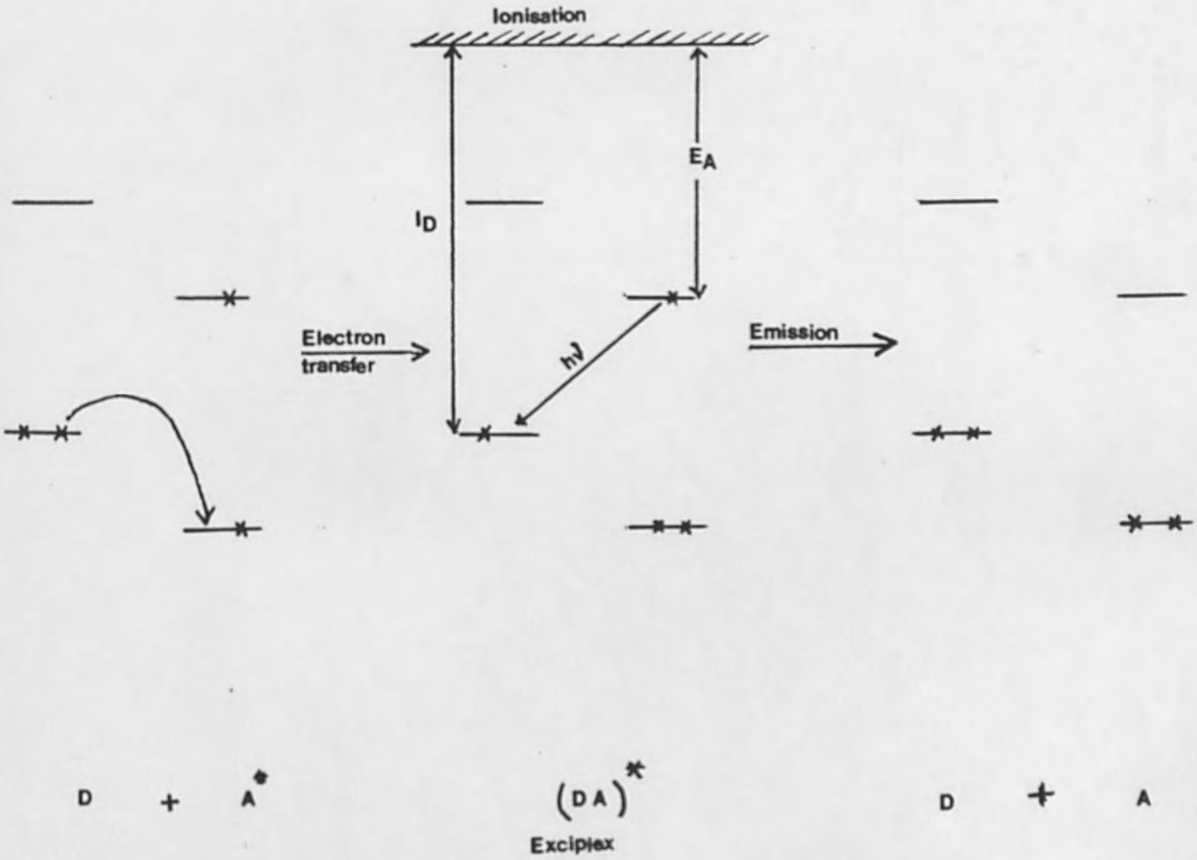


Figure 17: Molecular orbital treatment of exciplex formation and emission (acceptor excited).

1.1.26.1 Delayed fluorescence:

Delayed fluorescence in which the luminescence decays more slowly than normal 'prompt' fluorescence from the same molecule. The most closely investigated mechanisms for delayed fluorescence are triplet-triplet annihilation and thermally activated delayed fluorescence.

1.1.26.2 Triplet-triplet annihilation:

Under certain conditions the long lived triplets (T_1) may collide with one another in solution and "annihilate" each other,

simultaneously producing one molecule in the excited singlet state (S_1) and the other in the ground state (S_o). The fluorescence emission of S_1 may be observed and has a lifetime approximately half that of phosphorescence.[28] The accepted mechanism[29] is as follows:

$$S_o \xrightarrow{h\nu} S_1 \quad \text{absorption} \qquad (a)$$

$$S_1 \xrightarrow{K_f} S_o + h\nu' \quad \text{normal fluorescence} \qquad (b)$$

$$S_1 \xrightarrow{K_{isc}} T_1 \quad \text{intersystem crossing} \qquad (c)$$

$$T_1 \xrightarrow{K_p} S_o + h\nu'' \quad \text{phosphorescence} \qquad (d)$$

$$T_1 + T_1 \xrightarrow{K_5} X \quad \text{triplet-triplet annihilation} \qquad (e)$$

$$X \xrightarrow{K_6} S_1 + S_o \quad \text{spin allowed} \qquad (f)$$

$$X \xrightarrow{K_7} S_o + S_o \quad \text{deactivation} \qquad (g)$$

$$S_1 \xrightarrow{K_f} S_o + h\nu' \quad \text{delayed fluorescence} \qquad (h)$$

The important steps are equation (e) and (f) in which two excited triplets, on collision, redistribute their energies via the entity X so that one is promoted to S_1 and the other collapses to the ground state.

Energy transfer from donor triplets may be used to produce acceptor triplets, which upon annihilation will produce an excited singlet capable of emitting a photon of higher frequency (greater energy) than the absorbed light. The requirements for such a phenomenon

are met if the donor has an S_1 state which lies below that of the acceptor but a T_1 state which lies above that of the acceptor. The phenanthrene-naphthalene system fulfills this requirement.[30] The mechanism of sensitised naphthalene fluorescence is given as follows:

$$P_0 \xrightarrow{3500\text{Å}} P_1 \dashrightarrow P_3 \qquad \text{(i)}$$

$$P_3 + N_0 \longrightarrow N_3 + P_0 \qquad \text{(j)}$$

$$2N_3 \longrightarrow N_1 + N_0 \qquad \text{(k)}$$

$$N_1 \longrightarrow N_0 + h\nu \quad (3250\text{Å}) \qquad \text{(l)}$$

Where P and N refer to phenanthrene and naphthalene and the subscripts 0, 1, and 3 refer to ground, lowest singlet and triplet states respectively.

1.1.26.3 Thermally activated delayed fluorescence:

In this phenomenon, light absorption followed by intersystem-crossing and vibrational relaxation gives triplets in their zero-point vibrational level. Thermal activation through the energy gap ΔE followed by reverse intersystem crossing ($T_1 \rightsquigarrow S_1$) gives excited singlets which then fluoresce. These facts are explained by the mechanism depicted in Fig. (18).

The delayed fluorescence technique provides a powerful tool for examining the behaviour of relatively low concentrations of triplets in solutions. The flash photolysis technique is another alternative but it requires a high concentration of triplets. The delayed fluorescence provides information about the rates of all three intersystem crossings and permits triplet-triplet quenching to be observed directly.

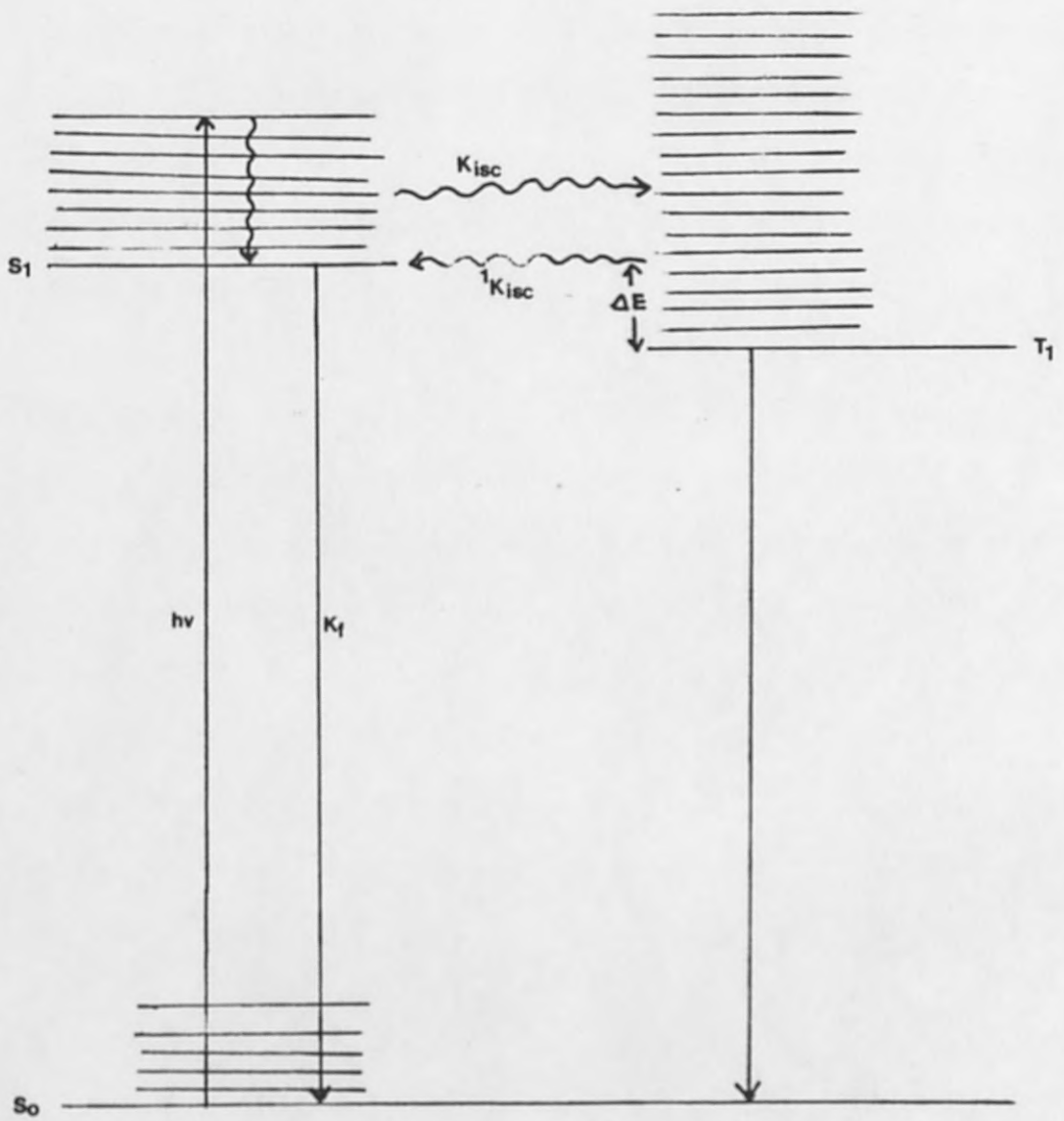


Figure 18: Energy levels for thermally activated delayed fluorescence.

1.1.27 Spin orbit coupling and heavy atom effect:

For organic molecules, spin-orbit interactions usually provide the major mechanism for intersystem crossing. Since the electron is charged and 'spinning' it is expected to have spin angular momentum as well as magnetic moment. The electron inverts its spin, i.e.

changes the direction of its magnetic moment in a S ⟶ T transition. Clearly this calls for a magnetic interaction. The required magnetic interaction is provided by the magnetic field produced by the orbital motion of the charged electron. The magnetic moment of the spinning electron becomes coupled to the orbital magnetic field and hence it is termed as 'spin orbit coupling'.

The spin orbit coupling cannot occur in an S orbital because an electron in an S orbital has an associated angular momentum of zero. Since the coupling of orbital and spin motion requires exchange of angular momentum and hence no spin orbit coupling is expected. Figure (19) which is an over simplified planar model of an electron in a P orbital. The magnetic torque (force) is generated by an electron travelling in an orbital which has a shape of "figure 8" about the nucleus, and a spin-flip can occur with a simultaneous orbital momentum change.

The spin-orbit coupling takes place only if (i) the orbital transition involved possesses the character of a $P_x \longrightarrow P_y$ orbital jump, for example $^1n\pi^* \longrightarrow {}^3n\pi^*$ (Fig. (20), and (ii) the orbital transition is localized on a single atom.

The triplet state produced under spin-orbit coupling can be written in the following form. Where s^K is the Kth singlet state and E_T and E_s are the energies of the triplet and the perturbing singlet states respectively. ψ_s^o and ψ_T^o are the wave functions of 'pure' singlet and triplet states respectively.

$$\psi_T = \psi_T^o + \Sigma_K \frac{\langle \psi_{sK}^o / H_{so} / \psi_T^o \rangle}{(E_T - E_{sK})} \cdot \psi_{sK}^o \qquad (m)$$

H_{so} is the Hamiltonian operator.

$H_{so} = K\,\zeta(L.S.)$

where L is the orbital angular momentum operator and S is the spin angular momentum operator, ζ is a factor dependent on the nuclear field.

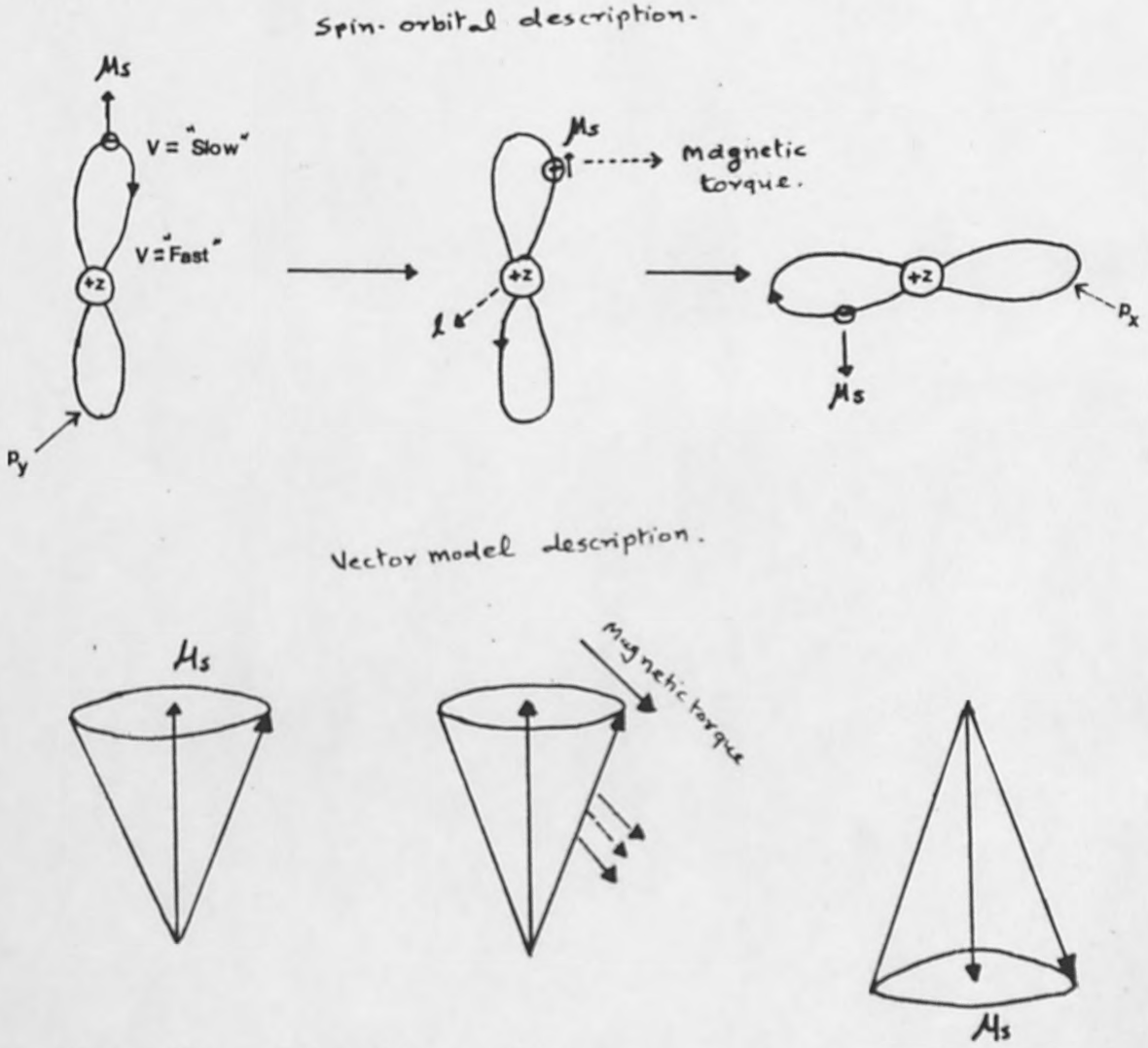


Figure 19: Spin orbit coupling.
μ_s = electronspin magnetic moment
L = orbital angular momentum

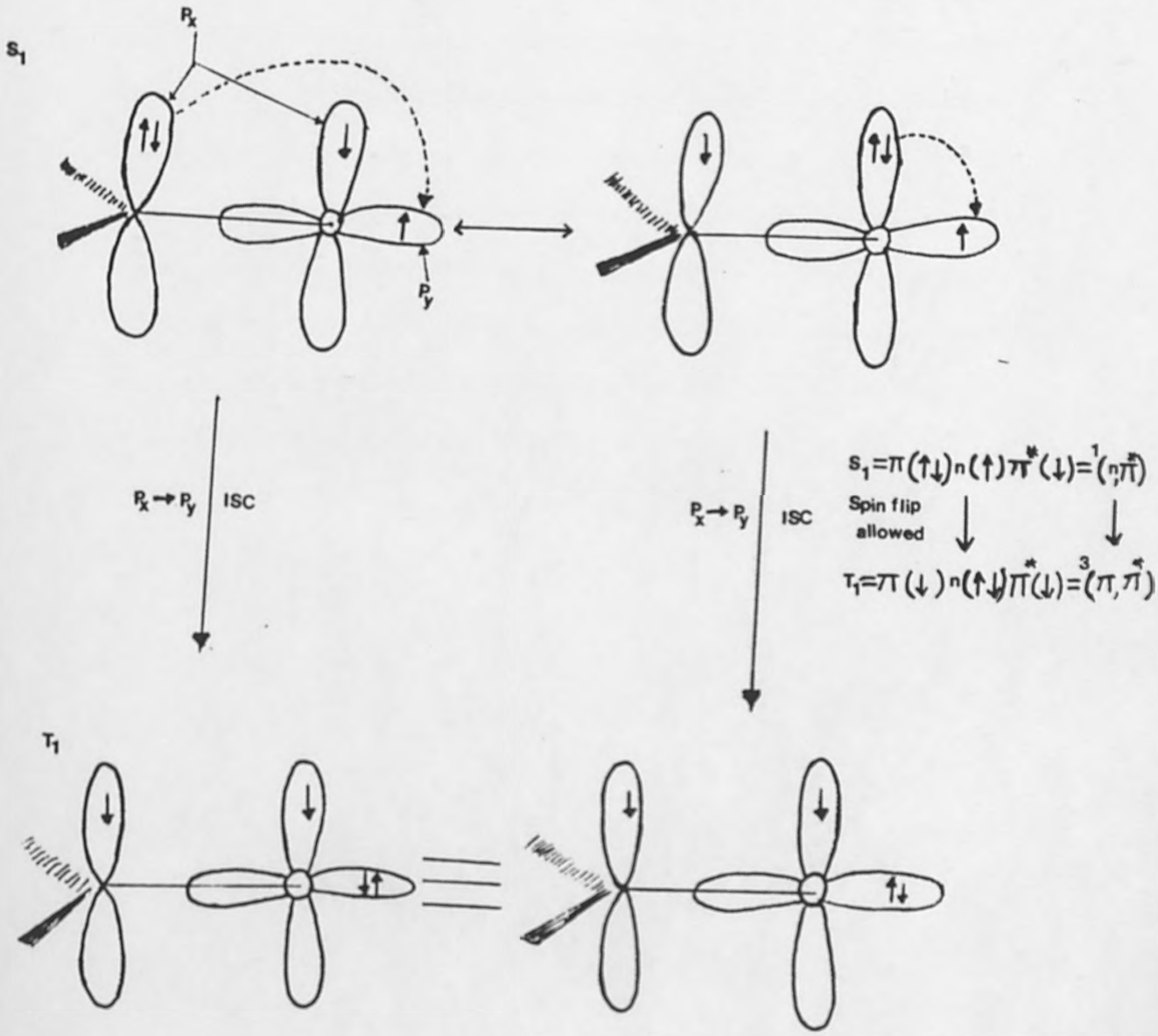


Figure 20: Quantitative orbital description for spin orbit coupling $^1(n,\pi^*) \longrightarrow {}^3(\pi,\pi^*)$ ISC in C=O group.

The probability of the S ⟶ T transition depends upon the energy gap between the states concerned and upon the size of matrix elements such as $< \psi^o_{sK} / H_{so} / \psi^o_T >$ in the above equation (m). This quantity increases very rapidly with increasing atomic number giving rise to the heavy atom effects.

The probability of electron spin flips would be increased if a heavy atom with high atomic number is present in the system. There are both internal and external heavy atom effects depending upon whether the heavy atom is incorporated into the molecule itself, or into the environment. The S $\longrightarrow$T absorption is greater in 1-iodonaphthalene than it is in 1-chloronaphthalene. This is due to an internal heavy atom effect. The dramatic enhancement of S $\longrightarrow$ T absorption in 1-chloronaphthalene in ethyl iodide solution over that observed in ethanol is due to an external heavy-atom effect.

1.2 Investigation of important properties of organized systems:

1.2.1 Surfactants:

A surfactant is a surface active material that contains both polar (or ionic) and non-polar moieties. A typical detergent (surfactant) structure is RX, where R is a hydrocarbon chain of 8-18 carbon atoms or some other hydrophobic residue, and X is a hydrophilic group.[31,32] There are usually four main types of detergents classified according to the nature of X; (i) non-ionic, (ii) cationic R^+X^- (e.g. cetyl trimethyl ammonium chloride), (iii) anionic $\overline{R}X^+$ (e.g. sodium lauryl sulphate) and (iv) zwitterionic (e.g. betaines).

1.2.2 Micelles:

The field of micellar chemistry is extremely large and diverse.[33] The word micelle has been used in a variety of ways. According to the Webster dictionary,[34] a micelle is a unit of structure built up from polymeric molecules or ions as either (a) an ordered region in a natural or synthetic fibre (as in cellulose, silk or viscose

rayon), (b) a highly associated particle of a colloidal solution (colloidal micelles of soaps and detergents - J.W. McBain) or (c) an organic colloidal particle ranging in size from one micron to one millimicron as found in coal and shales. The definition (b) is the one which concerns us and was first used in 1913 by J.W. McBain.[35]

The concept of micelles met with some resistance in the early days of its development before it was finally accepted, as can be realized from the following quotation of McBain.[36]

> "So novel was this finding that, when in 1925 some of the evidence for it was presented to the colloid committee for the advancement of science in London, it was dismissed by the Chairman, a leading international authority, with the words,
>
> 'Nonsense, McBain!'

Soon after, Hartley and many other scientists like Ekwall, Harkins, Debye, Mysels, Stigter and Overbeck contributed to the pioneering research of micelles.[33]

There are four principle types of synthetic surfactant micelles and they depend on the nature of the polar head group.

(1) Anionic: the surface active head group is an anion, e.g. as in potassium laurate $CH_3(CH_2)_{10}COO^- K^+$ and sodium dodecyl sulphate, $CH_3(CH_2)_{11} SO_4^- Na^+$.

(2) Cationic: the surface active head group is a cation, e.g. as in hexadecyl (cetyl) trimethyl ammonium bromide, $CH_3(CH_2)_{15} \overset{+}{N} (CH_3)_3 Br^-$ and dodecyl pyridinium chloride.

(3) Nonionic: the water soluble moiety contains hydroxyl groups or a poly oxy ethylene chain, e.g. polyoxyethylene p-t-octyl phenyl ether $C_8H_{17}C_6H_4O(CH_2CH_2O)_{10}H$.

(4) Ampholytic or zwitterionic: in this type of surfactant micelle the molecule can behave as either an anionic, non-ionic or cationic species, depending on the pH, e.g. the Zwitterionic form of N-dodecyl-N,N-dimethyl betaine, $C_{12}H_{25}\overset{+}{N}(CH_3)_2CH_2COO^-$.

1.2.3 The dynamic structure and shape of the micelles:

The fascinating property of an aqueous surfactant solution is the phenomenon of self organization above a certain critical concentration (CMC), whereby different molecules associate spontaneously to build up structural entities of colloidal dimensions. The interior of the micelle contains the hydrophobic (water insoluble) alkyl chain of the detergent while the hydrophilic (water soluble) head groups are located at the surface and are in contact with the aqueous environment. The micellar systems are microheterogeneous in character. The electrostatic potential and the polarity prevailing in the interior of aggregates differ from those in the bulk aqueous phase.

A cross section of an idealized surfactant micelle is given in Fig. (21).

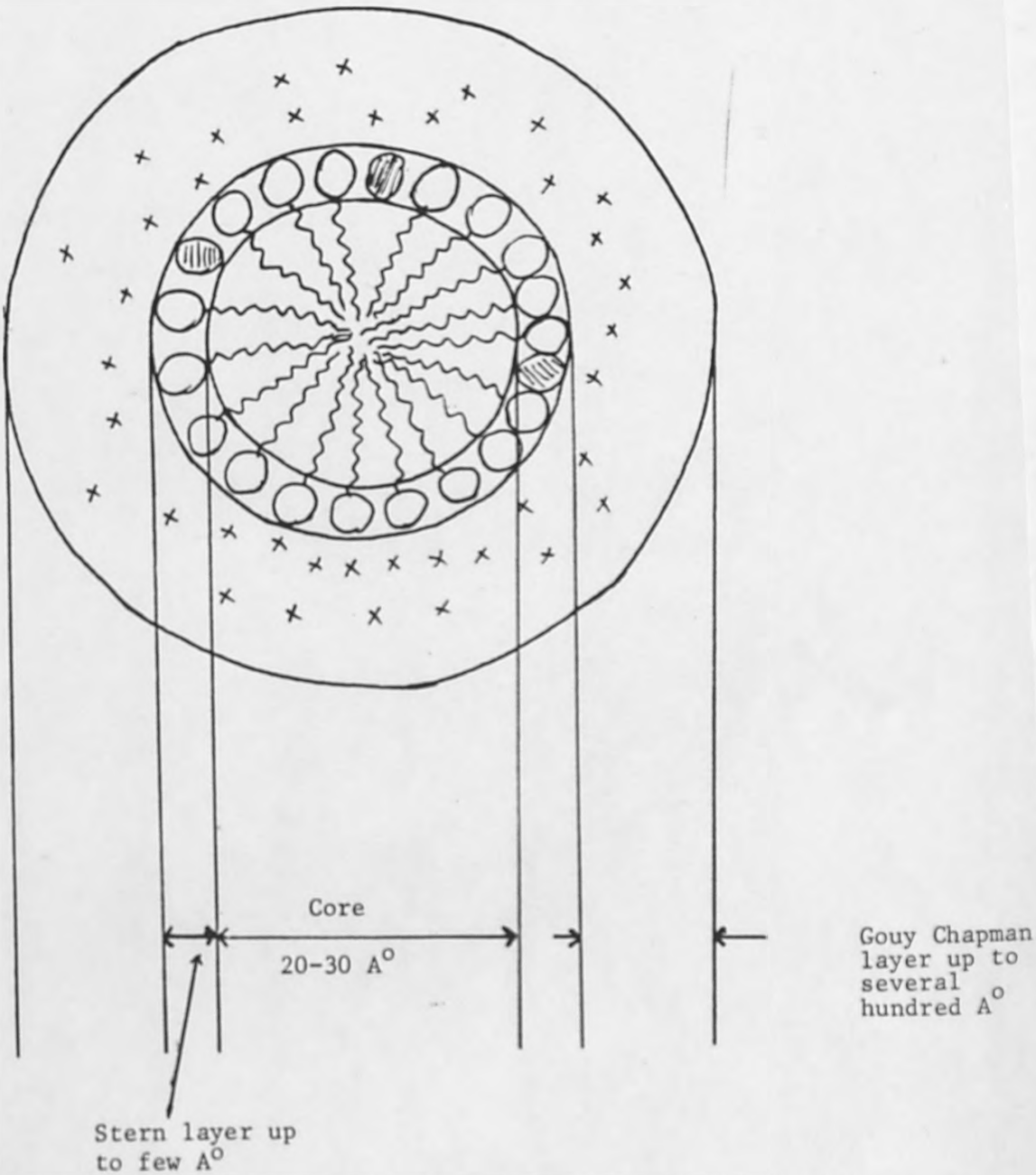


Figure 21: A two dimentional schematic representation of the regions of spherical micelle.

Micelle core: Contains the hydrocarbon tails of the detergent molecules (10-28Å).

Boundary or stern layer: Consists of the detergent head groups and bound gegenions, few Å.

Outside or Gouy chapman layer: Consists of unbound counter ions up to several hundred Å.

An average shape of a micelle may not necessarily be spherical as shown in Fig. (21), e.g. it can also be either ellipsoid or irregular in shape.

The amphipathic (ionic or polar derivatives of hydrocarbons) molecules have a tendency to collect at any interface where the hydrophobic groups can be partially or completely removed from the contact of water and the hydrophilic group can remain intact with bulk water. These general tendencies account for their surface-activity, i.e. the ability to adsorb to air-water or oil-water interfaces and to surfaces of hydrophobic solids such as carbon or to macromolecules such as proteins. The same dual tendencies and the built-in asymmetry of the molecules allows them to form soap films and bilayers (Fig. (22)).

The balance of attractive forces between the non-polar parts of the monomer units and repulsive forces between the head groups limits the size of surfactant micelles. The average number of monomer units in a micelle (the aggregation number 'n') can range from 10 to 100 for ionic micelles and to greater than 1000 for nonionic micelles.[37,38] The higher aggregation number for nonionic micelles is due to the steric repulsion between head groups being less than the electrostatic repulsion between ionic head groups of ionic micelles.

Micelles are usually considered to be spherical and of uniform size at concentrations within an order of magnitude of the CMC. These assumptions cannot be absolutely accurate and it is now accepted that micelles are often polydisperse and are not necessarily

spherical.[39] The micelle size can be influenced by temperature[40] pressure,[41] ionic strength,[42] charge,[43] hydrocarbon chain length,[44] head group[45,46] and the type of counter ion.[47]

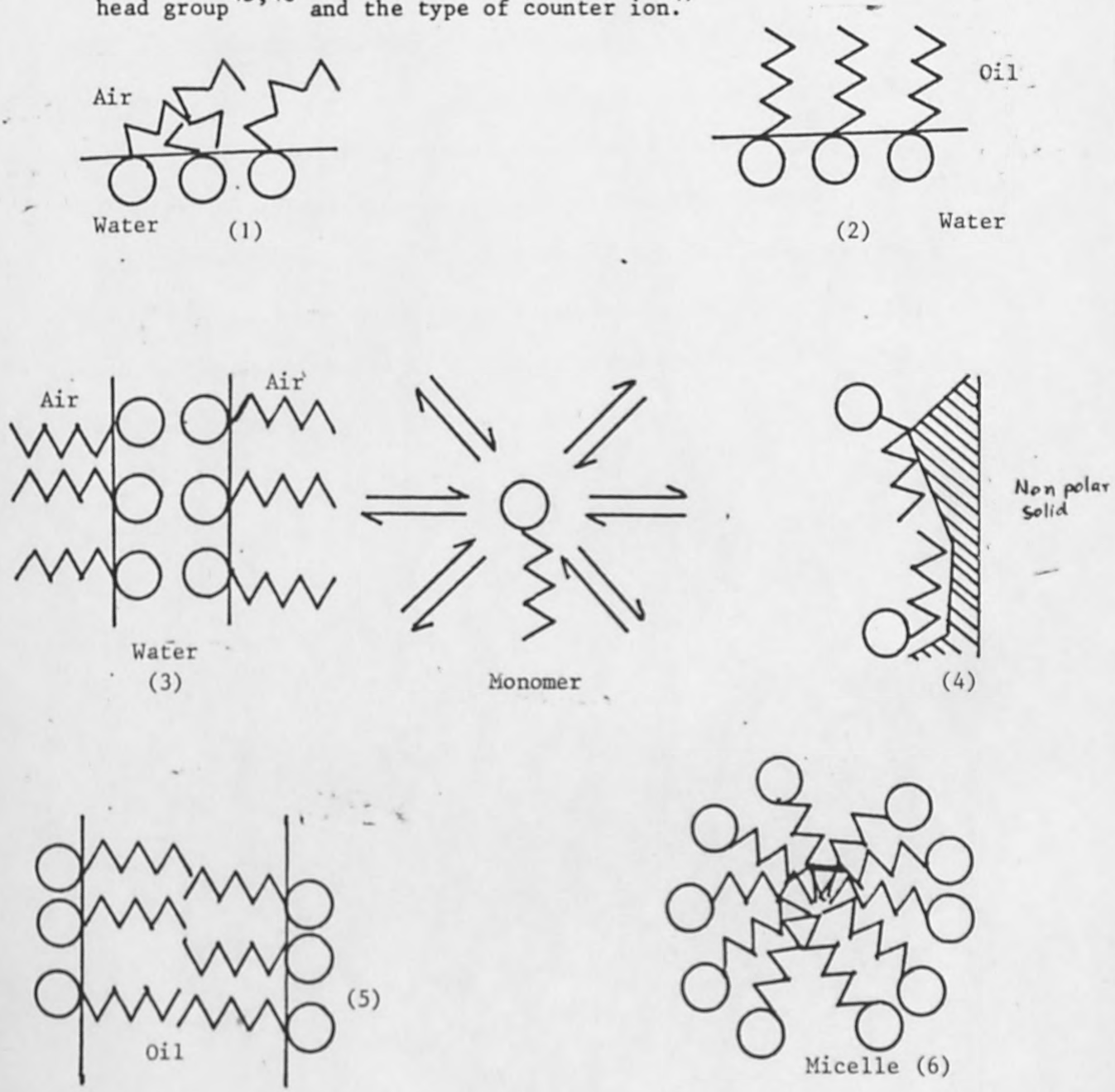


Figure 22 Schematic representation of surface activity and micelle formation. (1) Air-water interface (2) Oil-water interface (3) Soap films (formation of organized structures (4) Adsorption to non-polar solids (as also to polymers and proteins), (5) Formation of bilayer (a model for membranes), (6) Micelle.

→ Hydrophilic and
→ Hydrophobic end..

Increasing the hydrocarbon chain length causes an increase in the size of a micelle. For ionic surfactants the micellar size falls with increasing temperature.[48] This is due to thermal agitation decreasing adhesion between monomer molecules and so shifting the equilibrium in favour of monomeric species. Micelles of nonionic surfactants increase rapidly in size with rising temperature.[49,50] This is probably due in part to increased monomer hydrophobicity and in part to geometric factors based on the different configurations of polyoxyethlene chains at different temperatures affecting the mode of packing of the monomers in the micelles.

The equilibrium between micelles and monomers is generally very fast. This so-called 'monomer jump' is diffusion controlled and occurs in about 10^{-9} seconds.[51]

1.2.4 Critical micelle concentration:

Knowledge of critical micelle concentration (CMC) is vital to any study of surfactant chemistry. On increasing the concentration of a surfactant solution there is an initial concentration range over which micelles will be formed. The CMC is the concentration at which micelle formation first becomes detectable.[33,52] Many physico-chemical properties of surfactant solutions can be used for the determination of the CMC. Some physico-chemical properties if plotted against the concentration of surfactant solution appear to change at a different rate above and below the range of CMC. The concentration at which the micelles appear corresponds to the change in the slope of the plot in Fig. (23).

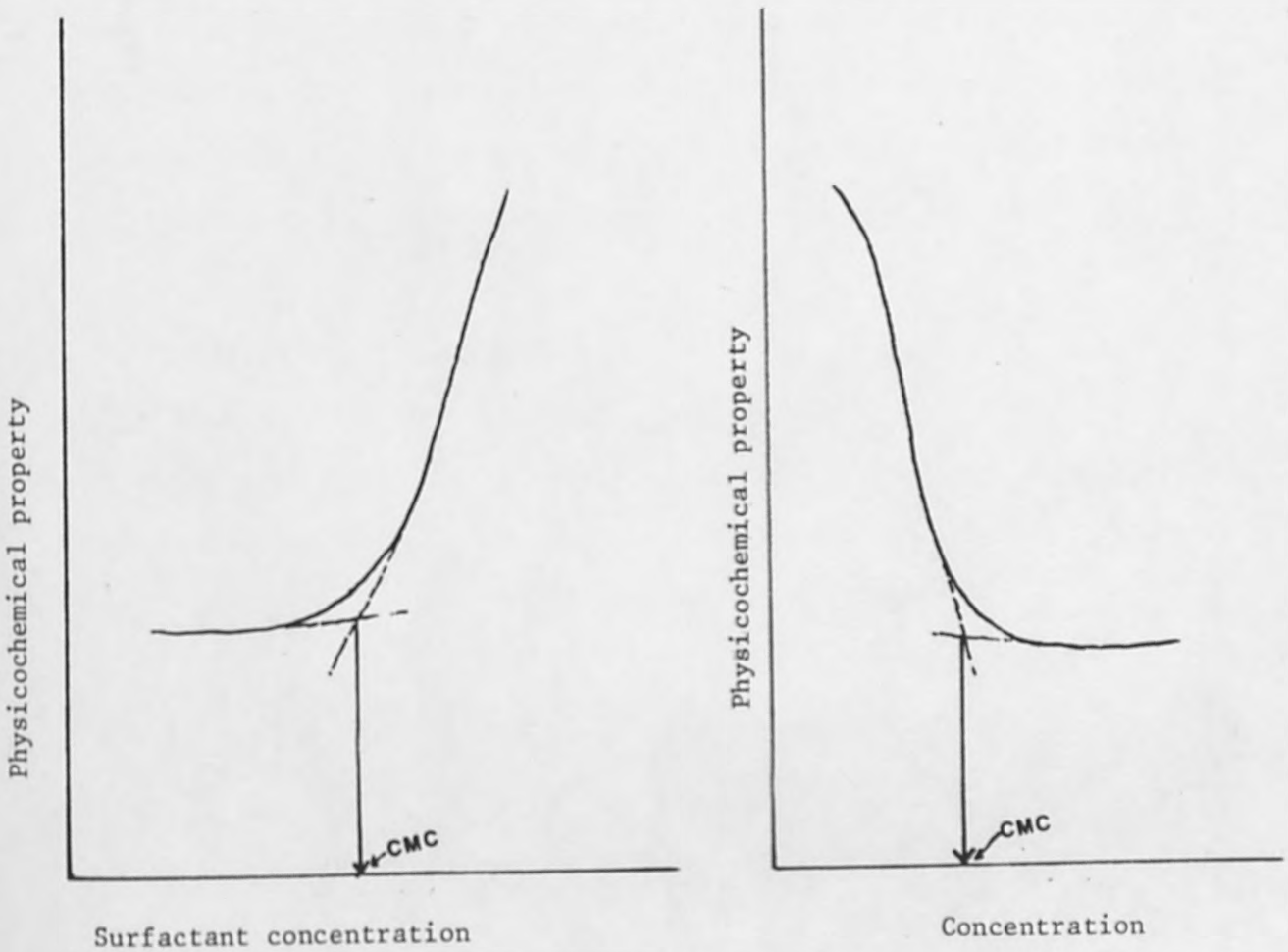


Figure 23: A plot of surfactant's physical property against its concentration.

1.2.5 Methods of measuring the critical micelle concentration:

There are a number of methods which can be applied to the determination of the CMC of surface active agents. The experimental methods whereby the CMC of solutions of surfactants may be determined are briefly described below.

1.2.5.1 Electrical conductance:

In this method the conductance of ionic surfactants is measured as a function of the surfactant concentration. There will be an abrupt change in equivalent conductivity of the solution of surfactant at the CMC. The measurement of electrical conductance of the solution of surface active agents is the most reliable data in terms of accuracy and of quantity and hence it outweighs all other measurements of the properties of colloidal surface active agents.[69]

1.2.5.2 Transference number:

The transport number of solution of the surfactant is measured as a function of its concentration. The mobility of the micelle forming ion changes at the CMC and consequently its transport number changes. Thus the CMC of the detergent solution can be determined.[70]

1.2.5.3 Dye absorption:

The CMC is determined using a change in dye colour. The amount of dyestuff is kept at a constant concentration (1×10^{-5} M) while the concentration of detergent solution is gradually decreased. A marked change in the colour of the solution will occur at the CMC because of the total solubilization of the insoluble dye particles in the micellar solution.[53] With anionic surfactants pinacyanol chloride and rhodamine G may be used and with cationic surfactants sky blue FF, eosin, fluorescein and dichlorophenol indophenol may be used. The CMC can be affected by the presence of dye ions[53] but the amount of dyestuff used is usually too small to change the CMC appreciably. The disadvantage of this method is the ambiguity of CMC determinations at high salt or alcohol concentrations. The

advantage of this method however, is that it provides rather accurately a measure of small changes or differences in the CMC.[54]

1.2.5.4 Solubilization:[55]

The solubility of either hydrocarbon or dyestuff remains almost constant until the concentration of surface active agent reaches the CMC and then it increases rapidly and almost linearly at the beginning. The CMC values determined by this method are lower than those observed from other measurements because of the presence of added hydrocarbons or dyestuff. The saturation limit of solubilization of liquid or dyestuff by a solution of detergents may be followed conveniently in terms of the optical density of the solution. Excess of organic liquids are readily emulsified by surfactants and can be seen when saturation is reached. The end point may be determined instrumentally either by transmission measurements or light scattering.

1.2.5.5 Surface tension[56,57]:

The surface tension of aqueous solutions of surface active agents decreases very rapidly until the CMC is reached and then stays constant above the CMC. The CMC can be determined from the inflection in the plot of the surface tension vs. log concentration of surfactant. Since this method can be used successfully with purified nonionic surfactants it is particularly valuable.[71]

1.2.5.6 Refractive index:

The use of refractive index in the determination of CMC has been demonstrated by Hess et al.[58] and Klevens.[59] As this method does

not involve the addition or the application of a strong external field or force no change in CMC can occur throughout the experiments. The method can be applied to any type of surfactant using any kind of solvent. Careful temperature control and accurate determination of the concentration of the solution are very necessary requirements for this method.

1.2.5.7 Light scattering:

The aggregation number can be determined by this method. The aggregation of surfactant is reflected in the increase of scattered light. The CMC can be determined from the abrupt increase in the slope of the plot of light scattering vs. concentration. Very careful elimination of dust particles and other impurities from the surfactant solution is necessary to obtain accurate results. Light scattering measurements are useful because the aggregation number can be obtained from these measurements. They also afford a measure of dissymmetry of a particle[60] and of the amount of charge at the centre from the slope of scattered light vs. concentration.[61,62]

1.2.5.8 Osmotic pressure:

The measurement of osmotic pressure can provide direct and important information relating to the CMC and the properties of the solutions of surfactants, provided various experimental problems can be overcome. Hess and Suranyi have attempted to overcome the difficulties of finding a suitable semi-permeable membrane whereby the solution is placed in a container and the solvent is constrained in a capillary or in a series of capillaries, such as a fritted disc. Hence, the liquid-vapour surface is used as the membrane and the pressure on the

solvent is adjusted until vapour equilibrium is attained between solvent and solution; the criterion of equilibrium is the absence of distillation.[55]

1.2.5.9 Vapour pressure:

The CMC of the surfactant solution is determined from the graphs of vapour pressure depression vs. concentration. The dew point method using thermistors has been applied.[63,64] Thermistors are thermally active resistors and act as the temperature sensing elements. They are incorporated in with an A.C. current to measure the difference in resistance. In this method, a drop of water is placed on one resistor and a drop of the solution of surfactant on the other and both immersed in a humidified chamber. The resistance of the thermistor is changed by the temperature difference assumed by the two drops of water and the surfactant solution respectively. A calibration curve is determined by measuring the resistance changes with various concentrations of a salt whose thermodynamic properties are known (usually potassium chloride). The calibration curve can be plotted in the form of Δr vs. νgm where Δr = the observed resistance change, ν is the number of ions given by the standard salt, g is the osmotic coefficient and m is the concentration. Such a plot is a straight line within experimental error. From the Δr observed for the surfactant under investigation νgm is read from the calibration curve and g can be calculated from the known νm of the surfactant solution. For practical purposes g (the osmotic coefficient) may be defined as the observed lowering of the vapour pressure divided by the ideal lowering of the vapour pressure.

1.2.5.10 Solubility:

The solubility of ionic surfactants at lower temperatures shows a steady increase with rising temperature, but if solubility becomes equal to the CMC - i.e. if micelle formation occurs - there will be an abrupt increase in the solubility-temperature relation. The temperature at which this abrupt change occurs is known as the 'Kraft point' and the concentration at which it occurs is the CMC at that temperature. The determination of solubility has been made using pyrex test tubes containing water and surfactant to form an excess of solid phase. The equilibrium was approached from the unsaturated and supersaturated states. The solubility was calculated by collecting the surfactant after evaporation of the saturated clean solution of the surfactant. The calculation was made as the number of grammes of surfactant dissolved in 100 grammes of water. The disadvantage of this method is that, in some cases, it takes a very long time to approach an equilibrium state.[65,66]

1.2.5.11 Sound velocity:

The CMC can be determined from the break point of the velocity vs. concentration of surfactant graph.[67] The velocity of the surfactant solution can be measured by an acoustic interferometer.[68]

1.2.5.12 Diffusion:

Mysels and Stigter[72] measured the diffusion coefficient by tagging the micelle with water-insoluble radioactive dye. The rate of micellar diffusion is related to the size and shape of the hydrated micelle. The micellar diffusion can be plotted against the concentration of the surfactant and hence CMC can be determined.

1.2.5.13 Viscosity:

The CMC of surfactant can be determined by plotting a viscosity vs. concentration graph. A viscometer is used for the measurement of the viscosity of the surfactant solution. Wright and Tartar have measured the viscosity and density of sodium dodecyl sulphonate detergent as a function of concentration and temperature.[73]

1.2.5.14 Electrophoretic mobility:

The electrophoretic mobility of poly vinyl acetate emulsions in the presence of various emulsifying agents and salts has been studied by Munro and Sexsmith.[74] The CMC of these emulsions have been determined by plotting the graph of mobility vs. concentration. Discontinuities in the curve occur at the CMC of the surfactant.

1.2.5.15 Ultraviolet and infrared absorption:

The ultraviolet absorption spectra of the paraffin chain quaternary ammonium iodides (e.g. dodecylpyridinium iodide) in aqueous solution undergo an abrupt change in terms of wavelength at the CMC.[75] The CMC of alkyl ammonium carboxylates in organic solvents was also determined from the concentration dependence of the ultraviolet and infrared absorption spectrum.[76] Abrupt change also occurs in the plot of molar extinction coefficient vs. the surfactant concentration at the critical micelle concentration of the surfactant.[75]

1.2.6 Application of photoluminescence techniques in micellar systems:

The photophysics of organic molecules that are solubilized in micelles provide information on the composition, structure and dynamics of

the micellar environment. In turn, photochemical reactions in micelles display characteristics that distinguish them from comparable reactions in homogeneous solutions.[33,37,52,77] The photophysical methods offer advantages such as simplicity, wide scope and extreme sensitivity and often require a very low solute (probe) concentration. The following properties of the luminescent probes are measurable from the emission of a lumophore.[78]

(1) Emission spectrum (intensity of emission as a function of wavelength for a fixed absorbed intensity and fixed excitation wavelength).

(2) Excitation spectrum (intensity of emission at fixed wavelength as a function of absorbed intensity and variable excitation wavelength).

(3) Luminescence decay (fall-off of the intensity of the emission spectrum as a function of time after an excitation pulse).

(4) Quantum yield of luminescence (the number of photons emitted relative to the number of photons absorbed).

(5) Polarization of luminescence (the orientation of the emitted light vector relative to the orientation of the absorbed light vector).

(6) Quenching (a decrease in luminescence intensity or increase in decay rate as a function of added solute or changing environment).

(7) Sensitization (an increase in luminescence intensity or decrease in decay rate as a function of added solute or changing environment).

(8) Energy transfer (electronic excitation energy transferred from an initially excited lumophore to a second lumophore).

The properties of micellar aggregates have been investigated by applying the above described properties of the luminescent probe.[78-81]

Luminescent probes act as sensors and 'reporters' of micro-environments, as in this process excitation of the probe molecule takes place and then emission of photons occurs which 'reports' the microenvironment of the system as shown in Fig. (28a).

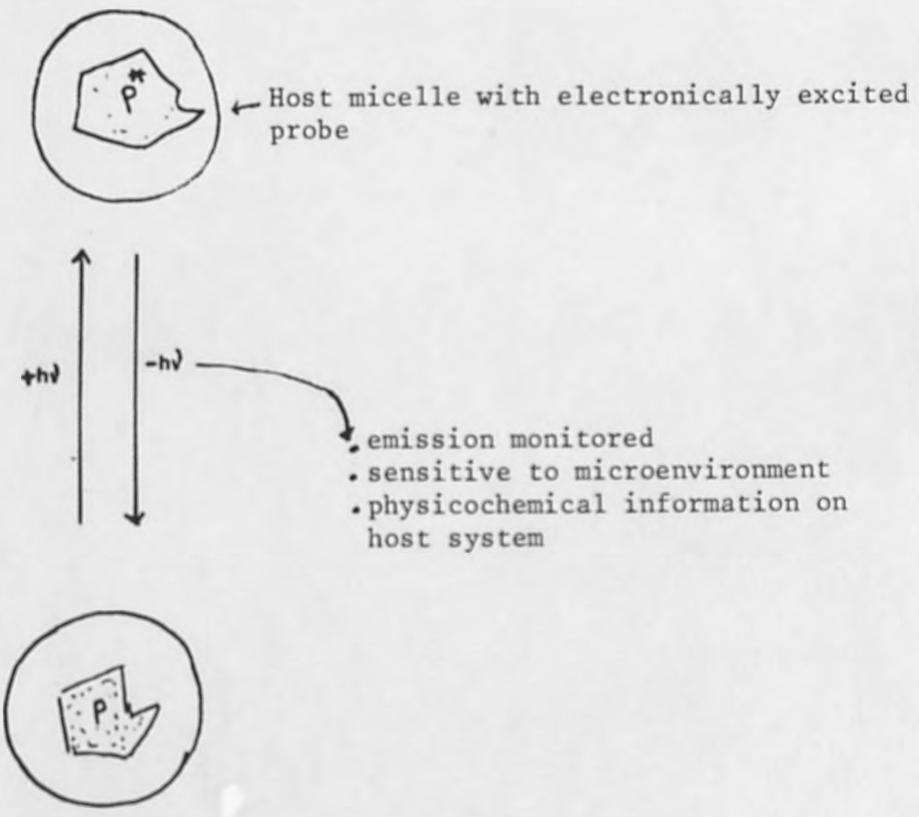


Figure 28a: Luminescent probe as sensor and reporter of microenvironment.

Luminescent probes can provide information for characterisation of microenvironments when they exhibit a particular affinity for a given environmental site, whereas others can be used to examine a variety of environments (e.g. micellar environment and bulk aqueous environment).

Fluorescent probes have been widely employed in the study of the structures and dynamics of many systems, e.g. to determine CMC, polarity, microviscosity, diffusional property, entry-exit rates, aggregation numbers and water penetration in the micelle core.

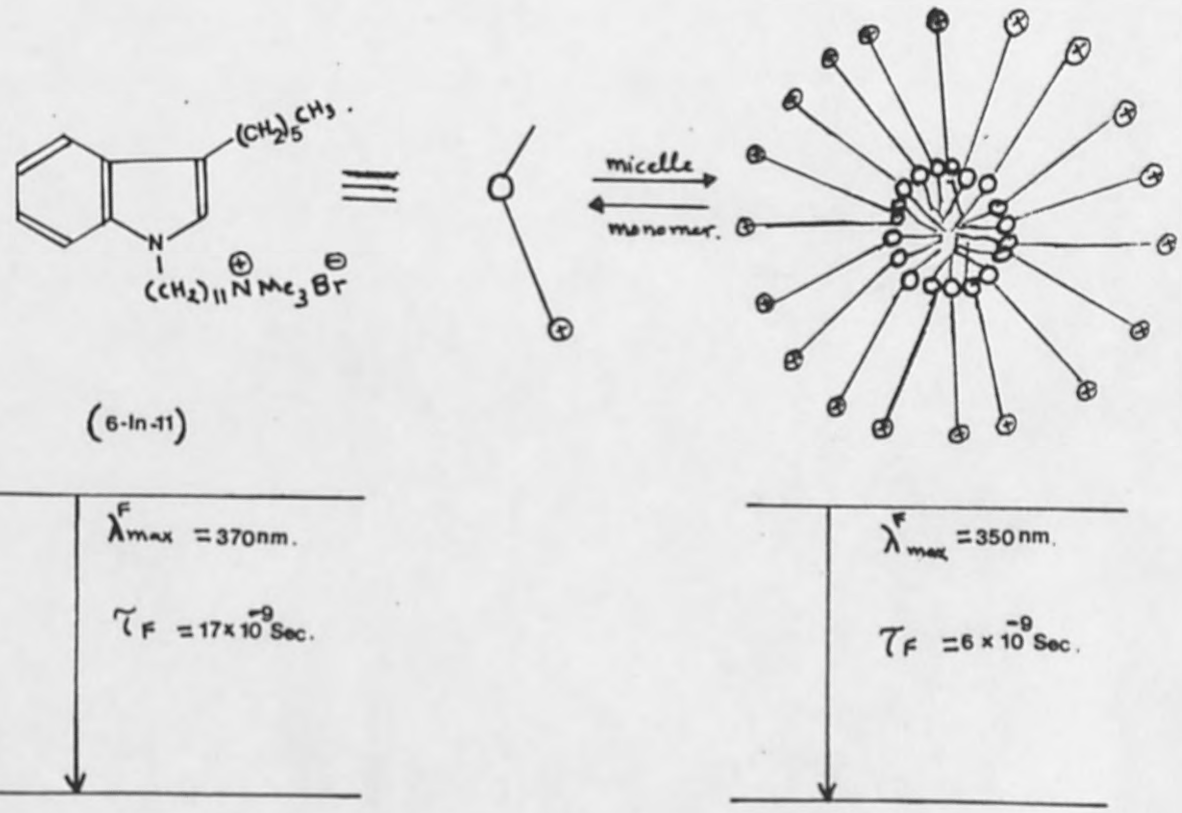
1.2.7 Determination of CMC of micellar systems by fluorescent probes:

The nature of the microenvironment of the probe can often be assessed by examination of the absorption and emission spectra of the probes. The environment can affect the fluorescence excitation and emission spectra, vibrational structure, shift in the position of emission wavelength maximum, quantum yield of fluorescence and lifetime of the fluorescence.

A probe when incorporated into the liquid like hydrocarbon centre of a micelle (micelle core) will fluoresce at shorter wavelengths than if it is located in the aqueous environment, which is found at the surface of the micelle.

It is possible to synthesise detergents containing a 1,3-di-alkyl indole nucleus. These possess a luminescent probe (the indole nucleus) as an integral part of their structure. The fluorescence

from the indole chromophore in aqueous or polar media (e.g. water, ethanol) occurs towards the red of that produced with non-polar solvents, for example, 1,3-dialkyl indoles show a fluorescence wavelength maximum at 305 nm and 370 nm in cyclohexane and water respectively. The fluorescence lifetimes of indoles are strongly solvent dependent (4×10^{-9} sec and 16×10^{-9} sec in cyclohexane and water respectively).[82,83] This property of the fluorescence has been employed in the determination of the CMC of surfactants.



(6-In-11)

The CMC of host surfactant hexadecyl trimethyl ammonium bromide (HDTBr) was determined by adding HDTBr to dilute aqueous solution (10^{-5} M) of (6-In-11) indole compound.[82] This caused a sudden shift in the fluorescence λ_{max} of the indole (6-In-11) when the concentration of the host surfactant approached its CMC. The inflection point of the curve of the plot of surfactant concentration vs. fluorescence wavelength maximum of the chromophore occurs at a concentration of HDTBr (8.8×10^{-4} M) which is very close to the known[52] CMC of HDTBr (9.2×10^{-4} M). The fluorescence lifetimes of indole (6-In-11) as a function of concentration of HDTBr is shown in Table 1. This also indicates the dependence of the fluorescence lifetimes on the detergent concentration. The CMC of decyl trimethyl ammonium bromide was also determined as above using fluorescence λ_{max} vs. the host surfactant concentration. The concentration of chromophore (6-In-11) was kept at a very low value ($\sim 10^{-5}$ M).

Table 1

Dependence of (6-In-11) fluorescence lifetimes (τ_F) upon HDTBr concentration[a]:

[HDTBr] M	$\tau^{360\ nm}$
0 M	17 nsec
5×10^{-4} M	18 "
9.2×10^{-4} M	10 "
1.4×10^{-3} M	9 "
2.7×10^{-3} M	9 "

a: [6-In-11] = 2×10^{-5} M or less. Value ± 1 nsec.

Turro and Schore[82] have also prepared 1,3-dimethyl indole (DMI), N-butyl,3-methyl indole (BMI), 11-(3-methyl-1-indolyl) undecyl trimethyl ammonium bromide (1-In-11) and 6-(3-hexyl-1-indolyl)-hexyl-trimethyl ammonium bromide (6-In-6). Their fluorescence properties were investigated, e.g. fluorescence wavelength maximum and fluorescence lifetime in the presence of different host surfactants, e.g. tetramethyl ammonium bromide (TMABr), hexa-decyl trimethyl ammonium chloride (HDTCl) and HDTBr.

These indolic compounds show similar behaviour in dilute aqueous solutions having λ^{F}_{max} = 371 ± 1 nm and τ_F = 18 ± 2 nsec. Addition of HDTBr and HDTCl have no effect on fluorescence spectra of the above indolic compounds until the CMC is reached, at which point a gradual shift of fluorescence λ_{max} to shorter wavelength is seen. At high HDTBr and HDTCl concentrations (above the CMC) the spectra of all four indole derivatives show a fluorescence λ_{max} = 354 ± 1 nm and τ_F = 9-10 nsec (Table II).

Wolf[84,85] has reported the measurement of quantum yields of the blue fluorescence of Acridine in alkaline aqueous solutions of anionic, cationic and nonionic detergents. The CMCs were determined using values of fluorescence quantum yields determined for different surfactant concentrations.[85] 4-Cyano-4'-propyloxy biphenyl and 4-cyano-4'-octyloxy biphenyl compounds have also been employed as fluorescent probes to determine the CMC of different cationic, anionic and nonionic surfactants by plotting a graph of the fluorescence wavelength maximum against the concentration of the surfactants.[86]

Table II

Fluorescence data for aqueous solutions of indoles

Compound[a]	Additive[b]	λ^F_{max} [c]	τ_F [d]
DMI	-	372	16
"	TMABr	371	17
"	HDTCl	358	10
"	HDTBr	355	9
BMI	-	371	17
"	TMABr	372	17
"	HDTCl	355	9
"	HDTBr	352	10
(1-In-11)	-	371	17
"	TMABr	371	16
"	HDTCl	357	10
"	HDTBr	353	10
(6-In-6)	-	370	18
"	TMABr	370	18
"	HDTCl	355	9
"	HDTBr	353	10

a: Indole concentrations 1.4 to 2.0 x 10^{-4} M.

b: Additive concentrations 2.5 to 2.7 x 10^{-2} M.
TMABr = tetramethylammoniumbromide.

c: Values in nm, ± 1 nm.

d: Values in nsec ± 1 nsec.

The CMCs of cationic surfactants containing a phenoxy group located at three different positions on long alkyl substituents of the ammonium cation and cetyl trimethyl ammonium bromide were determined by employing the fluorescent probes 4-methyl, 7-anilino coumarin (MAC) and 4-methyl, 7-diethyl amino coumarin (MDC). The CMCs were determined by plotting graphs of λ^{F}_{max} and fluorescence intensity against the concentration of the surfactants.[87]

Relative intensities of vibrational structures of the fluorescence spectrum are sometimes perturbed by solvent interactions that may occur with the chromophore of the molecule, and this effect is called the 'Ham effect.'[88] The fluorescence and absorption spectra of organic molecules such as benzene or pyrene show mixed polarizations because of the vibronic coupling between the first (S_1) and second (S_2) singlet excited states. With pyrene, a strong solvent dependence was shown by its monomer fluorescence for the various vibronic (fine) structure intensities. In the presence of a polar solvent there is an enhancement in the intensity of the 0—0 band at the expense of others. This property of pyrene has been employed in the fluorescent probe studies of different micellar systems as a function of the surfactant concentration. Hence the CMC of the surfactants were determined using this strong peturbation of the vibronic band which gave rise to variations in the pyrene monomer fluorescence.[89]

The CMC values of different surfactants obtained by the fluorescence method[82,84] were in agreement with the CMC values determined by other methods,[52] for example, electrical conductivity,[161] spectral change of dye[162] and solubility method.[163]

Although the fluorescent probes provide a useful and convenient method for the determination of the CMC of the surfactants caution should be taken when polar molecules are used as micelle probes, because of probe surfactant interactions well below the CMC. For example, the fluorescence from 1-dimethyl-amino naphthalene-5-sulphonyl glycine (115) was gradually enhanced and blue shifted (30-35 nm) by the addition of cetyl trimethyl ammonium bromide below and up to the CMC of the latter. No further changes were noted when CTAB was added above its CMC.[90] The magnesium salt of 8-anilinonaphthalene-1-sulphonate (116) gave a very low estimate of the CMC of sodium lauryl sulphate, possibly because of metal promoted probe-surfactant interaction.[91]

Pyrene-3-carboxaldehyde (117) is also an environmentally sensitive polar fluorescent probe (in methanol λ^{F}_{max} = 450 nm, with ϕ_F = 0.15, in hexane, λ^{F}_{max} = 410 nm, with ϕ_F = < 0.001).[92] However, a recent reexamination[93] suggests that changes in the fluorescence intensity and wavelength maximum of Py-CHO (117) are dependent on the protic or aprotic character as well as polarity of the medium. It was pointed out by the authors[93] that the behaviour of the polar probes such as Py-CHO may be difficult to interpret in the complicated micro-environment of a micelle. The non-exponential decays of Py-CHO were also noted in ethanol/water solvent mixtures.

Probe-surfactant interactions have been shown to increase with increasing hydrophobic structure in the probe. The uncharged merocyanine dyes (118) with alkyl groups longer than n-butyl show appreciable changes in their absorption spectra with added SLS

below its CMC.[94] From quenching of the fluorescence of a series of cationic pyrene derivatives (119) by the surfactant nitroxyl radical (120) it was concluded that undecyl derivative (n=11) (but not n=1 or n=5) associates with surfactant nitroxyl radical (120) at concentrations of the latter below its CMC.[95] The electronic and e.s.r. spectral evidence for the formation of mixed aggregates of surfactant nitroxyl radical (120) and sodium 5-(1-pyrenyl)pentanoate (121) in dilute (10^{-5} M) aqueous solutions in the mole ratio of 2:3 were also reported.[96]

1.2.8 Influence of polarity of microenvironment on the fluorescent probes

The microscopic polarity or microscopic dielectric constant of the micellar interior and interface is a fundamental property of these systems. It is an important characteristic for understanding micellar structure and function. The micellar systems are microheterogeneous in character and the electrostatic potential and polarity prevailing in the interior of the micelles differ from those of the bulk aqueous phase.

Several parameters of the luminescent probes (e.g. quantum yields of emission (ϕ), wavelength maximum (λ_{max}) and lifetime of the emission (τ)) are influenced by the local environment of the probe molecule, and the measurement of the emission using luminescent probes are the most convenient method for investigation of the micropolarity of the microenvironment.[78] Thomas et al.[92] reported the application of pyrene 3-carboxaldehyde (Py-CHO) for the evaluation of dielectric constants at the micelle water-interface. Pyrene-

3-carboxaldehyde shows large red shifts in a polar solvent environment, and with Py-CHO near the micelle-water interface the fluorescence spectral shifts have been used to estimate polarity at this water interface. Linear correlations of the emission maxima with the bulk solvent dielectric constant have been demonstrated and these correlations have been used as a rough measure of the polarity of the probe binding sites.

The polarity of the microenvironment of micelles mostly determines the solubilization site of the probe (solubilizate) in the micellar solutions. It also depends on the nature of the solubilizate (hydrophobic or hydrophilic). The term solubilization means the formation of a thermodynamically stable isotropic solution of a substrate (solubilizate) normally insoluble, or only slightly soluble in a given solvent, by the addition of a surfactant (or solubilizer).[52] Hydrophobic substances tend to be solubilized in the core of the micelles while polar or surface active species tend to remain close to the micellar surface. The hydrophobic region of the micelle consists of simple alkyl chains and hardly shows any specific interaction with the solubilizate. This part of the micelle is normally in a less polar environment than the other regions.

The perturbations in the luminescence parameters of the probes in micellar solutions occur due to the polarity of the microenvironment. For example, the solvent induced red shift in the wavelength maximum of the fluorescence of molecules like arylamino naphthalenes[90,91,97] (e.g. 1-anilino, 8-naphthalene sulphonate (ANS) and

N-phenylnaphthyl amine (NPN), indoles.[82]) In this type of compound fluorescence lifetime (τ_f), wavelength maximum of fluorescence (λ^F_{max}) and fluorescence quantum yield (ϕ_F) vary markedly with the solvent polarity. The quantum yields of the blue fluorescence of acridine in alkaline solutions of detergents are reduced drastically when the CMC of the surfactant is reached.[85] This is due to the change of the polarity of the microenvironment of the fluorescent probe acridine. Similar types of examples like 4-cyano-4'-propyloxy biphenyl, 4-cyano-4'-octyloxy biphenyl,[86] 4-methyl-7-anilino coumarine (MAX) and 4-methyl-7-diethyl amino coumarine (MDC)[87] showed similar types of change in their fluorescence wavelength maxima as the polarity of the medium was changed (i.e. from aqueous to hydrocarbon-like or micellar environment).

The influence of high pressure on the monomer fluorescence spectra of pyrene carboxaldehyde (Py-CHO) in aqueous detergent solutions was investigated by Turro et al.[98] The fluorescence intensity increases and the fluorescence wavelength maximum shows a slight red shift with increasing pressure. From these results it was concluded that the pressure increases the polarity or dielectric constant at the micelle-water interface. The dielectric constants (ε) experienced by the probe were estimated from the linear relationship between λ_{max} of the fluorescence and ε obtained by Thomas et al.[92] (i.e. λ^F_{max} (nm) = $0.52\varepsilon + 431.5$).

The polarity gradient of the micelle sodium lauryl sulphate (SLS) was investigated by using a series of n-(9-anthroyloxy) fatty acids (n = 2,6,9,12) as fluorescent probes.[99] The fluorescence behaviour of

these probes has been studied in saturated hydrocarbon solvents of increasing viscosity and solvents of increasing polarity. Incorporation of the four fatty acids in the micelles of SLS leads to a loss of structure in the emission spectra compared with that in the saturated hydrocarbon solvents. The observed decrease in intensity and increase in fluorescence wavelength maximum (λ^{F}_{max}) in order from 12 AS - 2AP is consistent with a graded increase in the polarity of the microenvironment. This was confirmed by carrying out fluorescence quenching studies using dimethyl aniline (DMA), Cu^{2+} ($CuSO_4$) and I^- (NaI) as quenchers. The location of the above probes was determined by finding their quenching efficiencies using Stern-Volmer plots of $[I_o/I]$ vs. concentration of quencher.[99] Where I_o = intensity of the fluorescence in the absence of the quencher and I = intensity of the fluorescence in the presence of the quencher.

The fluorescence wavelength maximum (λ^{F}_{max}) of p-N,N-dialkylaminobenzylidenemalononitrile (122) shifts to a longer wavelength as the polarity of the medium increases. By comparing the λ^{F}_{max} of (122) in homogeneous solvents and those in micelles of various surfactants, the dielectric constants of cetyltrimethylammonium bromide, sodium dodecyl sulphate, potassium dodecanoate and Triton X-100 were estimated to be $\sim$ 36, $\sim$ 40, $\sim$ 40 and $\sim$ 28 respectively.[100] The graph of λ^{F}_{max} of (122) vs. known dielectric constants (ε) of different homogeneous solvents was plotted, and thus the dielectric constants for the surfactants were estimated from the straight line of the graph.[100]

1.2.9 Microviscosity of the microenvironment:

The fluidity or viscosity experienced by the probe molecules in a micellar environment is termed as "microviscosity" and it may differ

from that of the medium (aqueous) in which the micelles are present. The viscosity of the bulk medium (aqueous) may be termed as "macroscopic viscosity".

The microviscosity can be measured by the luminescent probes by applying the following luminescent parameters; (i) fluorescence depolarization and (ii) efficiency of excimer formation. The above fluorescence parameters depend on the magnitude of the microviscosity experienced by the probe.

1.2.10 Measurement of microviscosity by fluorescence depolarization:

The fluorescence depolarization method is based on the competing rates of rotational diffusion and fluorescence decay in the probe molecules. It provides information concerning the probe mobility.[101]

When a randomly oriented fluorescent molecule is irradiated by plane polarized light only the molecules that have the direction of their absorption oscillator parallel to the plane of polarized light will be excited. In micellar media, molecular rotation will further randomize the excited molecules and the degree of polarization in the emission is defined as

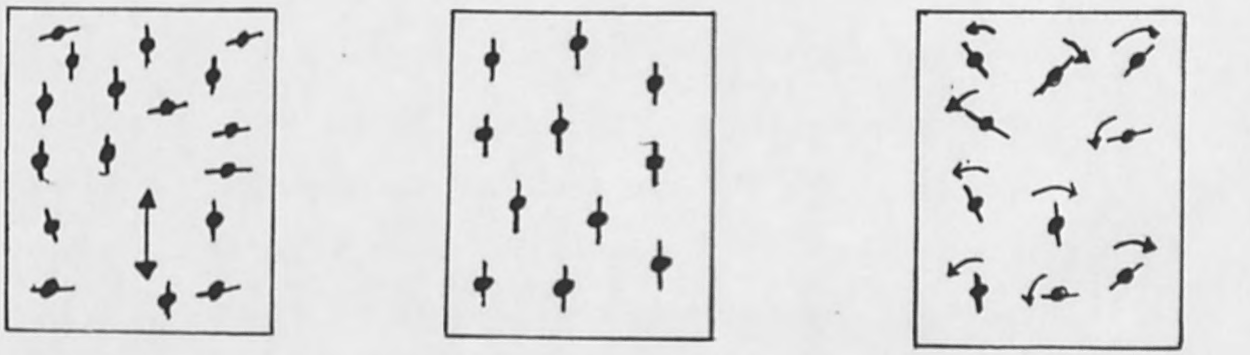
$$P = (I_{11} - I_{\perp})/(I_{11} + I_{\perp})$$

where I_{11} and $I_{\perp}$ are the fluorescence intensities observed through polarizers oriented parallel and perpendicular to the plane of polarization of the exciting beam.

The polarization P depends on the competition between the rates of emission and rotational diffusion as expressed in the equation below.

$$\left[\left(\frac{1}{P}\right) - \left(\frac{1}{3}\right)\right] / \left[\left(\frac{1}{P_0}\right) - \left(\frac{1}{3}\right)\right] = 1 + \tau_f \underline{K}T/(\eta V).$$

Where P_0 is the observed polarization in a medium of high viscosity at low temperature (where there is minimal reorientation of the excited molecule prior to emission), τ_f is the average emission lifetime, V is the effective volume of the probe molecule in cc. (assumed to be a sphere), η is the viscosity (poise), $\underline{K}$ is Boltzmann's constant and T is the absolute temperature. The fluorescence depolarization experiment is illustrated in Fig. (29).



Plane polarized light (↕) irradiation of randomly oriented probe mixture.

Selective excitation of properly oriented probes.

Rotational diffusion depolarizes the probes.

Figure 29: Fluorescence depolarization experiment.

Shinitzky and co-workers[101] have modified the Perrins equation for commonly used planar arene probes. For cases where the absorption and emission oscillators of the arene probe are parallel, as generally occurs in the longest wavelength absorption band, the following equation was derived where $\bar{\eta}$ is the "microviscosity" of the system.[101]

$$\left[\left(\frac{1}{P}\right) - \left(\frac{1}{3}\right)\right] / \left[\left(\frac{1}{P_0}\right) - \left(\frac{1}{3}\right)\right] = 1 + \tau \underline{K} T/\bar{\eta} V$$

Generally the ideal probes for fluorescence depolarization studies should possess the following properties.

They should have (i) rigid structures to avoid depolarization arising from side group rotations, (ii) show high and constant P_0 values in the longest wavelength absorption band to eliminate errors due to slight shifts in the absorption spectrum, (iii) have lifetimes of 1-8 ns, which will lead to measurable degrees of depolarization in media with viscosities of 1-100 cP and (iv) have intrinsically large values for their extinction coefficients and quantum-yields and hence high sensitivity in fluorescence measurements.

Molecules such as perylene and 2-methyl anthracene were used in steady state fluorescence depolarization studies to measure microviscosities for the inner hydrophobic regions of micelles of dodecyl trimethyl ammonium bromide (DTAB), cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulphate (SDS).[101,102] The values of microviscosity with 2-methylanthracene and perylene as fluorescent probes in DTAB micelles were 26 cP and 17 cP respectively. For CTAB micelles the values of microviscosity were 30 cP and 19 cP when 2-methyl anthracene

and perylene were used as fluorescent probe respectively.[101] SDS micelles gave the microviscosity values of 15 cP and 36 cP (aged micelles) when 2-methyl anthracene was applied as a fluorescent probe.[102] Use of cyanine dye in SDS micelles gave the microviscosity as 30 cP.[103] The lower values of microviscosity obtained with perylene compared with 2-methyl anthracene for DTAB and CTAB micelles may have arisen from contributions to depolarization from rotation of the host micelles.

Turro et al.[104] have evaluated the microviscosity of CTAB micelles by studying fluorescence depolarization of probe 11-(3-hexyl-1-indolyl) undecyltrimethyl ammonium bromide (6-In-II$^+$) and perylene. The results were correlated with comparable data in homogeneous solvents of known viscosities. The functionalized surfactant indole (6-In-II$^+$) was used as a probe because its chromophore in micelles of HDTBr has been established by previous studies to be located in the micellar interior.[105] The effect of the addition of several alcohols (ethanol, n-propanol, n-butanol) on the microviscosity of CTAB micelles was also investigated. In each case the microviscosity was found to decrease with increasing alcohol concentration.

The microenvironment of the fluorescent probe (6-In-II$^+$) has been investigated in the presence of poly(styrene sulphonate) (NaPss) macroanions.[106] The microviscosity experienced by the probe was measured by the fluorescence depolarization method. It was found to be 150 cP. The probe (6-In-II$^+$) was found to be in a strongly hydrophobic environment when it became associated with NaPss macroanions, which was confirmed by fluorescence wavelength maximum and

lifetime measurements. The large value of the microviscosity for the probe associated with NaPss (∿ 150 cP) may be due to the strong restriction of the movement of the probe, which results from the striking electrostatic and hydrophobic forces between the probe and the macroanions.[106] The CTAB and 1-hexadecane sulphonate system also shows a very large value of microviscosity, i.e. ∿ 400 cP. This was due to the very strong attractions between cationic CTAB micelles and the anionic 1-hexadecane-sulphonate.[101]

1.2.11 Microviscosity measurements by the efficiency of excimer formation:

The microscopic viscosity may be determined by intermolecular excimer formation,[107] but the analysis for micellar systems requires the use of solute (probe) distribution statistics (Poisson statistics). Intermolecular excimer formation is a bimolecular process occuring between a molecule in the first excited singlet state and a similar molecule in the ground state. Therefore, a relatively high concentration of the excimer forming molecule is required to ensure that an adequate fraction of the micelles are more than singly occupied and hence capable of excimer fluorescence. The introduction of a probe molecule into a micelle can in principle lead to a distortion of the structure of the hydrocarbon core. Such a distortion, when it occurs, would be expected to become larger with an increased concentration of probe molecules in a micelle. The requirement for the presence of a high concentration of the probe molecules in the micelles can be avoided by employing intramolecular excimer formation as a probe of microviscosity. In this situation at a maximum of one probe molecule may be present per micelle. In this method, the

excimer to monomer fluorescence ratio (I_{χ}/I_{m}) from micelle solubilized probes is compared with the ratios obtained in homogeneous solutions of varying (known) macroscopic viscosities.

Fluorescent probes like 1,3-diphenyl propane and 1,3-di(1-pyrenyl) propane were used to evaluate the microviscosity of sodium dodecyl sulphate (SDS) micelles.[108] The value of the microviscosity obtained with dipyrenyl propane was 19 cP and with 1,3-diphenyl propane was 4 cP. This large difference in fluidity reported by the two diaryl alkanes, may be because the smaller molecule, diphenyl propane, can move to a more fluid part of the micelle interior, whereas the movements of the larger dipyrenyl propane are determined by the less fluid parts of the SDS micelle.[108]

Compounds such as 4-biphenyl derivative (123)[109] and 1,3-di(1-naphthyl)propane[105] were used for intramolecular excimer formation with SDS, CTAC and CTAB micelles to determine their microviscosity.

The microviscosities were obtained by correlating the observed relative intensity of excimer to monomer emission with the known macroscopic viscosity of the homogeneous solvents. (Graph of I_{χ}/I_{m} vs. viscosity of homogeneous solvents was plotted).[105,109]

Law[100] has determined the microviscosity of the micellar environments of potassium dodecanoate, sodium dodecyl sulphate, cetyl trimethyl ammonium bromide and Triton X-100 micelles by comparing the quantum yields (ϕ_f) of the fluorescence emission of 2-[6-(2,2-dicyanovinyl)-1,2,3,4-tetrahydro-2,2,4-trimethylquinol-1-yl] ethylbenzoate(122) in

micelles and in homegeneous organic solvents of known viscosity. The fluorescence quantum yield of (122) increases with the viscosity of solvents whose viscosities are more than 2 cP. A plot of log ϕ_f vs. log η for alcohols of chain-length less than 6 carbons is found to be linear. Since ϕ_f of (122) is only sensitive to the solvent viscosity and this log ϕ_f vs. log η relationship has been exploited as a measure for the microviscosity.

1.2.12 Distribution of probe molecules in micellar solution:

The micellar/aqueous partitioning of ground state probe molecules is 'reported' via their fluorescence emission. The fluorescence of the probe is faster than probe exit-entrance rates and hence it reflects the initial ground state distribution.

The solute partitioning into micelle/aqueous environment has been investigated by the fluorescence lifetime measurement of naphthalene at low concentrations ($< 10^{-4}$ M).[110] The fluorescence lifetime shows clear evidence of a two-component decay for solutions near the CMC of cetyl trimethyl ammonium bromide (CTAB). The long lived decay (τ_f = 34 ns) is assigned to naphthalene molecules dissolved in the bulk aqueous phase and the short lived decay (τ_f = 10 ns) is assigned to naphthalene molecules associated with micelles. Statistical distribution of solute among the micelles can be determined by "Poisson statistics". It can be expressed by the following equation,

$$P(n) = \frac{\langle S \rangle^n}{n!} \exp(-\langle S \rangle)$$

where P(n) is the probability of finding a micelle containing n solute molecules and <S> is the "mean occupancy number" or the ratio of the bulk concentration of solute molecules to the bulk concentration of micelles. The large values for <S> cannot hold for Poisson statistics because the size of the micelle is finite and the inclusion of too many solute molecules will eventually cause gross disturbances of the micellar characteristics.[78]

1. 2.13 Fluorescence quenching processes in the aggregated system: Fluorescence quenching is a diffusion controlled process and various dynamical properties of micellar systems and lipid vesicles can be investigated by this process. Usually there are two types of fluorescence quenching processes that can occur in the micellar systems as shown in Fig. (30). (i) Static quenching and (ii) dynamic or nonstatic quenching.

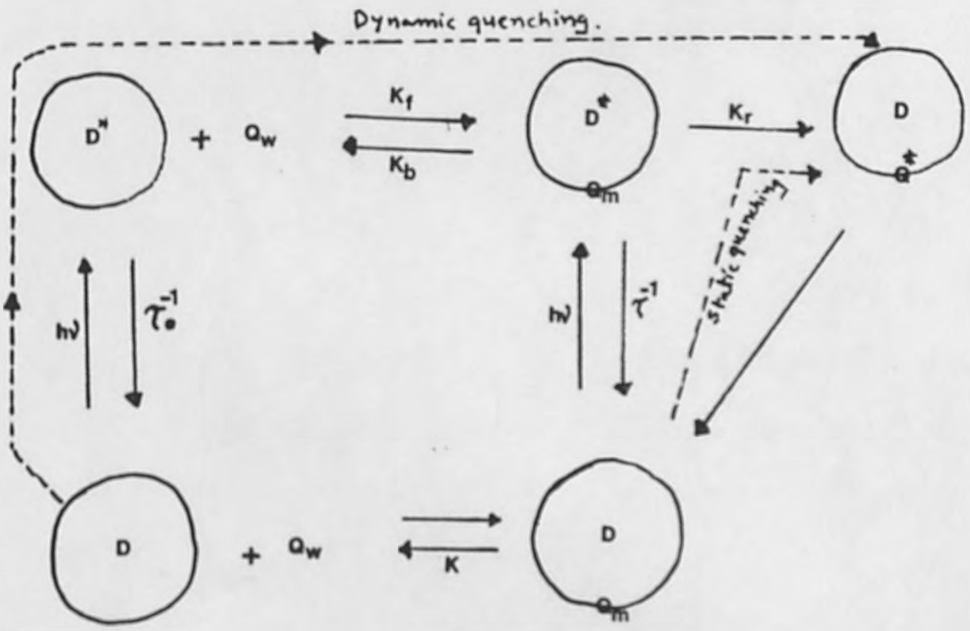


Figure 30: Static and dynamic quenching process in micellar system.

Circles represents micelles.

τ_0 = Lifetime in the absence of quencher.

Q_w = Water solubilized quencher.

τ = Lifetime in presence of quencher.

Q_m = Micelle solubilized quencher.

K_f = Forward rate constant of micellization (entry rate).

K_b = Backward rate constant of micellization (exit rate).

K_r = Unimolecular reactive rate constant of quenching in the micelle.

D = Donor or the fluorescent probe.

The above shown quenching process of the micellar systems by the fluorescent probe molecules and quenchers can further be divided into four different types of cases as follows:

(1) Static quenching; quencher is totally micellized:

In this type of quenching the fluorescence emission can occur only from that fraction of excited molecules (D*) containing micelles that are free of quencher molecules. Although the overall luminescence intensity is reduced, the measured lifetime of D* remains constant upon addition of quencher. The mean micelle aggregation number ($\bar{n}$) of the detergent solution can be evaluated by using this type of quenching process.[111] The determination of the mean aggregation number of detergents has been discussed in Section 1.2.15. The fluorescence quenching of pyrene by amines can also be categorized in this manner.[112]

(2) Static quenching; quencher is partially micellized:

In this case the quenching is static and the emission still occurs only from that fraction of D* containing micelles which

are free of quencher molecules. The lifetime τ of the emitting state is reduced by dynamic diffusional quenching by water solubilised quencher molecules Q_w. Information on mean micelle aggregation number, quencher binding constant and residence time have been obtained using the above type of quenching process. An investigation of the quenching of a completely micellized fluorescent probe 1,5-dimethyl naphthalene by a series of cyclic azoalkanes that exist to a significant extent in both aqueous and micellar environments has been carried out by Turro and co-workers.[113] The quenching data based on lifetimes and fluorescence intensity measurements suggested that only static quenching takes place inside the micelle (only single exponential decay of plot of log I vs.t was observed). The value of K_f and K (equilibrium constant between micelle and quencher molecules) has been obtained by plotting a graph of $(\tau^{-1}-\tau_0^{-1})^{-1}$ vs. detergent concentration (Det) at fixed quencher concentrations and from the known aggregation number $\bar{n}$ of the cetyltrimethyl ammonium bromide (CTAB) micellar solution. The above parameters were obtained from the equations below. Also measurements of the quenching of the fluorescence lifetimes of 1,5-dimethyl naphthalene by cyclic azoalkanes in micellar solutions of CTAB were obtained. The changes in the lifetime are given by the following equation.

$$\tau^{-1} = \tau_0^{-1} + K_f \, [Q_w]$$

where $[Q_w] = [Q]/(1 + K\,[M])$

$$\therefore \quad \frac{1}{\tau^{-1}-\tau_0^{-1}} = \frac{1}{K_f\,[Q]} \quad (1 + K\,[M])$$

$$\simeq \frac{1}{K_f [Q]} \left(1 + \frac{K}{\bar{n}} [\overline{Det}]\right) \quad \because [M] = [\overline{Det}]/\bar{n}$$

From the knowledge of K and K_f the exit rate of substrate from micelles (K_b) has been evaluated ($K = \frac{K_f}{K_b}$).[113,114]

(3) Non-static quenching quencher is totally micellized:

Non-static quenching is distinguished by non-exponential decay of luminescence. This is because the lifetime of donor D* in a given micelle depends on the number of cohabitant quencher molecules. The quenching of pyrene fluorescence by Cu^{2+} ions in SDS micelles is an example of this type of quenching.[115]

(4) Non-static quenching; quencher is partially micellized:

The quenching of pyrene fluorescence by methylene iodide and nitromethane in SDS micellar solutions can be categorized in this case. The distribution of the quenchers between micellar and aqueous phases was measured by determining their distribution constants by means of pulse radiolysis.[116]

Fluorescence quenching of 11-(3-hexyl-1-indolyl)undecyl sulphate (6-In-II^-) and 1-methyl indole was investigated using water soluble quenchers NO_2^- and CO^+.[117] The quenching rate in the micellar phase depends upon the electric charge of the micelle and the quencher. If the charge of the quencher is the same as that of the micelle, no quenching is observed. If the charge of the quencher is opposite to that of the micelle the quenching rates of (6-In-II^+) and (6-In-II^-) fluorescence are more than ten times faster than those in the water

phase. This may be attributed to the high local concentration of the quenchers in the micelle phase. The environment of the surfactant indole chromophores in micellar solution was found to be hydrophobic compared with that of water and this was confirmed by their spectral properties (e.g. fluorescence, lifetime τ_f). The location of 1-methyl indole in CTAB micelles was found to be on the surface of the micelles because the quenching of this probe by NO_2^- in CTAB solution proceeds by a mechanism of static quenching (the lifetime did not change significantly when the NO_2^- quencher was added up to 1.8 mM, whereas the fluorescence intensity decreases in CTAB micelles). 1-Methyl indole and the chromophore $(6\text{-In-II})^-$ were found to be at the interior of the micelle since the fluorescence quenching of both chromophores in SDS solution proceeds via a dynamic mechanism process. The location of 1-methyl indole was also confirmed by its spectral properties (i.e. fluorescence λ_{max}, absorption λ_{max} and fluorescence lifetime).[117]

The effect of alcohols on the fluorescence quenching of (6-In-II^+) by NO_2^- was also investigated.[104] The quenching rate constants were determined from the slope of a plot of fluorescence lifetime τ^{-1} vs. concentration of quencher using the Stern Volmer expression.[110]

$$\tau^{-1} = \tau_0^{-1} + K_q [Q]$$

The fluorescence quenching rate of NO_2^- in CTAB micellar solution with (6-In-II^+) probe decreased with increasing ethanol concentration and decreased even more significantly with the addition of n-butyl alcohol. The addition of alcohol to the micellar solution reduces its aggregation number and hence increases the micelle

concentration and micelle surface. The micelles become swollen considerably and this effect could reduce the positive electrostatic potential on the micelle surface and the viscosity in the micelle. The increase of the micelle surface and micelle volume, along with reduction of electrostatic potential lead to a lower effective concentration of NO_2^- at the micellar surface upon addition of alcohol and results in a slower quenching rate.[104]

The relative positions of fatty acids [2-(9-anthroyloxy)palmitic acid (2-AP) and 6-9-12-(9-anthroyloxy) stearic acid (6-AS, 9-AS, 12-AS)] in the SDS micelles have been characterised by fluorescence quenching experiments with dimethyl aniline (DMA), copper sulphate ($CuSO_4$) and sodium iodide as quenchers.[99] Because of the hydrophobic nature of the quencher DMA it would be expected to be located towards the centre of the micelle. The relative quenching efficiencies of the fatty acid fluorophores were confirmed by the Stern Volmer plot of (I_0/I^{-1}) vs. concentration of DMA (where I_0 and I are the fluorescence intensities in the absence and presence of the quencher DMA respectively). The quenching efficiencies were found to be in order of 12 AS > 9AS > 6AS > 2 AP. These results were further confirmed by examining the relative quenching efficiencies for a quencher, $CuSO_4$, located near the micelle surface. Since Cu^{2+} cations are expected to reside near the negatively charged sulphate groups of SDS the quenching efficiencies have been found to be in the reverse order to those observed with DMA. The entry of I^- ions into SDS micelles is inhibited by the surface charge and hence little quenching of the probes that lie deep in the micelles was observed (6-9 and 12-AS). However, some quenching was observed for 2 AP at high I^-

concentrations since this chromophore was found to be located near the surface of the micelles. These results confirmed that 6-AS, 9-AS and 12-AS, were located at a graded series of levels in the sodium lauryl sulphate micelles.[99]

The location of the above fluorphores (6-AS, 9-AS, 12-AS, 2-AP), anthracene and 9-methyl anthracene in CTAB micelles has also been characterised by carrying out fluorescence quenching experiments with sodium iodide and DMA. Since I^- binds strongly to the positively charged head groups of CTAB the quenching efficiency of the fatty acids shows an increase in order from 12-AS to 2-AP. The anthracene probe was found to be located at the surface of the micelle, since it showed a considerable reduction in its lifetime (τ_f) in micellar solution compared to hydrocarbon solvents. The 9-methyl anthracene chromophore solubilizes towards the micelle core since there was no quenching of its fluorescence lifetimes τ_f when it was incorporated into CTAB micelles.[118]

1.2.14 Micellar inhibition and catalysis of fluorescence quenching:

Two of the important functions of a quencher in the fluorescence quenching process in micellar solutions are micellar "inhibition" and micellar "catalysis" of fluorescence quenching. In the cases for which the quencher carries the same charge as the surface of the micelle the quenching of the chromophore may be substantially decreased relative to the bulk concentration of the quencher. Correspondingly, if the quencher possesses the opposite charge to the surface of the micelle the fluorescence quenching may be increased relative to the bulk concentration of the quencher. These

processes, called micellar 'inhibition' and micellar 'catalysis' respectively, are shown in Fig. (31).

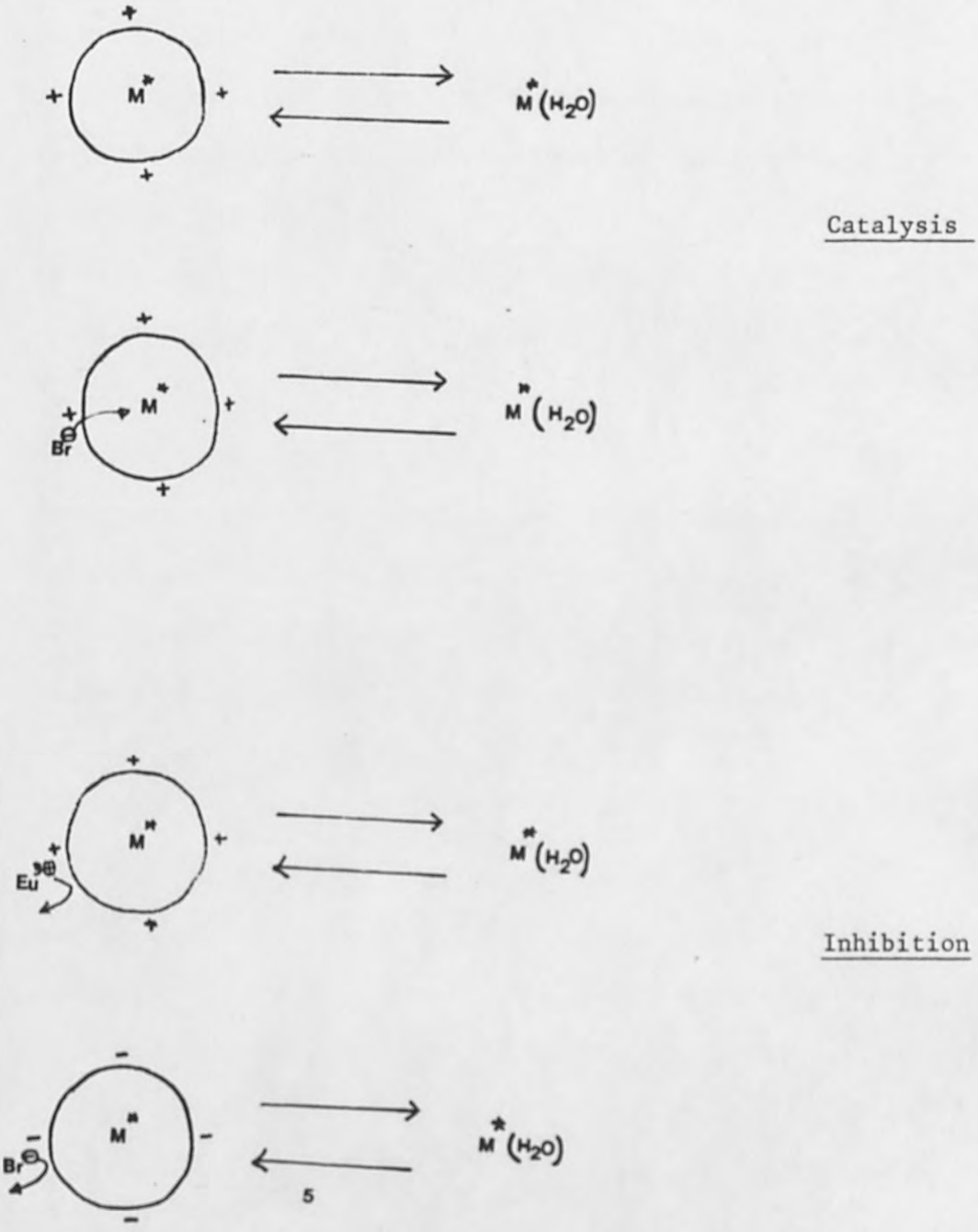


Figure 31: Schematic representation of 'catalysis' and 'inhibition' of fluorescence quenching in micellar solutions.

The processes of micellar "catalysis" and "inhibition" have been directly observed using the probe naphthalene in cationic (CTAB) and anionic (SDS) micellar solutions. The Br^- ions associated with the micelle as counter ions quench the fluorescence of naphthalene which is dissolved in the micelle of CTAB. Further addition of Br^- to an aqueous solution containing naphthalene and the micelles of CTAB results in the lower value of the fluorescence lifetime. In solutions containing anionic surfactant (SDS) the naphthalene associated with the micelle is protected from the quenching by Br^- ions.[110] Eu^{3+} acts as an 'inhibitor' when it is dissolved with pyrene in cationic micellar solutions.[119,120]

Molecular oxygen has also been found to be an effective quencher of the fluorescence in the micellar systems depending upon the location of the oxygen molecules and the probe molecules in the micellar solutions. A measure of oxygen penetration in to micelles was obtained by the study of pyrene fluorescence lifetimes under aerated, deaerated and oxygenated conditions.[121]

1.2.15 Determination of aggregation number (N):

The aggregation number is one of the most important structural parameters of micellar aggregates. The average number of detergent molecules in a micelle unit is called the aggregation number (N) or mean aggregation number ($\bar{n}$) and it can be measured using a method based on the quenching of the fluorescence of a luminescent probe by a hydrophobic quencher.[122] This method can be applied only if the static quenching of the probe occurs in the micellar solution. The quencher should be completely associated with the micellar interior.

The probe molecule D and the quencher molecules Q will be distributed among the micelles according to the Poisson statistics and the fluorescence will only come from the excited probe molecule D*, which is not associated with the quencher molecule Q in the micelle, because D* is completely quenched when it occupies a micelle containing at least one quencher molecule Q. The measured ratio of luminescence intensities (I/I^{o}) in the presence of Q to that in the absence of Q is related by the following expression

$$(I/I^{o}) = \exp\left\{ - [Q]/[M] \right\}$$

where $[M]$ is the micellar concentration and $[Q]$ is the concentration of quencher. I and I^{o} are fluorescence intensities in the presence and absence of the quencher respectively.

The $[M]$ can be related to the measurable macroscopic concentration of detergent $[Det]$ and mean aggregation number $\bar{n}$ by the following expression,[122]

$$[M] = \frac{[Det] - [\text{Free monomer}]}{\bar{n}}$$

The combination of the above expressions will lead to

$$\ln (I^{o}/I) = \frac{[Q]\,\bar{n}}{[Det] - [\text{Free monomer}]}$$

The aggregation number $\bar{n}$ and the concentration of free monomer which is in equilibrium with micelles can be evaluated by measuring I^{o}/I as a function of $[Q]$ at fixed $[Det]$ and by measuring I^{o}/I as a function of $[Det]$ at fixed $[Q]$. A plot of $\ln I^{o}/I$ vs. $[Det]$ at fixed concentration of Q gives a straight line and the slope is identified as $\{\bar{n}\,[Q]\}^{-1}$ and the intercept as $\{[Det] - [\text{Free monomer}]\}$.

Since [Q] and [Det] are known, $\bar{n}$ and [Free monomer] may be evaluated,

$$\therefore \quad \bar{n} = \frac{1}{\text{Slope} \times [Q]} = [Q]^{-1} \times \text{Slope}^{-1}$$

The mean aggregation number ($\bar{n}$) of the micelles of SDS was evaluated by using $Ru(bipy)_3^{2+}$ as a probe and 9-methylanthracene as a quencher by following the above described method. The effect of the addition of (NaCl) on $\bar{n}$ of SDS has also been investigated. It was found that the $\bar{n}$ increases ($\simeq$ 60 to 160) as the concentration of the electrolyte is increased (0.03 M to 0.6 M).

Another method to determine the micelle aggregation number (< 200 value) using totally micellized fluorescent probe and quencher is reported by Atik et al.[123] The aggregation number (N) can be estimated from the decay profile of pyrene fluorescence. The time dependence of pyrene monomer fluorescence at large t after pulsed excitation is

$$\ln (I_M/I_M^o) \quad \sim - (n + K_1 t)$$

where I_M^o and I_M are the fluorescence intensities of pyrene-monomer at t = 0 and t respectively, n is the mean occupancy number of pyrene in the micelle and K_1 is the decay rate constant of the excited pyrene monomer. The micelle aggregation number N can be calculated from the following equation

$$N = ([Det] - CMC)/n$$

when [Det] and CMC are the total concentration and the critical micelle concentration of the detergent respectively. The aggregation number of the detergent CTAB was measured by the above described

method and the effect of the addition of alcohols on the aggregation number was studied. The addition of alcohols have significantly reduced the aggregation number of the CTAB micelles.[104]

Zana et al.[124] have used the pyrene excimer formation method for the determination of the aggregation number of SDS micelles. The effect of the addition of sodium chloride on SDS micelles and its aggregation number has also been investigated.

When ratio P of the molar concentrations of pyrene (C_p) and micelle (C_m) (average number of P of probes per micelle) is close to 1 the fluorescence decay curve shows two decay components; a slow one corresponding to micelles having solubilized one pyrene molecule and a fast one associated with micelles having solubilized two or more pyrene molecules (excimer formation). From the ratio of the amplitudes of these two components one can obtain P and thus the aggregation number,

$$N = P(C - CMC)/C_p$$

where C is the surfactant concentration and CMC is critical micelle concentration.[124]

The aggregation number of the micelles formed by five-cationic, one anionic, two zwitterionic and one nonionic surfactant in aqueous solution have been determined at various concentrations by the pyrene excimer formation method.[125] It was also found that the micelle aggregation number of nonionic surfactants was increased with increasing concentration.

In summary, it can be concluded that the micelle aggregation number can be determined by (i) static quenching of the fluorescence of the luminescent probe by a completely micelle solubilized hydrophobic quencher, (ii) by obtaining the decay profile of the micelle solubilized pyrene monomer fluorescence which is quenched by micelle solubilized quencher and (iii) from the ratio of the amplitudes of the pyrene monomer to pyrene excimer formation in the micellar solution.

The addition of electrolytes to the micellar solution increases the micelle aggregation number, whereas the addition of alcohols to the micellar solution significantly reduces the aggregation number of the micellar solution.

1.2.16 Water penetration in micelle core:

The structure of micelles has been the subject of much speculation; in particular the degree to which water penetrates the micelle. Water penetration into the hydrocarbon core of a micelle could be an important factor in determining the properties of solubilized probe molecules in the micelles. An argument in favour of strong water penetration in the micelle was presented by Menger.[126] The results were mainly derived from ^{13}C NMR experiments by inserting a carbonyl group into micelles. The measurements of ^{13}C chemical shifts of carbonyl compounds was taken in different homogeneous solvents of known polarity and then a comparison was made with the ^{13}C chemical shift data of the micellar carbonyl compound. Octanal solubilized in cetyltrimethyl ammonium bromide micelles was found to be experiencing an environment whose average polarity resembled that of 2-propanol.[127] The idea of water penetration into

micelles was also supported by Muller and Birkhan[128] by a ^{19}F NMR study. Svens and Rossenholm[129] supported this argument by doing an x-ray study. Waka et al.[130] explained the lack of hetero-excimer emission in micellar solutions by the high polarity of the environment of the probes caused by the presence of water in the micellar core. However, on the other hand, Rossler and Wolf[131] failed to observe a photodecomposition of N-methyl carbazole in the micelle core. The photodecomposition of this compound occurs in water but not in hydrocarbon solvents.

The possibility and the extent of water penetration in the micelle core may depend on the nature of the ionic head groups of the detergent. 1-Methyl indole was found to be associated with the surface of CTAB micelles whereas with sodium lauryl sulphate micelles it was located in the interior of the micelles. The spectral (fluorescence) changes of the anionic (11-(3-hexyl-1-indolyl) undecyl sulphate indole detergent and 1-methyl indole in sodium lauryl sulphate micelles was not as large as that of cationic indole detergent [11-(3-hexyl-1-indolyl)undecyl trimethyl ammonium bromide] in CTAB micelles. This was considered to be due to the nature of the interior of micelles which depends strongly upon the nature of the ionic group. The surface of CTAB micelles is covered with $^{+}NMe_3$ groups and hence the penetration of water could be prevented due to tight packing of CTAB molecules in the micelles. The $^{+}NMe_3$ group is also a hydrophobic group. On the other hand, in sodium lauryl sulphate micelles the $-OSO_3^-$ group is highly hydrophilic and so water may penetrate easily into the interior of the micelle.[117]

The evidence for the porous clustered micelle structure was provided by the fluorescence lifetime study of xanthane dyes with micelles[132] and by charge transfer complexation in the micellar solutions of sodium lauryl sulphate (SDS) and hydrophobic donors like pyrene, 3-methyl indole and 1-benzyl, 1-4, dihydronicotinamide (BNAH) and the hydrophilic acceptor N,N'-dimethyl-4,4'-bipyridinium dichloride (paraquat, PQ^{2+}). The degree of ground state association between the hydrophobic donors and hydrophilic paraquat PQ^{2+} was strongly enhanced in SDS micellar solutions (when) compared to CTAB micellar or homogeneous methanol solutions. The location of the hydrophobic donor molecules in SDS micelles was found to be at a site which was in direct contact with the binding site of the hydrophilic PQ^{2+} molecules. This observation suggested that water and water-dissolved solute (PQ^{2+}) penetrate into the hydrocarbon region of the micelle.[133]

Acridine is non-fluorescent in organic aprotic solvents but it fluoresces blue in protic solvents like alcohol or water at pH > 11. This behaviour of acridine is due to formation of hydrogen bonded complexes between excited acridine and solvent molecules, which is only possible in protic solvents. The decrease of the fluorescence quantum yield of acridine in aqueous surfactant solutions above the CMC is due to separation of acridine from water molecules by solubilization in the micellar core. However, water molecules are considered to remain accessible to excited acridine molecules for the formation of the hydrogen bonded complexes necessary to emit limited blue fluorescence.[85] The solubilization site of 4-cyano-4'-propyloxybiphenyl (3-COB) derivative was found to be in a polar environment (polarity > ethanol). The fluorescence wavelength maximum

value of the probe in the micellar solutions of CTAB and SDS is similar to that in dimethyl formamide (DMF). This fact indicates that if 3-COB is dissolved in the core of the micelle it is not in a water-free hydrocarbon core. It could also be considered to be located near the polar head group in a water rich environment.[86] Vibrationally resolved fluorescence spectra of pyrene in SDS and CTAB micellar solutions showed similar vibrational structure to those in water.[134] The n-(9-anthroyloxy) fatty acids experienced as high a polarity in butanol as in SDS micellar solution. The high polarity experienced by these probes may be due to penetration of water in the micelle/water interface. This observation has been confirmed by the fluorescence lifetime decay curves which gave a double exponential function because of the two different environments of the probe molecules.[99]

It can be concluded from the above results that the fluorescent probe molecules experience a polar environment in the micellar solution. The water molecules penetrate the micellar interior and the nature of the interior of a micelle also depends strongly upon the nature of the ionic group. It is also likely that the properties of micelles (shape, aggregation number, water penetration etc.) will depend on the detergent structure and on environmental factors.

1.2.17 Phosphorescent probes in micellar solutions:

The slower processes (micro or miliseconds) connected with micellar systems, such as exchange of monomer with micelle, the complete collapse of micelle ('dissolution equilibrium') and exit and re-entry of the solubilizates in and out of the micelle can be conveniently

investigated by phosphorescence. Since a triplet excited state has a longer lifetime than a singlet excited state, it enables one to extend the time available for investigations of a micellar system from 10^{-9} to seconds. The micelle protects the solubilized triplet from impurities, and also inhibits the triplet state-ground state interaction (triplet-triplet annihilation) by solubilizing one molecule per micelle. The micellar environment tends to protect the excited triplet state of a probe located within the lipid phase from reactions with molecules, located in the bulk aqueous phase. It also protects it from quenching by impurities as well as from oxygen and hence the phosphorescence can be observed at room temperature in micellar systems.[78,79,81]

The phosphorescence emission at room temperature from a variety of aromatic molecules has been observed in micellar systems. For example, room temperature phosphorescence of 1,4-dibromonaphthalene was readily observed in nitrogen purged micellar solutions of cetyltrimethyl ammonium bromide, cetyl trimethyl ammonium chloride and sodium dodecyl sulphate detergents. This behaviour of 1,4-dibromonaphthalene compound was due to internal heavy atom effects. On the other hand the hydrocarbon compounds like naphthalene and triphenylene emitted phosphorescence in purified vacuum degassed solutions of 1,2-dibromoethane due to the external heavy atom effect.[135] Turro and Bolt[136] have synthesized 10-(4-bromonaphthal-1-oyl)decyl trimethyl ammonium bromide and analogous series of detergents and observed their phosphorescence at room temperature in aqueous solutions above their CMC value. The phosphorescence emission was confirmed by oxygen quenching experiments and by lifetime measurements

(> 1 ns). The aggregation number and CMC values of these probe detergents have been compared with those of CTAB and CTAC detergents, and the micellar properties of these probe detergents have been found to be closely parallel to those of conventional ionic detergents (CTAB, CTAC, etc.). The above phosphorescent probes have been employed to determine the detergent-micelle dynamics[137] and the association of polyelectrolyte (sodium polystyrene sulphonate) to detergent.[138]

It was noticed that thallium ions enhance the phosphorescence emission rate via intramolecular spin-orbit coupling. Hence it reduces the lifetime but enhances the yield (efficiency) in ionic micelles. Phosphorescence of the arenes like 1-bromopyrene, 1-bromonaphthalene, naphthalene, 1,2-benzanthracene, phenanthrene and biphenyl compounds in aggregated systems has been useful in measuring several kinetic features of the solubilization of probe molecules.[139,140]

Room temperature phosphorescence of naphthalene, pyrene and biphenyl series have been observed in thallium lauryl sulphate/sodium lauryl sulphate micellar environments.[141,142] The phosphorescence for 1-naphthoic acid and 2-naphthylmethyl ketone compounds was low and it was unmeasurable for 2-naphthaldehyde in the TLS/NaLS micellar environment. This could be due to unfavourable location of the compound relative to either the Tl^+ inside the micelle or location in the aqueous phase outside the micelle. Another reason could be the ineffectiveness of Tl^+ as a promoter of spin-orbit coupling for this type of substituted naphthalene. The average location of the above compounds in the micellar solution was examined by observing the

effect of microenvironment on their fluorescence wavelength maximum (λ^{F}_{max}). The λ^{F}_{max} of these compounds shifted to progressively longer values with increasing solvent polarity and the shift was more pronounced for 2-naphthaldehyde. These results suggested that these compounds are located in a more polar environment than naphthalene.. Very weak room temperature phosphorescence and small quenching of fluorescence was observed which could be due to a less protective environment. The room temperature phosphorescence of pyrene, 1-pyrene butyric acid, 1-amino pyrene and 1-pyrene sulphonic acid has been investigated in the micellar solution of TlLS/NaLS detergent. A strong micelle solubilized room temperature phosphorescence (MSRTP) was observed for 1-pyrene butyric acid and 1-amino pyrene while no measurable MSRTP was observed for 1-pyrene sulphonic acid. The possible reason for this type of behaviour is the same as discussed above for the naphthalene series. The MSRTP for biphenyl, 4-biphenyl carboxaldehyde and o-phenyl phenol has been also investigated in TlLS/NaLS micellar system. No measurable MSRTP was obtained for 2-biphenyl carboxylic acid, possibly due to an unfavourable location of the probe in the micellar system or the size of the carboxylic acid group impairing the formation of an excited state planar species.[142] It was observed from the above phosphorescent probes that electron donating substituents produced larger MSRTP intensities compared to electron withdrawing groups substituted on the lumophore.[142,144]

It was necessary to introduce heavy atom thallium as a counterion, in the form of thallium lauryl sulphate (30%), with sodium lauryl sulphate (70%) to induce room temperature phosphorescence of carbazole derivatives with electron withdrawing substituents on the

nitrogen atom.[145] If the chromophore spends most of its time in the bulk aqueous phase of the micellar solution and has only a limited solubility in the micelle it will have only weak, if any, MSRTP. For carbazoles the reduction in electron density on the nitrogen can be achieved by adding electron withdrawing substituents to it and this can affect their solubility properties by making them more soluble in the micellar aggregates. The cyano, iodo and chloro substituents will reduce the elctron density on the nitrogen. On the other hand the methyl and octadecyl substituents can only increase the electron density on nitrogen (positive inductive effect) and hence the molecule will be more polar and more soluble in an aqueous environment. However, on the other hand the hydrophobic nature of the octadecyl chain could overcome the increased nitrogen polarity and can drive this species into the micelle. This effect appears contradictory to the studies of the MSRTP of naphthalene, pyrene and biphenyl series, which found that electron withdrawing groups often quenched MSRTP.[142] The substituents have a different relation to the lumophore in carbazole series and are not electronically coupled directly into the ring system.[145]

1.2.18 Photochemical reactions in micellar systems:

1.2.18.1 Intramolecular hydrogen abstraction reaction:

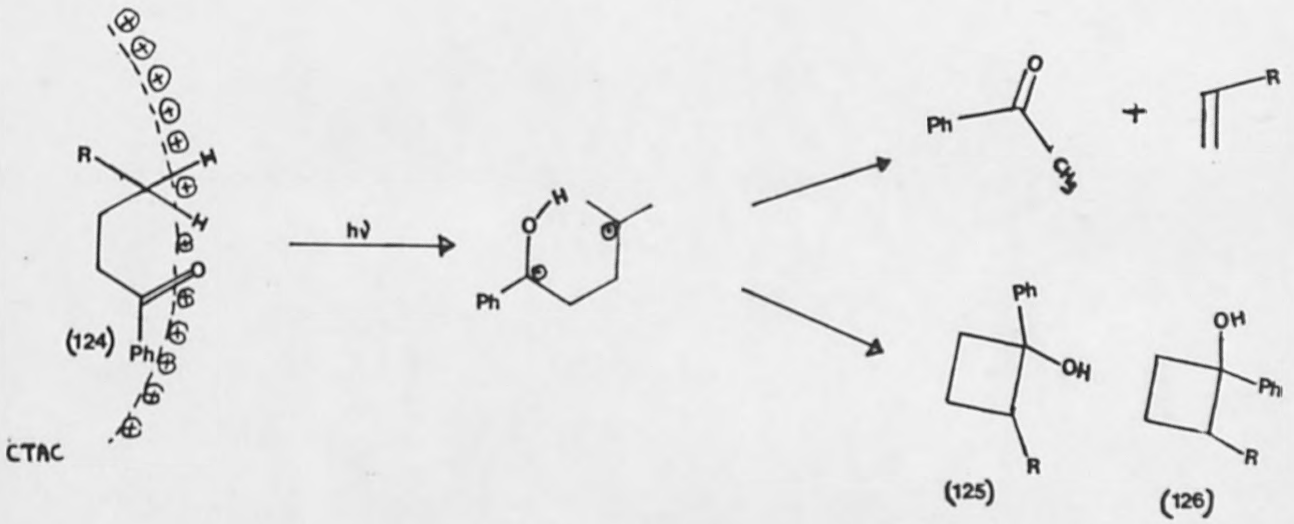
The hydrogen abstraction reactionsin micellar systems can provide information on the microenvironment of the system in which the hydrogen abstraction occurs. The efficiency of intramolecular hydrogen abstraction (Type II reaction) is enhanced upon proceeding from nonpolar to polar solvents. Thus it should be possible to employ hydrogen abstraction efficiency measurements to serve as

the probe of the environment in which the hydrogen abstraction occurs.

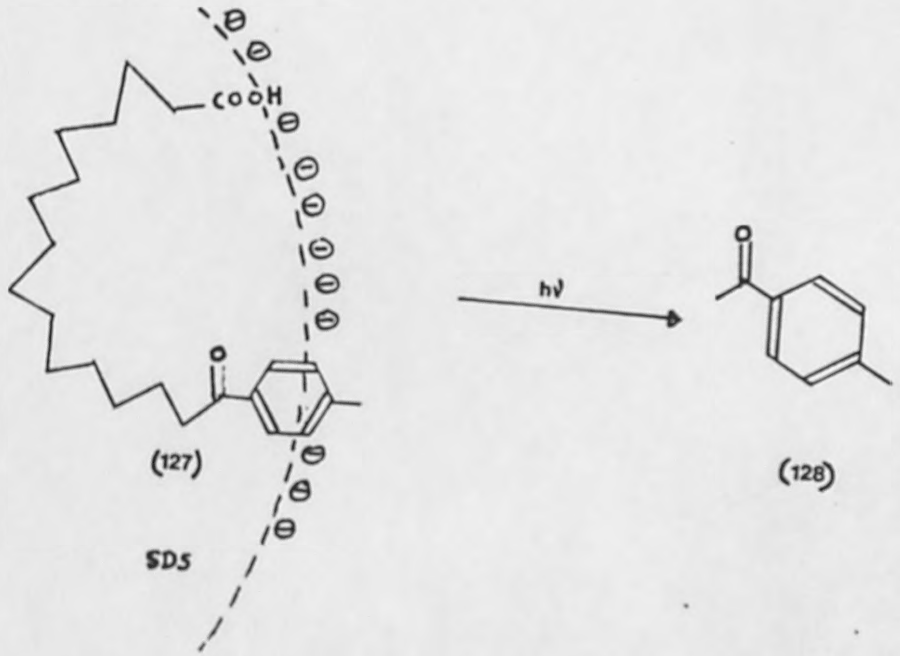
Intramolecular hydrogen abstraction (Type II reaction) of phenyl-heptyl ketone (octanophenone)(124) has been investigated in the micellar solution of CTAC.[146] The quantum yield of overall reaction of phenyl heptyl ketone and the ratio of stereoisomeric cyclobutanols (125) and (126) are solvent dependent. Thus measurement of the quantum yield and cyclobutanol ratio serves as a monitor of the local solvent properties of micelles. The values of the quantum yield of the Type II reaction of phenyl heptyl ketone in CTAC and the ratio of cyclobutanols are much closer to those for Type II reactions in t-butanol than those in benzene.[146] These results suggest that the ketones are not solubilized totally in the hydrocarbon core of the micelles. On the other hand, the quenching experiments by Eu^{3+} ($EuCl_3$ is a good quencher of Type II reactions in water) showed that europium cations (Eu^{3+}) do not quench the Type II reaction of octanophenone in the CTAC solution.[146] This suggested that no significant amount of the probe reacts in the aqueous phase. However, the ketone (or diradical intermediate) must spend at least some time in the polar stern layer of the micelle. The hydrogen abstraction can occur as shown in the Scheme (T-1).

Surfactant ketone 16-oxo-16(p-tolyl)hexadecanoic acid (127) was incorporated in sodium lauryl sulphate (SLS) micelles and the quantum yield of the Type II reaction was found to be higher (0.8) than that in benzene solution (0.2) and 4-methyl acetophenone (128) was the only volatile product detected, as shown in Scheme (U-1).[147]

SCHEME T-1



SCHEME U-1



The results can be interpreted to imply that hydrogen abstraction usually occurs when the fourteen carbon polymethylene chain is bent such that both ends lie near the micellar surface.[147]

1.2.18.2 Intermolecular hydrogen abstraction reactions in the micellar system:

Photo-induced intermolecular hydrogen abstraction reactions in micellar solutions can provide information on the structure of the micelles. For example photolysis of substituted benzophenones.[148-150] When 4-benzoylbenzoate anion (129) is irradiated in SDS micelles the intermolecular hydrogen abstraction occurs from the detergent methylene groups and is followed by attachment of the benzophenone moiety to the detergent. Abstraction occurs from the positions 5 to 11 of the chain and this non-selectivity of the hydrogen abstraction suggests extensive coiling and folding of the detergent chains.[148] However, on the other hand, photolysis of 2-(4-benzoylphenyl)propionate (130) in sodium tetradecanoate showed a particular selectivity in hydrogen abstractions on positions 5 through 8 with position 7 showing the highest selectivity.[149] (Fig. 32).

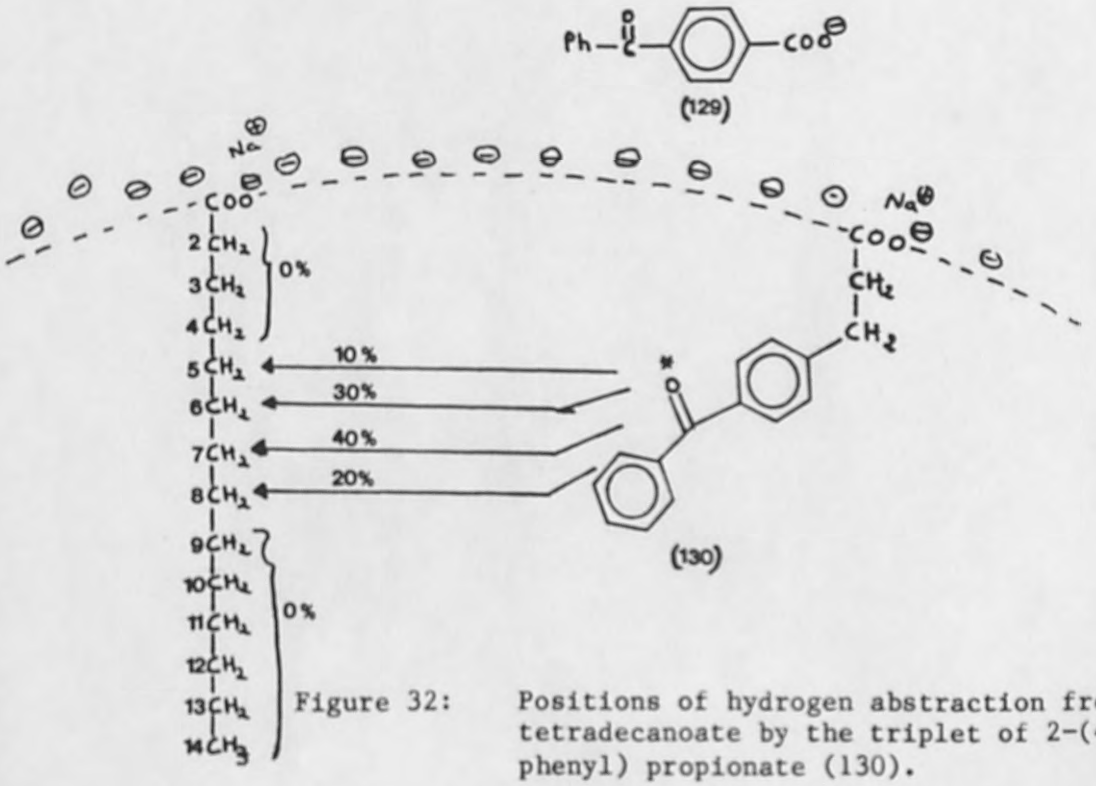
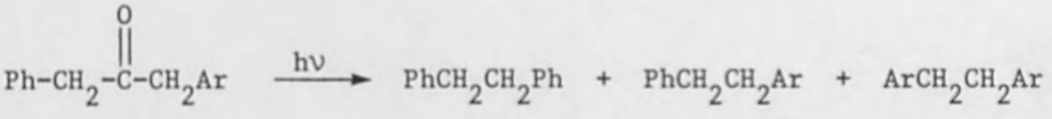


Figure 32: Positions of hydrogen abstraction from sodium tetradecanoate by the triplet of 2-(4-benzoylphenyl) propionate (130).

1.2.12.3 Photochemical fragmentation reactions:

Micellar environments can enhance the radical cage reactions of hydrophobic radical pairs relative to those in homogeneous solutions.[151,152] If a hydrophobic radical pair is generated in a micelle, the probability of cage reaction between spin correlated radical pairs increases relative to reaction of free radicals without spin correlation.

Photodecarbonylation of unsymmetrical dibenzyl ketones A-CO-B in homogenous solution occurs via a free radical mechanism to produce 1,2-diarylethanes in quantitative yields.[152] The products AA, AB and BB are formed in yields of 25, 50, and 25% respectively. In contrast,[151] photolysis of A-CO-B in micelles containing solutions of CTAC results in selective formation of AB (Fig. 33). The yield of A-B relative to (AA + BB) is more than 98% in micellar solutions of CTAC.



A-CO-B	AA	AB	BB
Homogeneous solution	25%	50%	25%
Micellar solution	∿ 0%	∿ 100%	∿ 0%

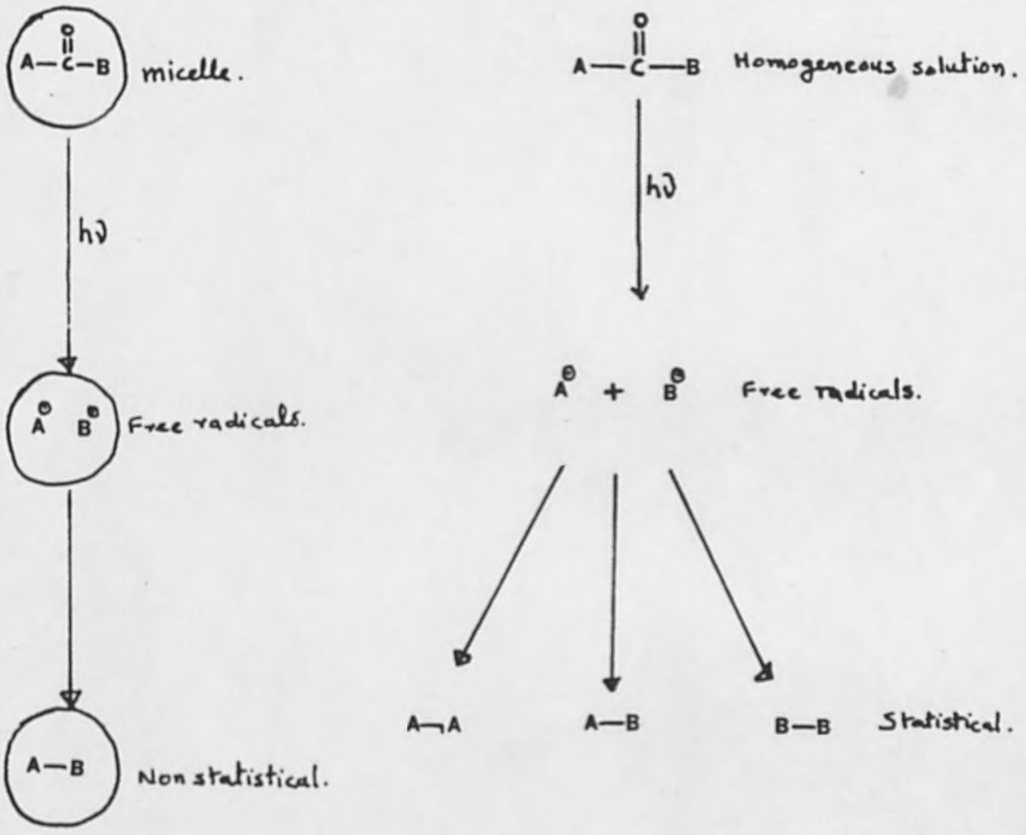


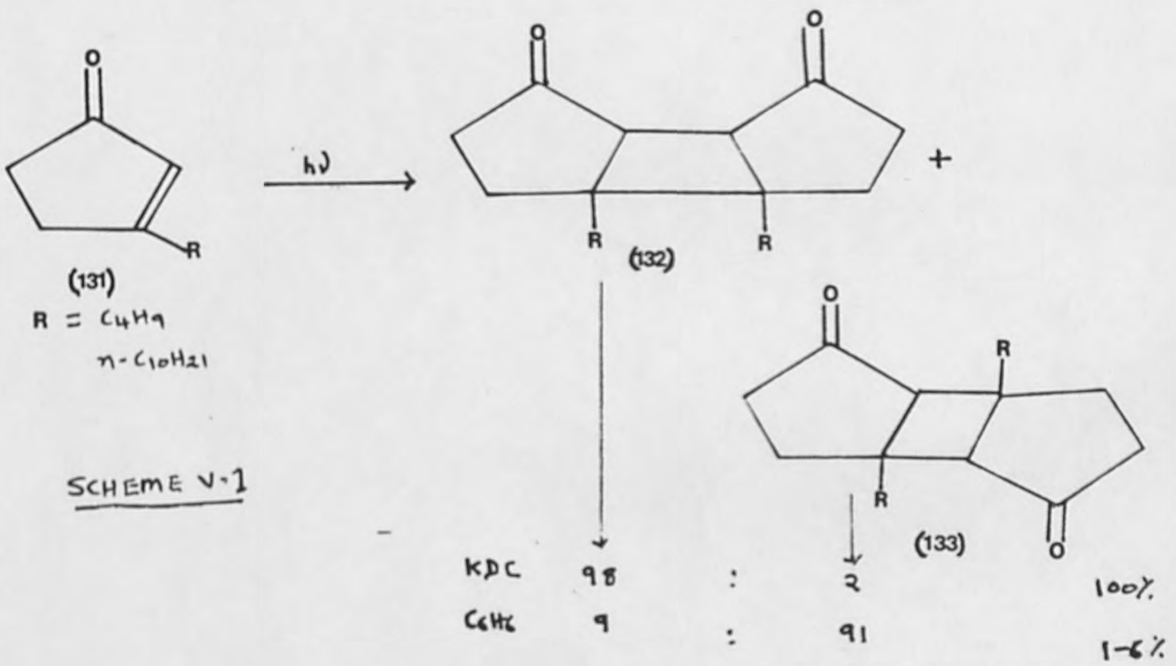
Figure 33: Photodecarbonylation of unsymmetrical benzyl ketones in a micellar solution (CTAC).

1.2.18.4 Photocycloaddition reactions in micelles:

The intermolecular cycloaddition reactions may be very efficient in micellar systems compared with those in homogeneous solutions. This may be due to high local concentrations of a substrate, which can be achieved by solubilization of the substrate into micellar aggregates.

Irradiation of 3-alkylcyclopentanes (131) in potassium dodecanoate (KDC) micelles leads to more efficient dimerisation of the compound compared to that occurring in homogeneous solution e.g. as in benzene.[153]

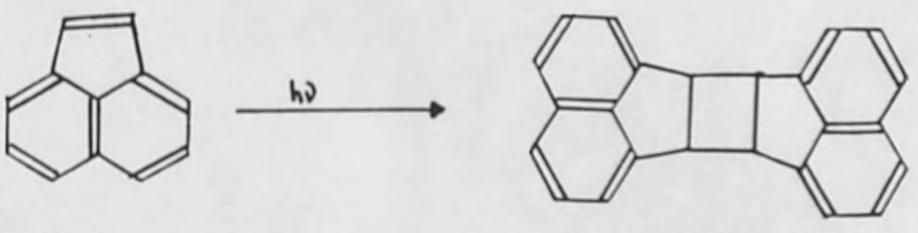
In addition to the high efficiency of photodimerisation of 3-alkyl-pentanoate (131) a high regio-specificity was also observed, the relative yield of head to head (132) to head to tail dimer (133) was opposite to that observed in homogeneous solutions (Scheme V-1).[153]



SCHEME V-1

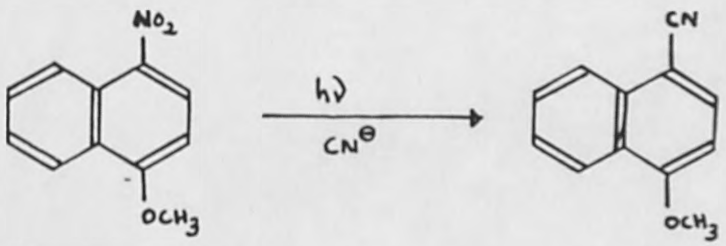
The photoinduced dimerisation of acenaphthalene (134) in the micellar solutions of nonoic and anionic surfactants occurs readily, even under low concentration conditions, such that no dimeric products were produced in benzene solutions (Scheme W).[154]

SCHEME W



1.2.18.5 Photoinduced substitution of aromatic compounds:

In the photoinduced substitution reactions in micelles, both reduction and enhancement in the reaction rates may be achieved depending on whether the charge of the detergent causes repulsion of the attacking nucleophile or causes organization of the attacking nucleophile and substrate. These effects have been observed in photoinduced substitution reactions of 4-methoxy-1-nitronaphthalene (135) containing CN^- ions. Formation of 4-methoxy-1-naphthalene carbonitrile (136) occured. Large enhancement in the quantum yield of the reaction was observed when the reaction was carried out in micellar solutions of cetyl trimethyl ammonium chloride, whereas the quantum yield of the reaction was very low when the reaction was carried out in sodium lauryl sulphate micelles.[155]



(135) (136)

1.2.19 Photo-redox reactions in micellar systems:

1.2.19.1 Electron transfer in transition metal ion micelles:

The photo-redox reaction can be expressed as follows:

$$A + D \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} A^- + D^+$$

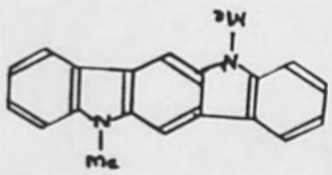
A = Acceptor
D = Donor

The photo-redox reaction may transfer a large fraction of incident light energy into chemical energy.[156-159,164] However, in the photo-redox process back reaction occurs very rapidly and hence

difficulty may arise in its practical application. This problem may be overcome by employing charged surfactant aggregates such as micelles in aqueous solutions as a reaction medium.

Cupric ions (Cu^{2+}) of surfactant copper lauryl sulphate $[Cu(LS)_2]$ can be photoreduced to cuprous ions (Cu^{+}) by suitable donor molecules, such as N,N'-dimethyl-5,11-dihydroindolo(3,2-b) carbazole (DI).[156,157] The introduction of copper ions as counterions of the surfactant reduces the fluorescence quantum yield and lifetimes of (DI) compared to sodium ions (Na^{+}) of sodium lauryl sulphate. This process occurs in less than a nanosecond and can compete with fluorescence and intersystem crossing.

$$DI + Cu^{2+} \xrightarrow{h\nu} DI^{+} + Cu^{+}$$



(DI)

The back reaction of the electron transfer from DI^{+} to Cu^{+} is slower than the exchange with counterions present in the Gouy Chapman layer. This allows the reduced metal ion (Cu^{+}) to escape from its native micelle into the bulk solution by exchange with one of the cuprous ions (Cu^{2+}) present in high local concentrations in the Gouy Chapman layer. The Cu^{+} ion can be used, after entering the aqueous phase, for a second redox process - such as the reduction of $Fe(CN)_6^{3-}$. The back reaction of the $Fe(CN)_6^{4-}$ with the oxidized donor DI^{+} is prevented by the negatively charged micellar surface. Hence, such a system is successful in storing light energy originally converted into chemical energy during a photo-redox process, Fig. (34).

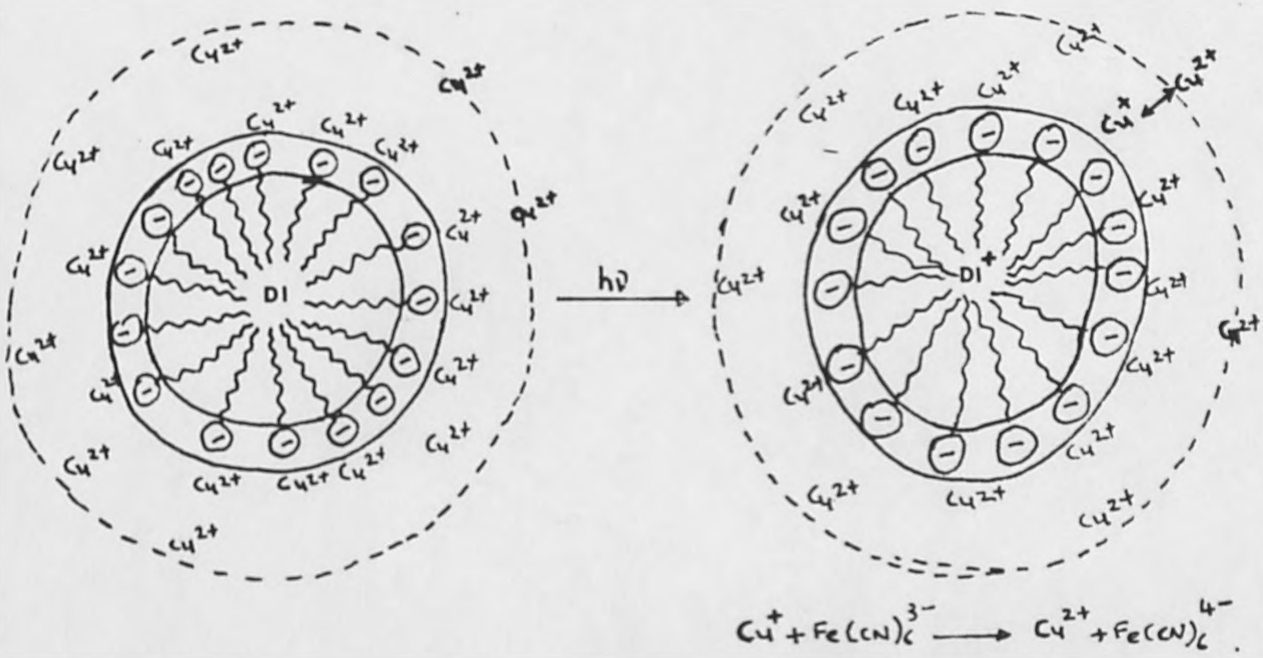
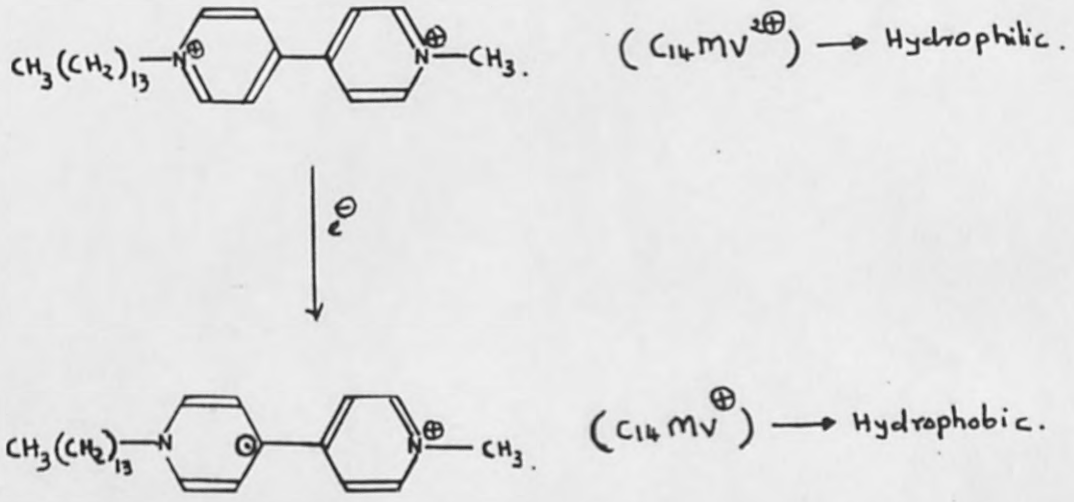


Figure 34: Electron transfer in copper sulphate micelles.

1.2.19.2 Methyl viologen surfactant assemblies as electron acceptors and their application in cyclic cleavage of water into hydrogen and oxygen:

The surfactant derivative of methyl viologen ($CnMV^{2+}$) (N-alkyl-N'-methyl-4-4'-dipyridinium dichloride, n = 12, 14, 16, 18) acts as an electron acceptor in the photo-induced electron transfer reactions of electron donor molecules such as ruthenium bipyridyl complexes $\left[Ru(bpy)_3^{2+}\right]$. The oxidized form of ($C_{14}MV^{2+}$) has strongly hydrophilic properties while its reduced form ($C_{14}MV^{+}$) is hydrophobic as shown in Scheme (X).[158]

SCHEME X



In a micellar solution of CTAC containing ($C_{14}MV^{2+}$) as an electron acceptor and zinctetrakis-(N-methyl-pyridyl)porphyrin ($ZnTMPyP^{4+}$) or a complex of ruthenium ($Ru(bpy)_3^{2+}$) as the photoactive electron donor, reduction of $C_{14}MV^{2+}$ to $C_{14}MV^{+}$ will occur as follows:

$$ZnTmPyP^{4+} + C_{14}MV^{2+} \xrightarrow{h\nu} C_{14}MV^{+} + ZnTMPyP^{5+}$$

$$Ru(bpy)_3^{2+} + C_{14}MV^{2+} \xrightarrow{h\nu} C_{14}MV^{+} + Ru(bpy)_3^{3+}$$

The forward electron transfer will go to completion without any subsequent back reaction, because the hydrophilic acceptor $C_{14}MV^{2+}$ will be reduced to $C_{14}MV^{+}$ and it will acquire hydrophobic character and hence it will be solubilized in the interior of the cationic surfactant micelles. The oxidized porphyrin ($ZnTMPyP^{5+}$) or $Ru(bpy)_3^{3+}$ will be prevented from approaching the interior of cationic micelles

by their repulsive surface charges. This type of electron transfer reaction can occur in homogeneous solutions (e.g. water) where the back reaction also takes place very rapidly, but can be prevented in the micellar environment as shown in Fig. (35).

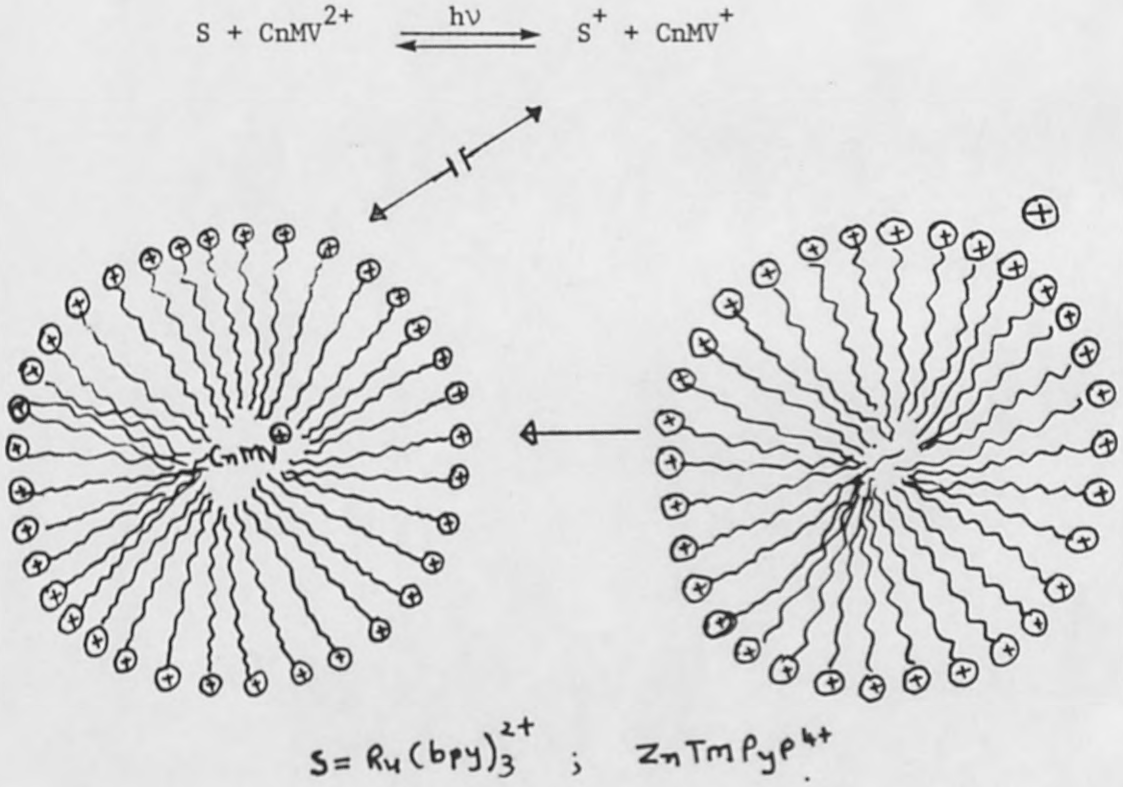


Figure 35: Principle of charge separation by cationic micelles in the photoinduced reduction of hydrophilic derivatives, e.g. $C_{14}MV^{2+}$.

The $C_{14}MV^{+}$ produced in the photo-redox process may be used to generate hydrogen from water in the presence of a noble metal catalyst. For example, continuous illumination of $ZnTMPyP^{4+}$ solutions containing $C_{14}MV^{2+}$, CTAC and platinum catalyst leads to the production of hydrogen.[158,159]

$$2C_{14}MV^{\cdot +} + 2H_2O \longrightarrow 2C_{14}MV^{2+} + H_2 + 2OH^-$$

The oxidized porphyrin ($ZnTMPyP^{5+}$) or ruthenium complex $Ru(bpy)_3^{3+}$ can afford water oxidation.[158]

$$4S^+ + 2H_2O \longrightarrow 4S + 4H^+ + O_2$$

The photo-induced reduction of methyl viologen (MV^{2+}) N-N-dimethyl bipyridine dication by sensitizer $Ru(bpy)_3^{2+}$ has been exploited to achieve cleavage of water into hydrogen and oxygen simultaneously.[159,160] The photo-redox process was performed in the presence of two redox catalysts deposited on colloidal titanium dioxide, one of which is colloidal platinum which effects reduction of water and the other e.g. RuO_2 effects oxidation of water as shown in Figure (36).

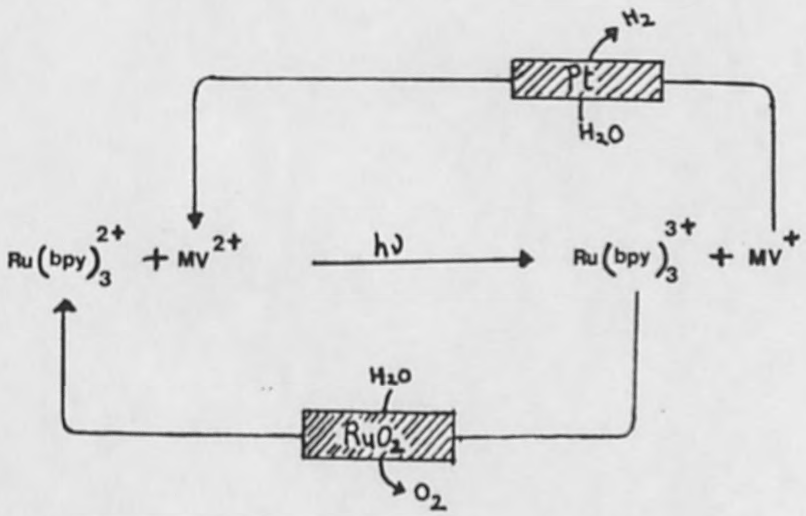
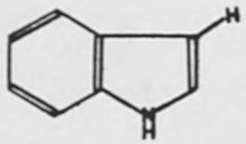


Figure 36: Cyclic cleavage of water by photoredox process.

CHAPTER TWO

RESULTS AND DISCUSSION

SCHEME V



C_2H_5MgBr + In(H)—H + $CH_3(CH_2)_nCOCl$ → In(H)—$CO(CH_2)_nMe$

n = 0,7,10,16 (see Scheme A)

n = 0,4,7,10,16

In(H)—$CO(CH_2)_nMe$ —$LiAlH_4$/dry ether, Reflux→ In(H)—$(CH_2)_{R_1}Me$

R_1 = 0,5,8,11,17 Scheme A & B

$CH_3(CH_2)_nCOCl$ + $HNMe_2$ → $CH_3(CH_2)_nCONMe_2$ + $POCl_3$ + In(H)—H

n = 0,4,7,10,16. (Scheme B)

In(H)—$(CH_2)_{R_1}Me$ + $Br(CH_2)_{10}CO_2H$ / KOH/DMSO → In—$(CH_2)_{R_1}Me$ | $(CH_2)_{10}CO_2H$

R_1 = 0,5,8,11,17 Scheme F

In(H)—$(CH_2)_{R_1}Me$ + $Br(CH_2)_{11}OH$ / KOH/DMSO → In—$(CH_2)_{R_1}Me$ | $(CH_2)_{11}OH$

R_1 = 0,5,8,11,17 Scheme F

In(H)—$(CH_2)_{R_1}Me$ + $Br(CH_2)_6Br$ / KOH/DMSO → In—$(CH_2)_{R_1}Me$ | $(CH_2)_6Br$

R_1 = 5,8,11,17 Scheme F

In(H)—$(CH_2)_{R_1}Me$ + $Br(CH_2)_{10}Br$ / KOH/DMSO → In—$(CH_2)_{R_1}Me$ | $(CH_2)_{10}Br$

R_1 = 0,5,8,11,17 Scheme F

In—$(CH_2)_{R_1}Me$ | $(CH_2)_{10}CO_2H$ —$NaHCO_3$→ In—$(CH_2)_{R_1}Me$ | $(CH_2)_{10}CO_2^{-}Na^{+}$

R_1 = 0,5,8,11,17 Scheme I

In—$(CH_2)_{R_1}Me$ | $(CH_2)_6Br$ —$+NMe_3$, C_2H_5OH, Reflux→ In—$(CH_2)_{R_1}Me$ | $(CH_2)_6\overset{(+)}{N}Me_3Br^{(-)}$

R_1 = 5,8,11,17 Scheme H

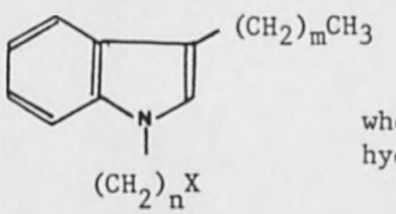
In—$(CH_2)_{R_1}Me$ | $(CH_2)_{10}Br$ —NMe_3, C_2H_5OH, Reflux→ In—$(CH_2)_{R_1}Me$ | $(CH_2)_{10}\overset{(+)}{N}Me_3Br^{(-)}$

R_1 = 0,5,8,11,17 Scheme H

2.1 Synthesis of substituted indoles using a variety of synthetic methods:

Compounds such as 11-(3-hexyl-1-indolyl)undecyl trimethyl ammonium bromide have been found to be versatile and powerful fluorescent probes for micelle structures.[82] They form micelles at above 10^{-4} M and can be incorporated into micelles of other cationic surfactants. These compounds are useful in determining the critical micelle concentration (CMC) of other cationic surfactants.

Following the above findings, a series of indolic surfactants were



where X = polar head group or hydroxy group

synthesised which were particularly suited for probing the structure of the micelles, because by varying both m and n it should be possible to vary the depth at which such fluorescent groups sit in a micelle and therefore make a depth profile of the micelle. By probing the fluorescence of these compounds, in aqueous solutions, we have determined their CMCs and found out what effect the chain length, providing the fluorescence is sensitive enough, has on the CMC.

The possibility of using anionic and nonionic indolic surfactants as fluorescent probes was also investigated. Indolic acids were synthesised to determine whether these probes can serve as CMC indicators and provide information concerning the similarities and

differences between the interior of cationic and anionic surfactants. Similarly, indolic alcohols were prepared to determine whether these compounds can be used as fluorescent probes in cationic, anionic and nonionic host surfactants.

The following classes of indolic surfactants have been synthesised as shown in Scheme V.

(i) Cationic surfactants (indolic trimethyl ammonium bromides).

(ii) Anionic surfactants (indolic acids and attempted synthesis of indolic sulphates).

(iii) Nonionic surfactants (indolic alcohols).

2.1.1 Synthesis of 3-acyl indoles:

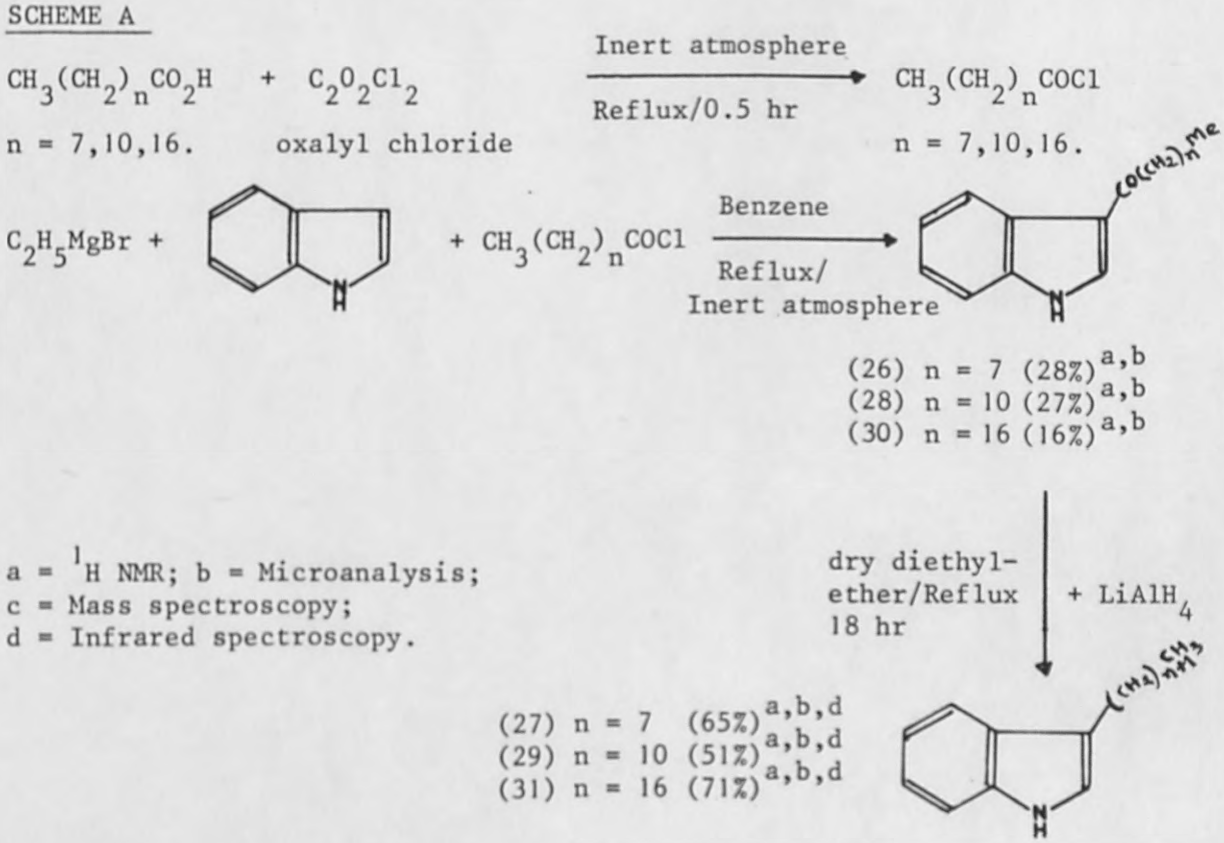
Indoles usually undergo electrophilic substitution at the 3-position[166]. Electrophilic reagents may also affect substitution at nitrogen, particularly if the alkali metal salts or Grignard derivatives of the indole are used. However, in most reactions of indolyl Grignard reagents with alkyl halides recorded in the literature, substitution takes place at the 3-position and only to a lesser extent at nitrogen. Jackson and Smith have investigated various aspects of these electrophilic substitution reactions with indoles and made an attempt to define more clearly the conditions under which substitution occurs in the various positions of the indole nucleus.[167-170] Indolyl magnesium iodide itself reacts

straightforwardly with allyl-bromide to give 3-allyl indole.[171] Turro and co-workers[82] followed the above method to synthesise 3-hexanoyl-indole which gave only 35% yield.

It was necessary for us to find an appropriate method to synthesise different 3-alkyl indoles which were to be converted to 1,3-dialkyl indole surfactants, for fluorescence investigations. We have followed Jackson's method and found that the yields obtained are very low (28%, 26% and 16%).

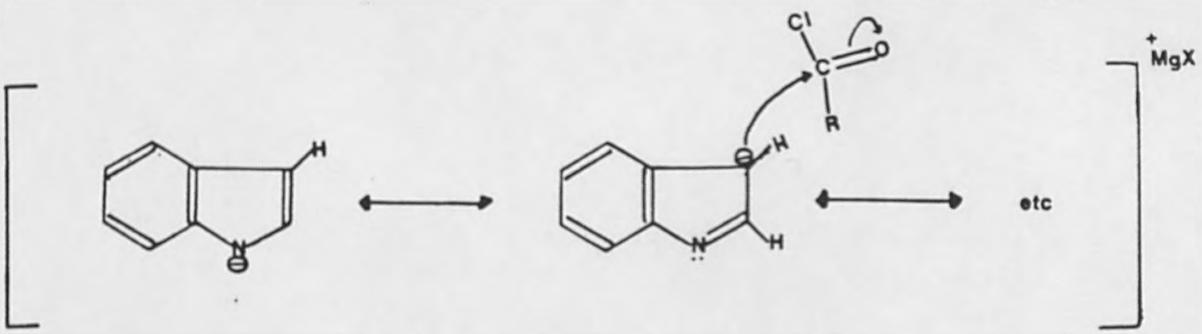
Acid chlorides were prepared from the corresponding acids (nonoic, lauric and stearic acids) and then reacted with indolyl magnesium bromide so as to obtain different 3-acyl indoles as shown in Scheme A. These 3-acyl indoles were then reduced to 3-alkyl indoles with yields of > 75% using lithium aluminium hydride.

SCHEME A



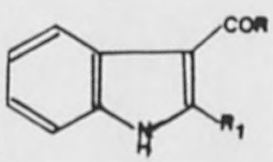
a = ^{1}H NMR; b = Microanalysis;
c = Mass spectroscopy;
d = Infrared spectroscopy.

The reaction proceeds via nucleophilic attack of an indolyl-magnesium bromide intermediate upon the acid chloride. The structure of the Grignard derivative derived from indole has been investigated by Reineck and co-workers.[172] They concluded from the NMR studies that the indole Grignard reagent is predominantly the ionic resonance hybrid as shown,



which could give the expected product ((26), (28) and (30)) as shown in Scheme A. The yields of 3-acyl indoles were low (< 30%). Therefore, it was necessary to investigate an alternative method which could improve the yields.

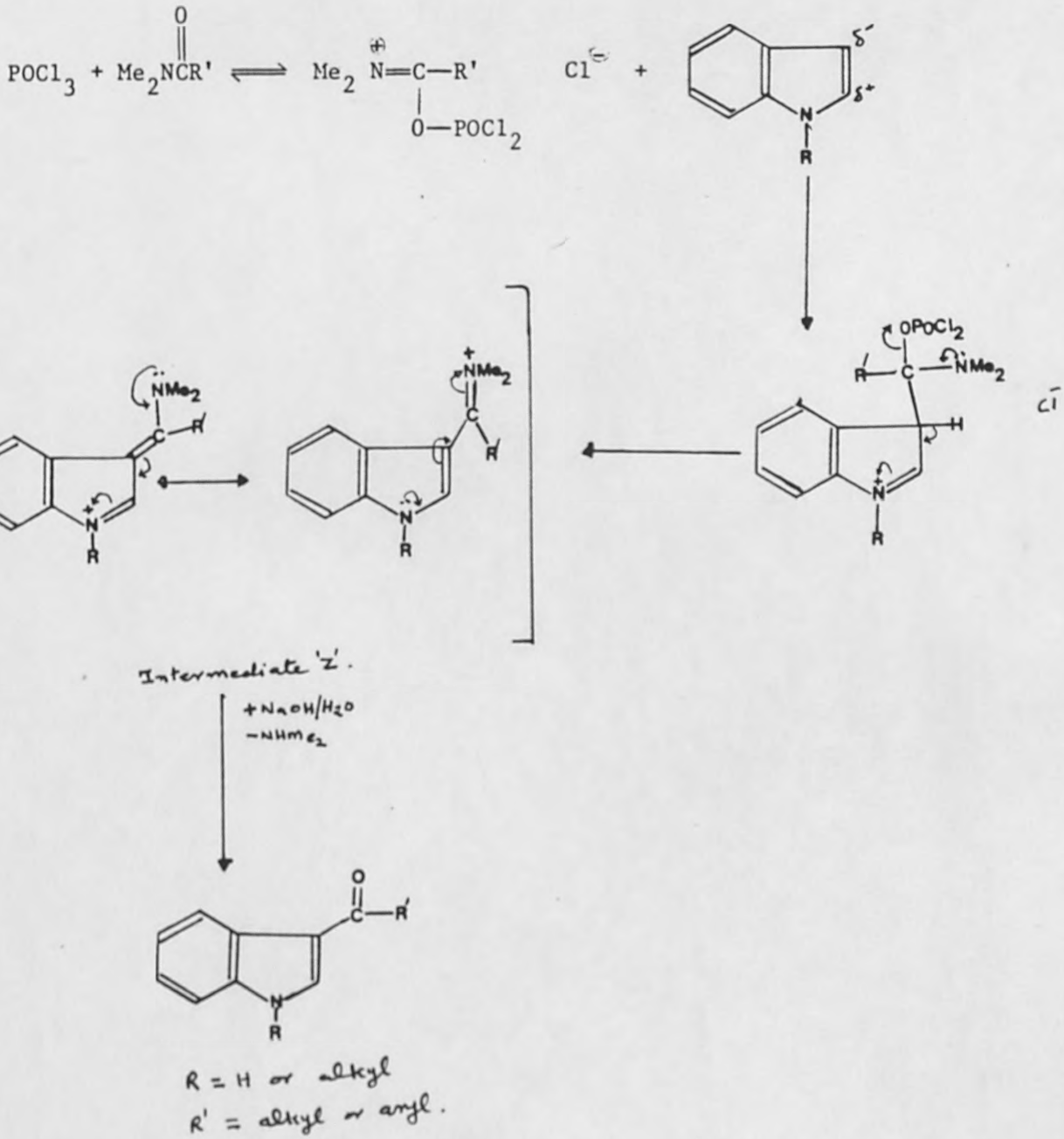
The introduction of a ketone function into certain indoles and pyrroles by means of phosphorus oxychloride and the appropriate amide has been reported by Anthony.[173] He prepared a variety of 3-acyl indoles and 3-acyl pyrroles using different amides and phosphorous oxychloride.



where R = CH_3, Ph, chloroacetyl, $-CH_2CH_3$, CMe_3 etc.

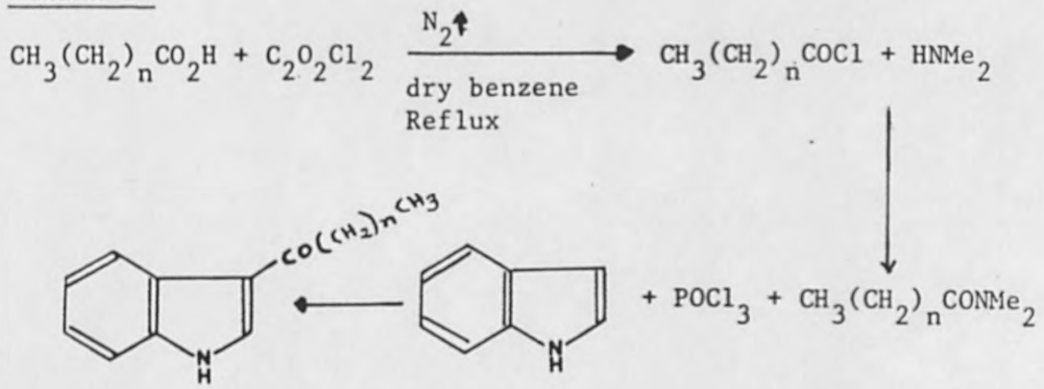
R_1 = Me, H etc.

Smith[174] has applied this procedure to the preparation of indole-3-carboxaldehyde and proposed a reaction mechanism which would require two replaceable hydrogens on the nucleophile. However, the formation of indole and pyrrole ketones with only one replaceable hydrogen was investigated.[173] The following reaction scheme may apply to acylation of indoles which contain either one or two replaceable hydrogens.[173,175]



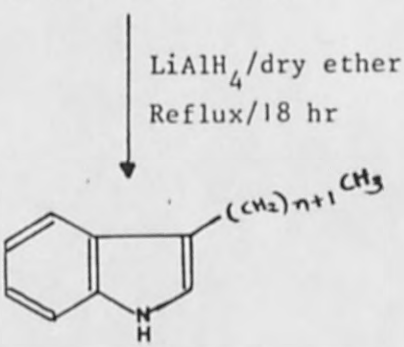
A water soluble compound was formed when water was added to the reaction mixture (before adding NaOH solution). This fact supported the proposed intermediate such as 'Z' above. When 3-alkyl indoles were synthesised with long alkyl groups (> C_{12}), the intermediate is partly soluble in water. Yields > 45% were obtained for all the products as shown in Scheme B.

SCHEME B



(26a) n = 7 (70%)[a,b,d]
(28a) n = 10 (77%)[a,b,d]
(30a) n = 16 (52%)[a,b,c,d]
(32) n = 0 (46%)[a,d]
(34) n = 4 (75%)[a,b,d]

(33) n = 4 (79%)[a]
(35) n = 7 (87%)[a,b,c]
(36) n = 10 (91%)[a,b,c]
(37) n = 16 (85%)[a,c]



(34b) n = 4 (89%)[a,d]; (27a) n = 7 (85%)[a,b,d];
(29a) n = 10 (71%)[a,b,d]; (31a) n = 16 (82%)[a,b,d].

The different chain length acids (nonoic, lauric, stearic and hexanoic acid) were reacted with oxalyl chloride to obtain the corresponding acid-chlorides which were subsequently reacted with N,N-dimethylamine (anhydrous) to obtain N,N-dimethyl carboxamides (33), (35), (36) and (37). These amides were then reacted with phosphorous oxychloride and indole to obtain the corresponding 3-acyl indoles (26a), (28a), (30a), (34) and (32) as shown in Scheme B. The yields were more than 50% in all reactions apart from the case of product (32), 46%. These yields are considerably higher than we obtained by Jackson's method (< 30%). The above 3-acyl indoles were then reduced by lithium aluminium hydride to give the corresponding 3-alkyl indoles (34b), (27a), (29a) and (31a) with yields greater than 70%.

2.1.2 Synthesis of N-alkyl indoles:

Our aim was to synthesise different N-alkyl indoles using different methods. We were then in a position to devise the most efficient and convenient method for the synthesis of different varieties of indolic products. Three types of methods were investigated.

(i) Phase transfer catalysis (PTC) using 18-crown-6.

(ii) PTC using polyethylene glycol(1540) and

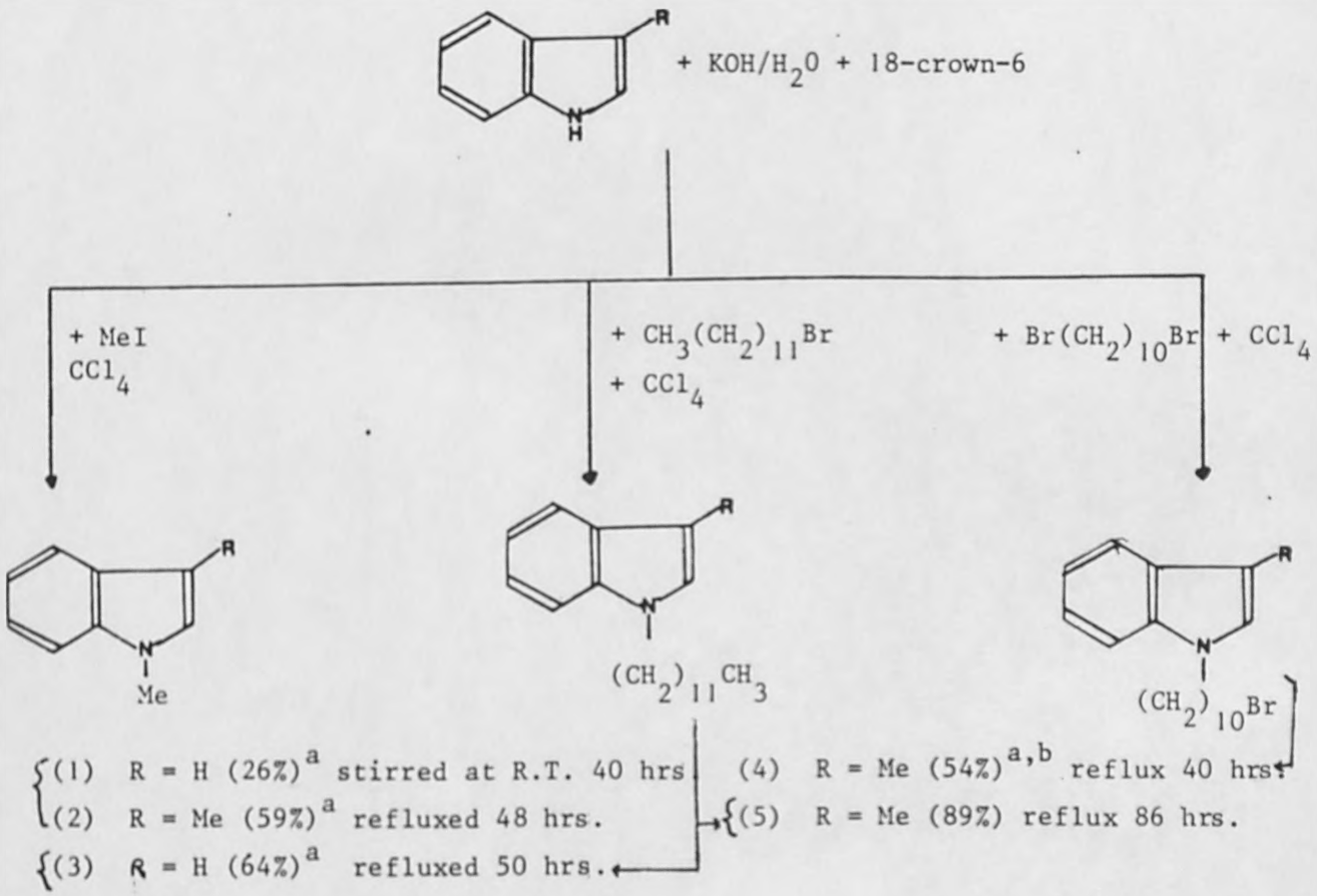
(iii) KOH/DMSO method.

The phase transfer catalysis reactions for N-alkylation and o-alkylation of different heterocyclic compounds are discussed extensively in Section 2.5. The reaction mechanism is also discussed.

(i) Reaction of indoles with alkyl halides using 18-crown-6- as phase transfer catalyst

The phase transfer catalyst 18-crown-6 has been used previously in many reactions[176,177] and its use in N-alkylation of indoles has been reported.[178,179] In this case the reaction of indole and skatole with iodomethane using 18-crown-6 as PTC gave 26% and 59% yields respectively. It has been noticed that yields were improved when the reaction mixture was heated under reflux for more than 40 hrs as shown in Scheme C. The yields were determined by the analysis of ^{1}H NMR.

SCHEME C

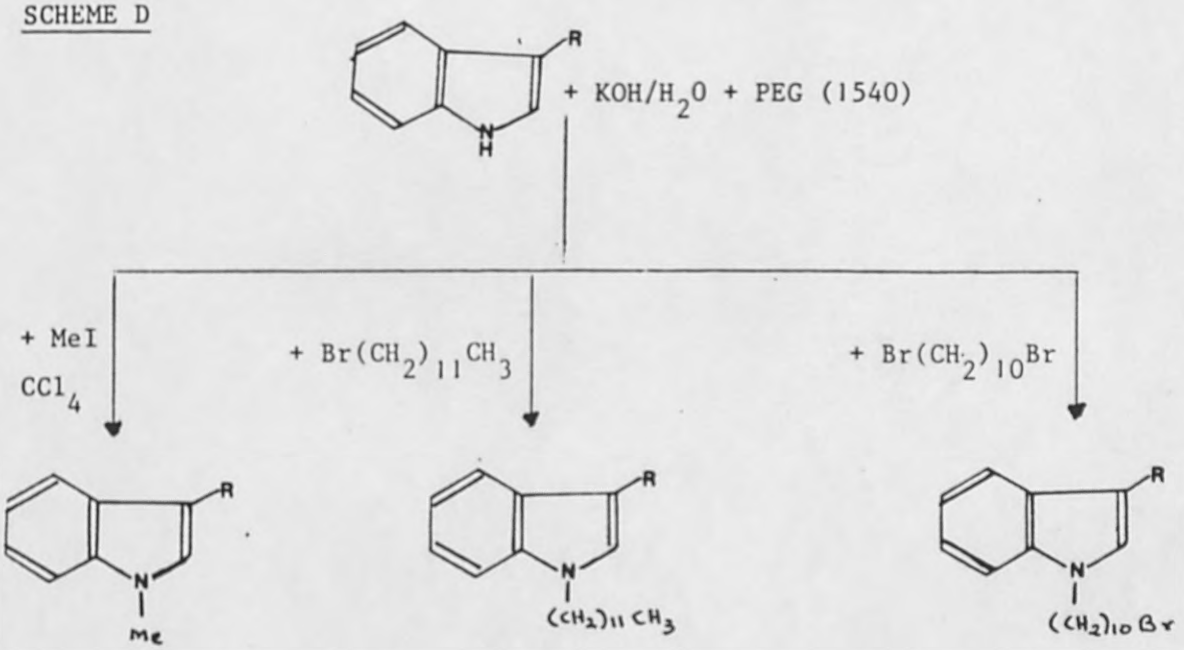


a = ^{1}H NMR. b = microanalysis (CHN).

(ii) N-alkylation of indoles using polyethylene glycol (1540) as PTC:

The polyoxyethylene dimethyl ethers have been previously used as PTC.[180,181] Straight chain polyethylene glycol (PEG 1540) has not previously been used as PTC in N-alkylation reactions. It will be interesting to find out if PEG acts as a PTC in our reactions. When skatole and indole were reacted with iodomethane in the presence of potassium hydroxide, water and PEG, as PTC, the expected products were obtained, but the reactions were not successful when bromododecane and 1,10-dibromo-decane were used as shown in Scheme D. The products were analysed by ^{1}H NMR spectroscopy.

SCHEME D



(1a) R = H (40%)[a]

(2a) R = Me (20%. reflux 48 hrs)[a] isolated product.

(3a) R = H (reflux 40 hrs) (no product)[a]

(4a) R = Me Reflux 48 hrs, minor product) R = H (no product).

a = ^{1}H NMR

(iii) N-alkylation of indoles using KOH/DMSO method:

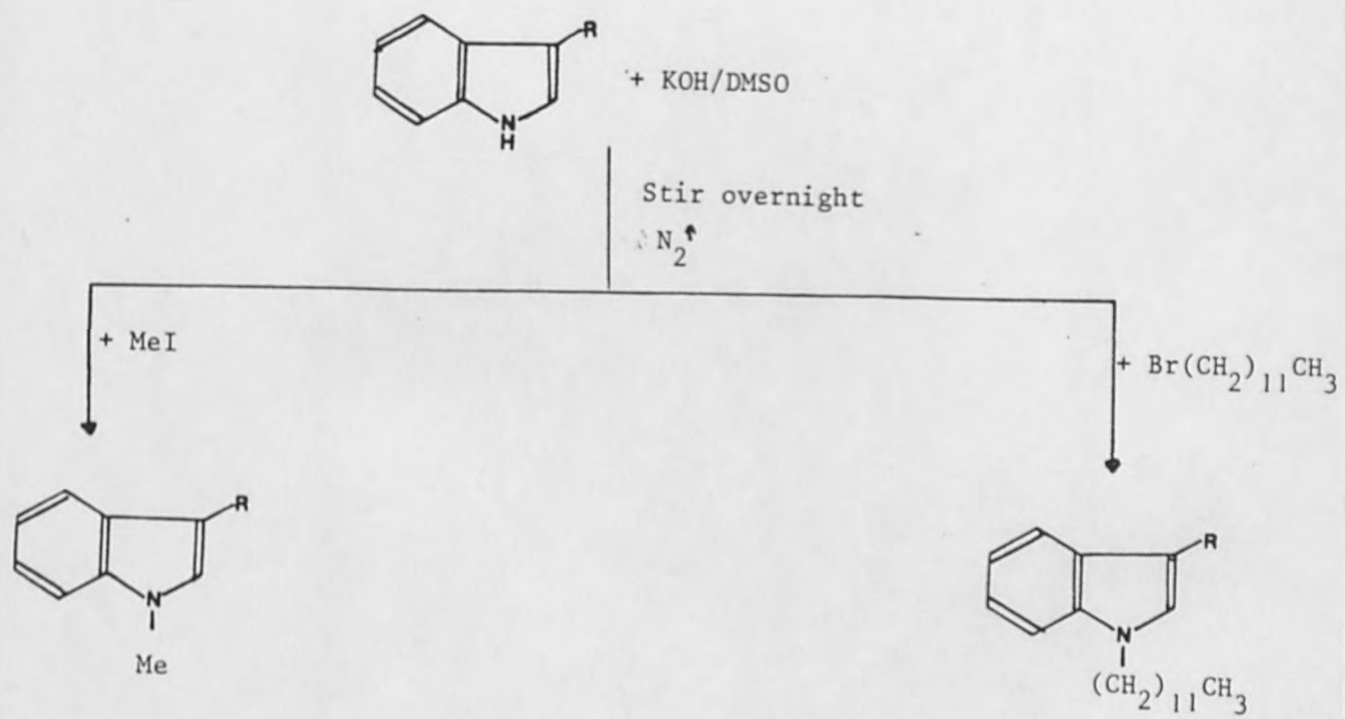
The use of dimethyl sulphoxide (DMSO) as a dipolar aprotic solvent[182] is well known and excellent results have been obtained, for example, o-methylation of phenoles,[183] n-alkylation of pyrroles and indoles.[21] In the case of alkylation of indoles, the reaction involves the formation of the potassium salts of indoles. Alkylation is then achieved, without the isolation of these potassium salts, by addition of excess of the appropriate n-alkyl halide at room temperature. In this procedure a small amount of potassium hydroxide is solubilised in the DMSO and the "naked" hydroxide ions so produced act as a powerful base for the removal of the acidic indole hydrogen.[182]

Rickborn[184] carried out a kinetic study on the rate of proton abstraction from carbon by alkoxide anions and found that it can be made to vary by as much as an estimated nine powers of ten by varying the solvent, i.e. from tert-butyl alcohol to DMSO.

We have synthesised N-methyl indole (1b) and N-dodecyl indole (3b) using potassium salts of indole in dimethyl sulphoxide with iodomethane and bromododecane respectively. The yields of the products were considerably higher (Scheme E, 69% and 74% respectively) than the yields obtained by the previous two methods, as shown in the schemes C and D. In addition, the KOH/DMSO system does not require any heating whereas in scheme C and D the reaction needs to be refluxed (> 40 hrs) in order to obtain higher yields. The indole starting material was obtained, along with the products, when N-

alkylations were carried out using PTC (^{1}H NMR). It was a difficult and lengthy process to isolate the product from the starting material. This problem did not generally occur when the N-alkylation was carried out in potassium hydroxide and DMSO. However, the removal of DMSO from the product required repeated washing (4 times) of the diethyl ether solution of the product with water and in some cases distillation.

SCHEME E



(1b) R = H (69%)[a]
isolated product.

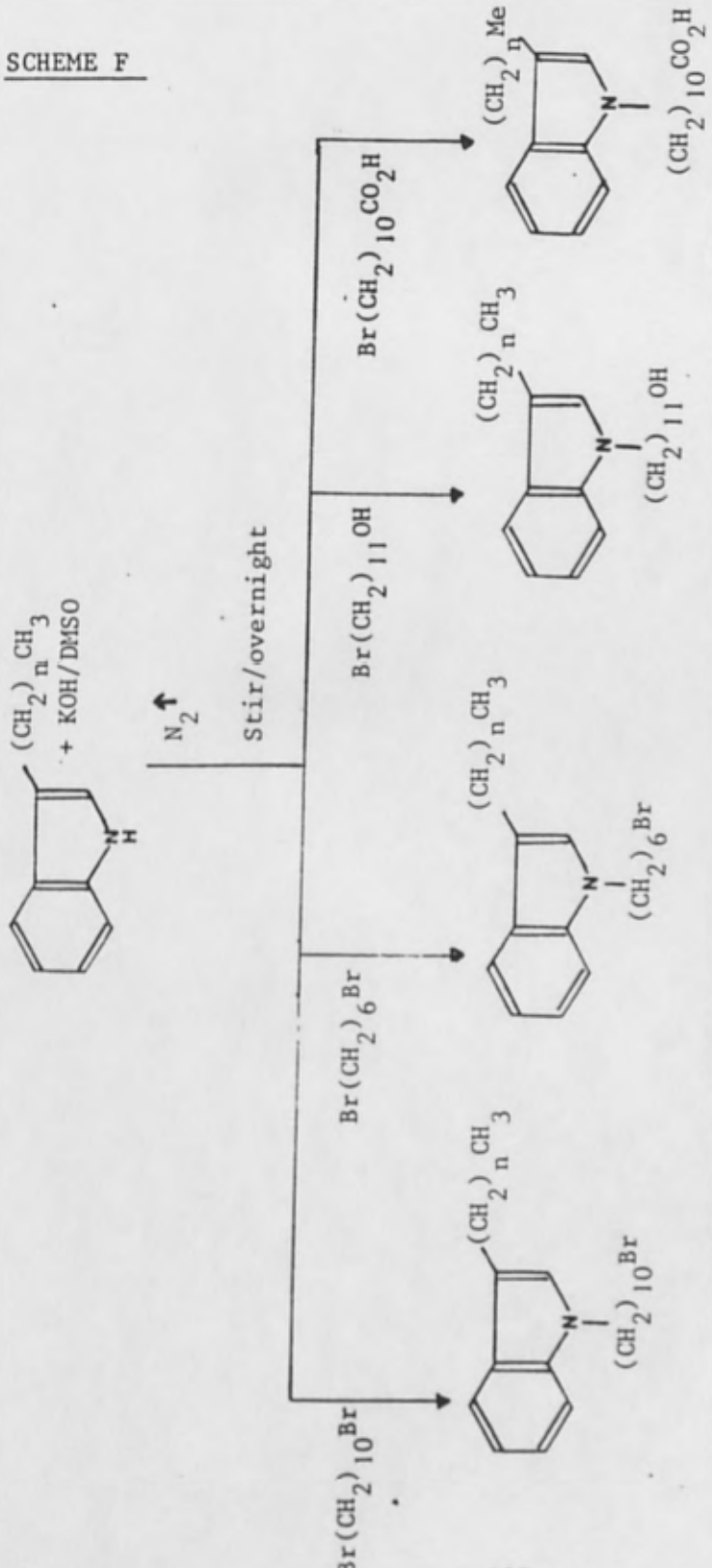
(3b) R = H (74%)[a]

a = ^{1}H NMR.

2.1.3 N-alkylation of 3-alkyl indoles:

N-alkylation of 3-alkyl indoles was carried out using KOD/DMSO method since it was found to be the most suitable and efficient method. The yields were varied according to the alkylating agents (alkyl halides, alcohols and acids) as shown in Scheme F.

SCHEME F



(4) n = 0 (54%)[a,b] (56) n = 5 (22%)[a,c] (51)-$(CH_2)_nCH_3$ = (53) n = 0 (69%)[a,b]

(59) n = 5 (47%)[a,c] (66) n = 8 (66%)[a,c] = H (63%)[a,b]. (64) n = 5 (65%)[a,b]

(11a) n = 8 (69%)[a,c] (76) n = 11 (40%)[a] (7a) n = 0 (67%)[a,b] (74) n = 8 (92%)[a,b,c]

(77) n = 11 (97% crude)[a,c] (83) n = 17 (45%)[a,c] (62) n = 5 (60%)[a,b] (81) n = 11 (95%)[a,b]

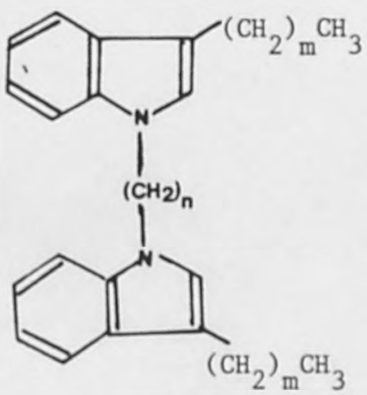
(85) n = 17 (46%)[a,c] (72) n = 8 (61%)[a,b] (88) n = 17 (67%)[a,b]

(49) -$(CH_2)_nCH_3$ = H (45%)[a,b] (79) n = 11 (54%)[a,b]

(87) n = 17 (38%)[a,b]

a = ^{1}H NMR spectroscopy; b = microanalysis (C,H,N); c = Mass spectroscopy.

1,10-Dibromodecane and 1,6-dibromohexane were reacted with 3-alkyl indoles to obtain different bromodecyl and bromohexyl indoles. 11-Bromoundecanol was reacted with 3-alkyl indoles to obtain different 3-alkyl indolyl N-undecyl alcohols (51), (7a), (62), (72), (79) and (87) in over 54% yields (except (87), 38%). Similarly, 11-Bromoundecanoic acid was reacted with 3-alkyl indoles to obtain different indolyl N-undecanoic acids (53), (64), (74), (81) and (88) in 65-95% yields. When indolyl bromides were prepared the indole dimers (50), (57), (60) and (67) were also obtained in minor amounts as by-products.



(50) $-(CH_2)_mCH_3$ = H

n = 10 (18%)[a].

(57) m = 5, n = 6 (13%)[a,c]

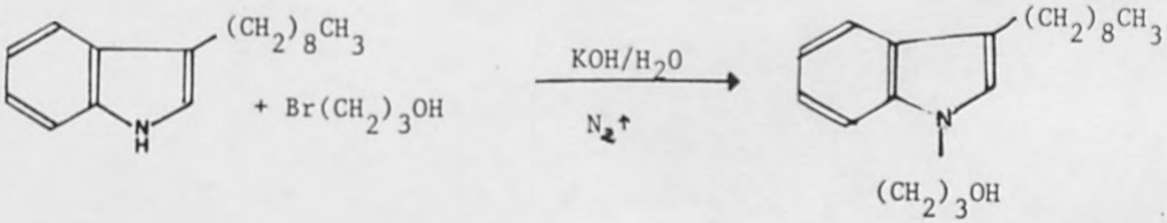
(60) m = 5, n = 10 (17%)[a,c]

(67) m = 8, n = 6 (minor)[a,c].

a = ^{1}H NMR; c = Mass spectroscopy.

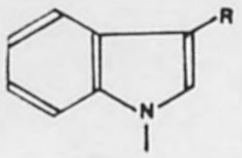
It was difficult to purify these 1,3-dialkyl indolyl bromides for analytical purposes. They were distilled twice or more under high vacuum (0.01 mm Hg) using Kugal rhör. TLC showed impure material, column chromatography was unsuccessful and it was not convenient to purify by preparative TLC because of the large amount of material requiring purification. However, the ^{1}H NMR were in reasonable agreement with the expected product. They were not needed in an absolutely pure form for further reactions since quaternisation with trimethyl amine allows the removal of any organic impurity such as indole dimer. Attempts were made to purify some of the indoles by HPLC but were unsuccessful. The impurity could not be separated on a reverse phase column using acetonitrile/dichloromethane, methanol/water and methanol /acetonitrile solvent systems.

The indolic alcohols were purified to analytical purity by using preparative TLC with silica gel and pet-ether (60-80°C)/ethyl acetate eluting solvent systems.



(71) 53%[a,c]

3-Nonyl indole was reacted with 1-bromo-3-propanol to obtain 3-(3-nonyl-1-indolyl)propyl alcohol (71) in 53% yield. Attempts were made to purify this product (71) analytically by preparative TLC but were unsuccessful. Attempts were made to synthesise 1-bromo hexan-6-ol (109) for the preparation of 6-(3-alkyl-1-indolyl) hexanols (110).



R = alkyl

(110)

SCHEME G

$$HO(CH_2)_6OH + HBr/H_2O \xrightarrow[76\ hr]{75^oC} Br(CH_2)_6OH + Br(CH_2)_6Br$$

48%

(109)

A mixture of 1,6-hexanediol, 48% HBr and water were heated at 75°C for 72 hrs while being continuously extracted with cyclohexane.[120] Removal of cyclohexane gave a very small amount of expected product, 6-bromohexanol (109) along with a major amount of 1,6-dibromohexane (Scheme G).

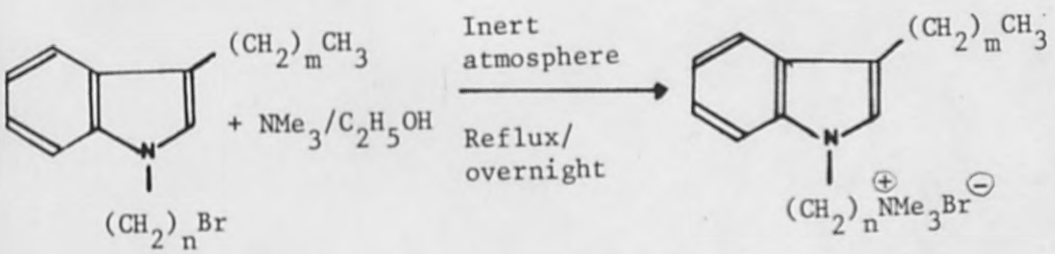
It was found that when a carbonyl group is attached to the indole nucleus in the 3-position, the 1-position can be readily alkylated with an alkyl halide and potassium carbonate.[185] An attempt was

made to synthesise 11-(3-acetyl-1-indolyl)undecanoic acid (92) by reacting 3-acetyl indole with 11-bromoundecanoic acid in dry acetone and potassium carbonate but was unsuccessful. Shafiee and Sattari[186] have prepared N-alkyl indoles by reacting the substituted indole with thallium (I) ethoxide and an alkylating agent in dry benzene.

2.1.4 Quaternisation of bromo-alkyl indoles with trimethylamine:

Turro and co-workers[82] have made 11-(3-methyl-1-indolyl) undecyl trimethyl ammonium bromide by reacting 1-(11-bromo-undecyl)-3-methyl indole with redistilled trimethylamine in absolute ethanol under reflux for 6 hrs. We did not find it necessary to redistill anhydrous trimethylamine. The 1,3-dialkyl indolyl bromides were reacted directly with anhydrous trimethylamine in absolute ethanol to give the corresponding trimethyl ammonium salts of indoles as shown in Scheme H.

SCHEME H



(52) m = 0, n = 10 (63%)[a,b]; (58) m = 5, n = 6 (56%)[a,b];
(61) m = 5, n = 10[a,b]; (68) m = 8, n = 6 (35%)[a,b];
(70) m = 8, n = 10 (74%)[a,b]; (69) m = 11, n = 6 (60%)[a,b];
(78) m = 11, n = 10 (36%)[a,c]; (84) m = 17, n = 6 (56%)[a,b].
(86) m = 17, n = 10 (36%)[a];

a = ^{1}H NMR; b = microanalysis; c = mass spectroscopy.

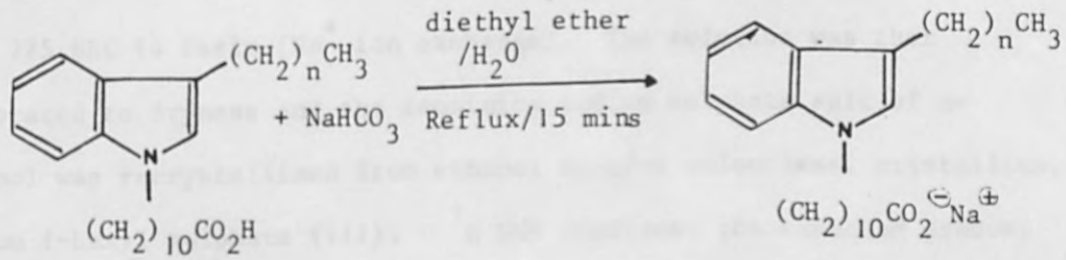
Since all of these compounds were very hygroscopic the yields were determined approximately. These compounds were purified by freeze drying and analysed by micro-analysis (CHN) which showed one or more molecules of water to be present. ^{1}H NMR spectra were consistent with the proposed structure. 6-(3-Alkyl-1-indolyl)hexyl trimethyl ammonium bromides are found to be less hygroscopic than the 10-(3-alkyl-1-indolyl)decyl trimethyl ammonium bromides.

2.1.5 Preparation of sodium salts of indolic acids:

$$CH_3(CH_2)_{10}CO_2H + NaHCO_3 \xrightarrow[\text{Reflux/15 mins}]{H_2O} CH_3(CH_2)_{10}CO_2^{-}\ Na^{\oplus} \qquad (54)$$

Lauric acid in ethanol was reacted with an equimolar amount of sodium bicarbonate solution in water. The reaction mixture was heated under reflux for 15 minutes and the product (54) was purified for fluorescence investigations.

SCHEME I



(53) n = 0.
(64) n = 5.
(74) n = 8.
(81) n = 11.
(88) n = 17.

(55) n = 0 (79%).
(65) n = 5 (38%)[a].
(75) n = 8 (41%)[a].
(82) n = 11 (33%)[a].
(89) n = 17 (71%).

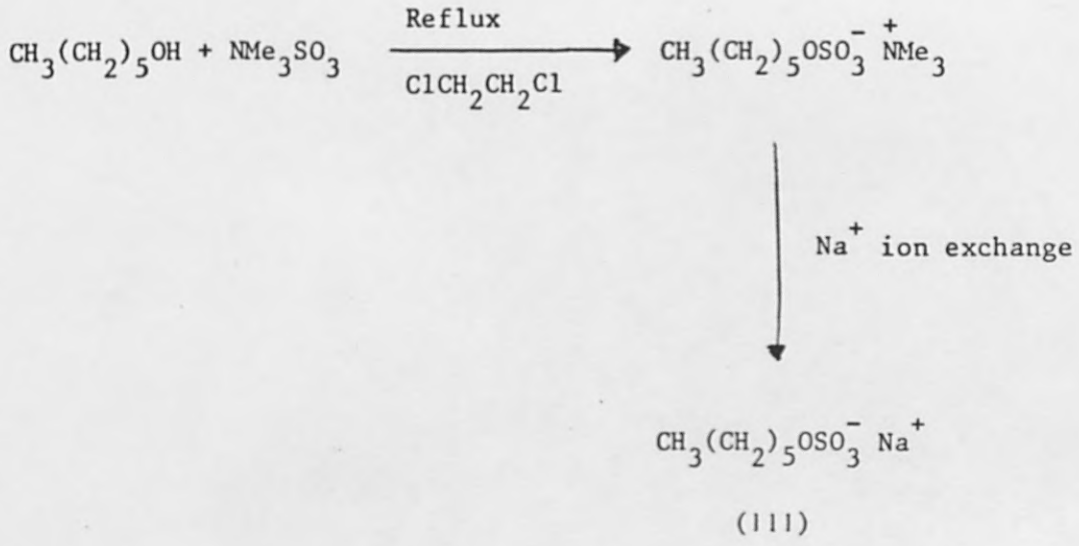
a = ^{1}H NMR.

10-(3-Alkyl-1-indolyl)undecanoic acids ((53), (64), (74), (81) and (88)) were reacted with equimolar amounts of sodium bicarbonate in water to obtain the corresponding sodium salts ((55), (65), (75), (82) and (89)) as shown in Scheme I.

These products ((55), (65), (75), (82) and (89)) were washed with sodium dried diethyl ether and dissolved in absolute ethanol to remove any unreacted sodium bicarbonate. The proton NMRs (in $CDCl_3$) were similar to those of the starting material acids. However, these products were soluble in water (starting material acids are insoluble in water) and hence considered to be pure enough for use as fluorescent probes.

2.1.6 Attempted preparation of sodium 11-(3-alkyl-1-indolyl) undecyl sulphates from the corresponding indolic alcohols:

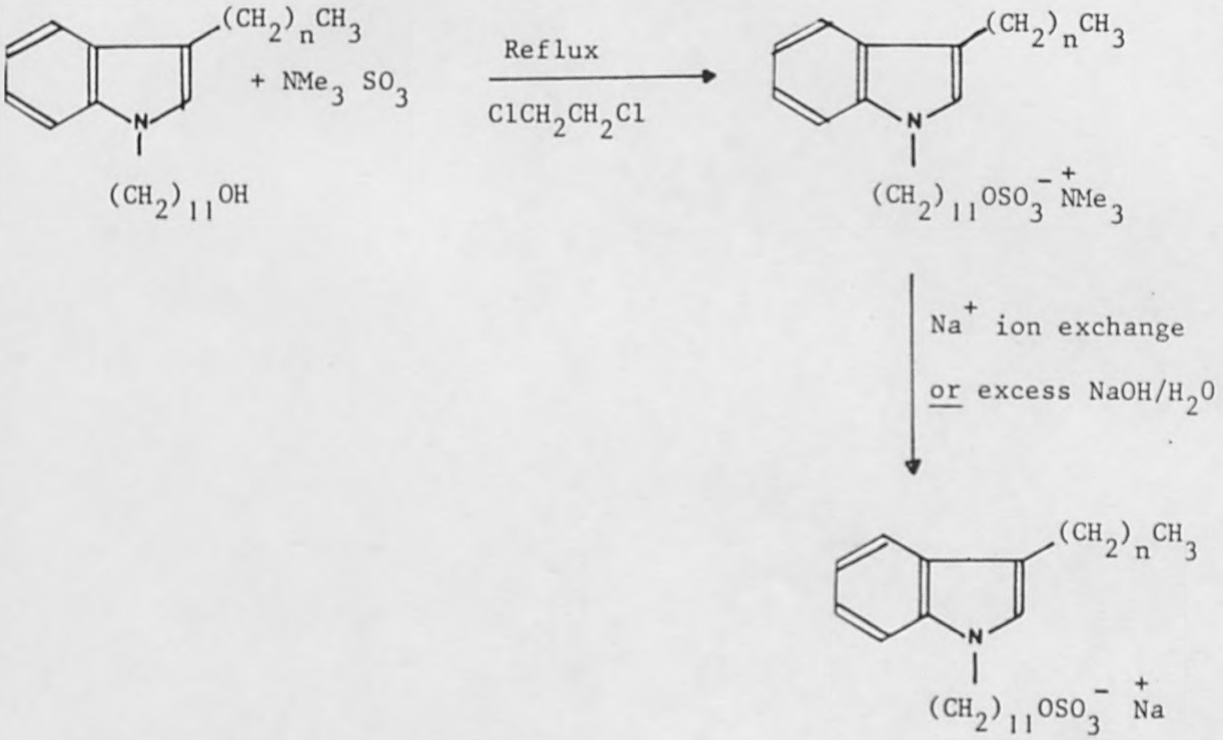
Pure n-hexanol was added to 1,2-dichloroethane containing trimethylamine sulphur trioxide complex and the mixture was heated under reflux for a period of 24 hrs. The solvent was removed under reduced pressure and the trimethyl ammonium 1-hexyl sulphate was dissolved in water and passed through an ion exchange column containing zeokarb 225 SRC 14 resin (Na^+ ion exchange). The solution was then evaporated to dryness and the remaining sodium sulphate salt of n-hexanol was recrystallised from ethanol to give colourless, crystalline, sodium 1-hexyl sulphate (111). ^1H NMR confirmed the expected product.



(III)

A similar method was employed using 11-(3-alkyl-1-indolyl) undecanols instead of n-hexanol to obtain the sodium sulphate of these indoles (Scheme J).

SCHEME J



(63) n = 5 (14%)[a,c,d];
(73) n = 8 (minor amount)
(80) n = 11 (impure).

The proton NMR of these products was consistent with the proposed structure. However, the product could not be purified further. The products could not be crystallised from organic solvents, since they were sticky orange coloured solids.

2.1.7 Synthesis of indolic surfactant 6-(3-citronellyl-1-indolyl)-hexyl trimethyl ammonium bromide (47):

Many indolic surfactants have been previously made with straight hydrocarbon chains at positions one and three of the indole nucleus (Section 2.1.4). Indole (47) was synthesised as shown in the Scheme K. The purpose of synthesising this surfactant with a double bond in the hydrocarbon chain of indole was to investigate how this type of surfactant behaves in a micellar environment when it is used as a fluorescent probe. This should show whether the presence of methyl groups and a double bond in the chain affects the way chains pack in the micelles.

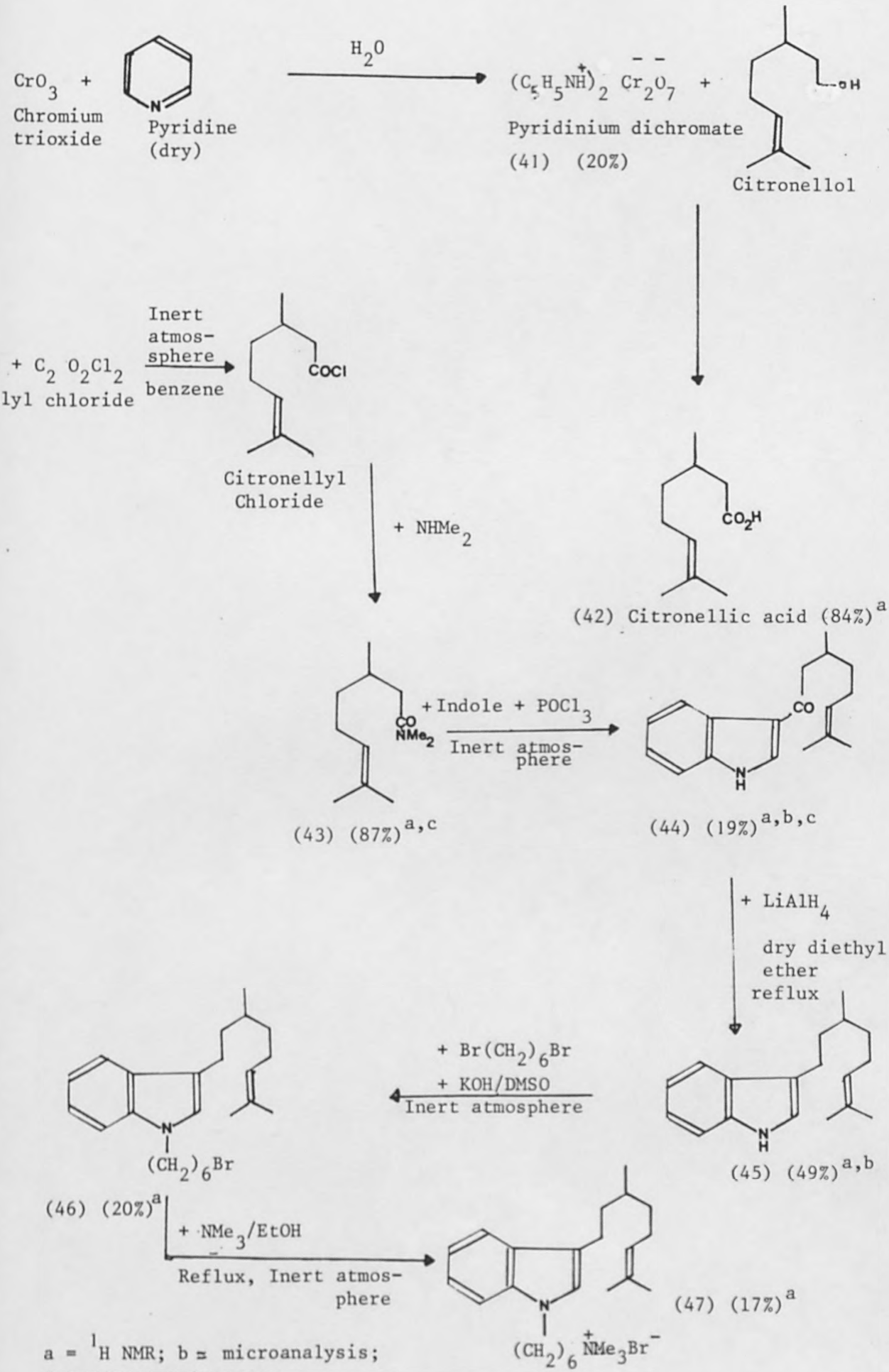
Attempted synthesis of citronellic acid by reacting pulegone with hydrogen chloride (HCl) gas and sodium hydroxide gave only 9% yield.[187] An alternative method to synthesise citronellic acid (42) was found and is shown in Scheme K.

Pyridinium dichromate (41) was prepared by reacting chromium trioxide with pyridine at $<30^{o}C$. The product (41) was recrystallised from water and acetone at $-20^{o}C$. Citronellol was stirred with pyridinium dichromate (41) and dimethyl formamide, under nitrogen, overnight at $20^{o}C$, to give citronellic acid (42). This was reacted with oxalyl-

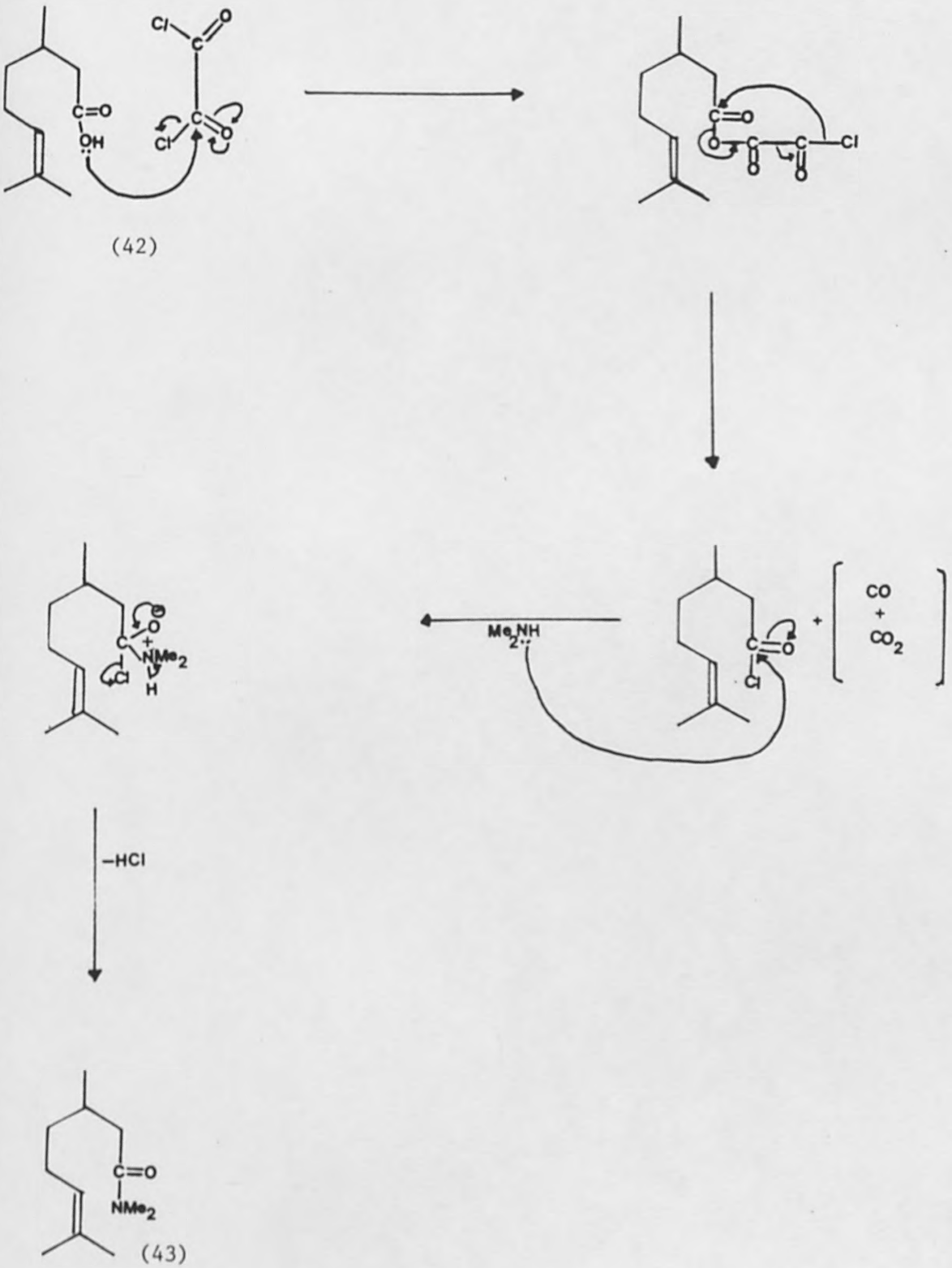
chloride under nitrogen to give citronellyl chloride which was then reacted with N,N-dimethyl amine to obtain 3,7-dimethyl octenamide (43). This amide (43) was reacted with phosphorus oxychloride and indole to give 3-(1-keto-3,7-dimethyl octene)indole (44). This product (44) was then reduced by lithium aluminium hydride to give 3-(3,7-dimethyloctene)indole (45) in 49% yield.

The above prepared indole (45) was reacted with 1,6-dibromohexane using KOH/DMSO method to obtain 6-(3-citronellyl-1-indolyl)-hexyl bromide (46) in 20% yield. This product (46) was then reacted with trimethylamine (50%) in absolute ethanol and refluxed overnight to obtain 6-(3-citronellyl-1-indolyl)hexyl trimethyl ammonium bromide (47) in 17% yield. This product was hygroscopic and hence it was difficult to make it analytically pure.

SCHEME K



a = ^{1}H NMR; b = microanalysis;
c = mass spectroscopy.



(42)

(43)

Mechanism for (42) to (43).

2.1.8 Synthesis of n-hexyl mesylate (107) and n-hexyl triethylene glycol-ether (108):

A few methods for the preparation of pure nonionics have been devised by Clark and Naik,[188] e.g.

$$RBr + NaO-(CH_2CH_2O)_nH \longrightarrow RO(CH_2CH_2O)_nH + NaBr$$

$$n \lesssim 5.$$

$$RO(CH_2CH_2O)_nH \xrightarrow[NEt_3]{CH_3SO_2Cl} RO(CH_2CH_2O)_nSO_2CH_3$$

mesylate

$$\downarrow + NaO(CH_2CH_2O)_mH$$

$$-(CH_2-CH_2-O) = EO \qquad RO(CH_2CH_2O)_{m+n}H + CH_3SO_3^- Na^+$$

To build up higher EO chain nonionics from the lower homologues they are converted into the mesylates and then further EO units are added as shown above (Williamson ether synthesis).

We synthesised the trigol derivative (108) of n-hexanol by reacting n-hexanol, triethylamine and sulphonyl chloride to form the mesylate ((107), methane sulphonyl derivative) and then this mesylate (107) was reacted with the sodium salt of trigol to give n-hexyl triethylene glycolyl ether (108) as shown in Scheme L.

SCHEME L

$$CH_3(CH_2)_5OH + NEt_3 + MeSO_2Cl \xrightarrow[\text{Stir/13 hrs}]{\text{Inert atmosphere}} Me(CH_2)_5OSO_2CH_3$$

0 to 10°C

mesylate (107) (73%).

$$HO(CH_2CH_2O)_3H + Na \longrightarrow Na^+ O^- (CH_2CH_2O)_3H + Me(CH_2)_5OSO_2Me$$

trigol

N_2 | 100-110°C, 3 hrs

$$CH_3(CH_2)_5O(CH_2CH_2O)_3H$$

(108) (79%) > 95% pure g.

g = glc.

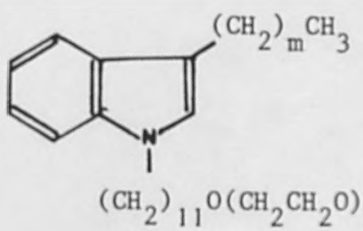
The reaction proceeds through the very reactive sulphene intermediate.

$$CH_3SO_2Cl + Et_3N \longrightarrow CH_2{=}SO_2 + Et_3NHCl$$

sulphene

$$CH_2{=}SO_2 + ROH \longrightarrow ROSO_2CH_3 \quad \text{(mesylate)}$$

The above product (108) was analysed by GLC. Similar types of trigol derivatives can be made using 1,3-dialkyl indolyl alcohols.

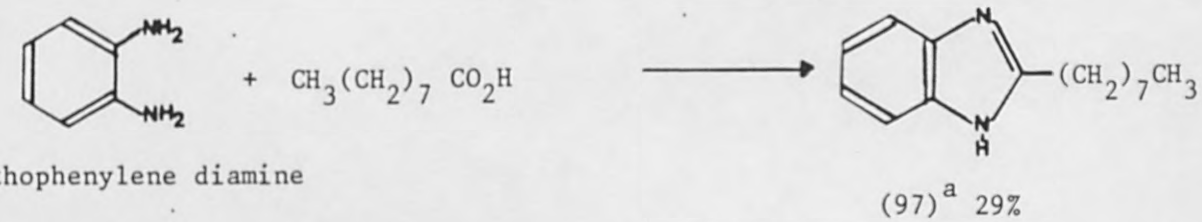


m = 0, 5, 8, 11, 17.

2.2 Attempted synthesis of 1,2-dialkyl benzimidazolyl bromides and their trimethyl ammonium bromide surfactants:

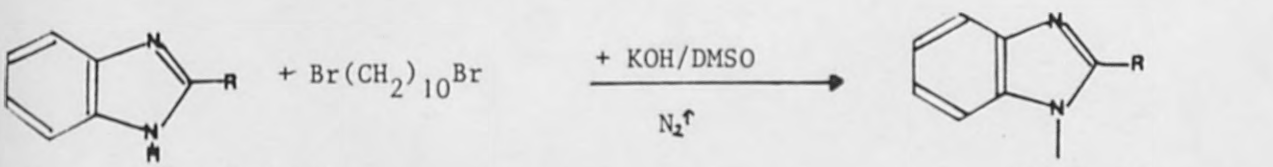
It was proposed to synthesise 1,2-dialkyl benzimidazoles and to investigate whether the fluorescence of these compounds behaves in a similar way to that of indoles when they are converted to surfactants. The investigation would also enable us to find out whether the benzimidazole chromophore stays in the hydrocarbon environment or the aqueous environment of the micelle when the hydrocarbon (alkyl) chain is altered to the 2-position.

SCHEME M



Orthophenylene diamine

(97)[a] 29%



R = H, R = $(CH_2)_7CH_3$

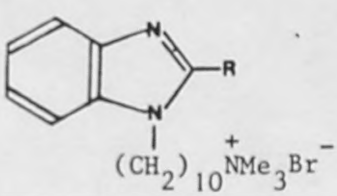
(94) R = H (74%)[a,c]

(98) R = $-(CH_2)_7CH_3$ (50%)

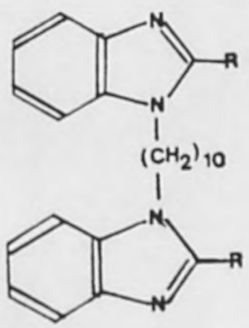
NMe_3/EtOH
Reflux

(99)[a] R = $-(CH_2)_nCH_3$;

(96) R = H (70%)[a].



1-(10-Bromodecyl)-benzimidazole (94) was prepared by reacting benzimidazole with 1,10-dibromodecane in the presence of potassium hydroxide and dimethyl sulphoxide. The quaternisation was carried out using anhydrous trimethylamine (50%) in absolute ethanol. The product (96) was freeze-dried. 2-Octylbenzimidazole (97) was synthesised by heating o-phenylene diamine and nonoic acid.[189] It was then reacted with 1,10-dibromodecane in the presence of potassium hydroxide and dimethyl sulphoxide to obtain 1-(bromodecyl)2-octyl benzimidazole (98). The product was quaternised with trimethylamine and the quaternised product (99) was freeze-dried (Scheme M). Both quaternary salts (96) and (99) contained dimer (95) and (100) respectively as revealed by ^{1}H NMR and mass spectra. Fluorescence probing could not be carried out.

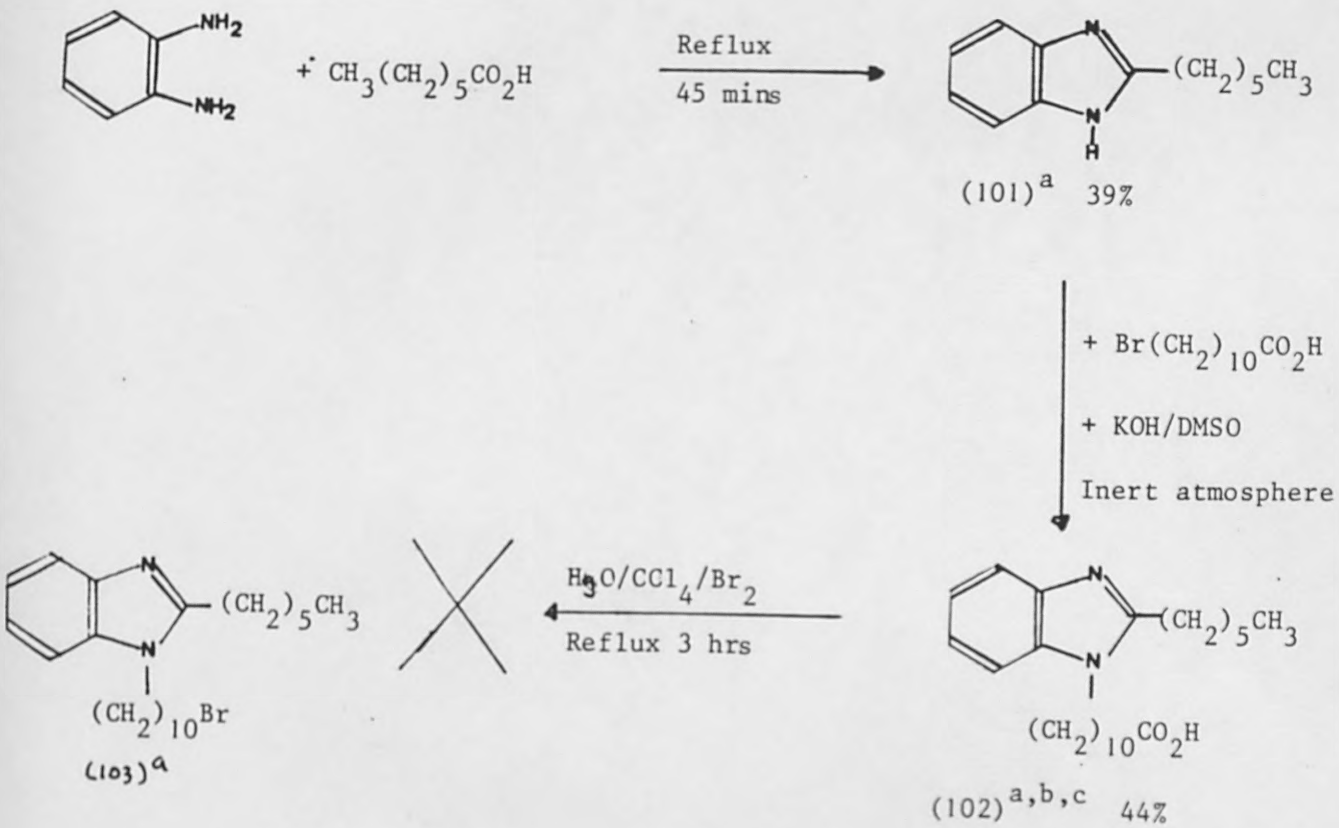


(95) R = H; (100) R = $(CH_2)_7CH_3$

2-Hexyl benzimidazole (101) was synthesised by heating o-phenylene diamine and n-heptanoic acid.[189] It was then reacted with 11-bromo-undecanoic acid in the presence of potassium hydroxide and dimethyl sulphoxide to obtain 1-(carboxy-decyl)-2-hexyl-benzimidazole (102) in 44% yield. This acid (102) was then reacted with yellow mercuric oxide and bromine in the presence of carbon tetrachloride and

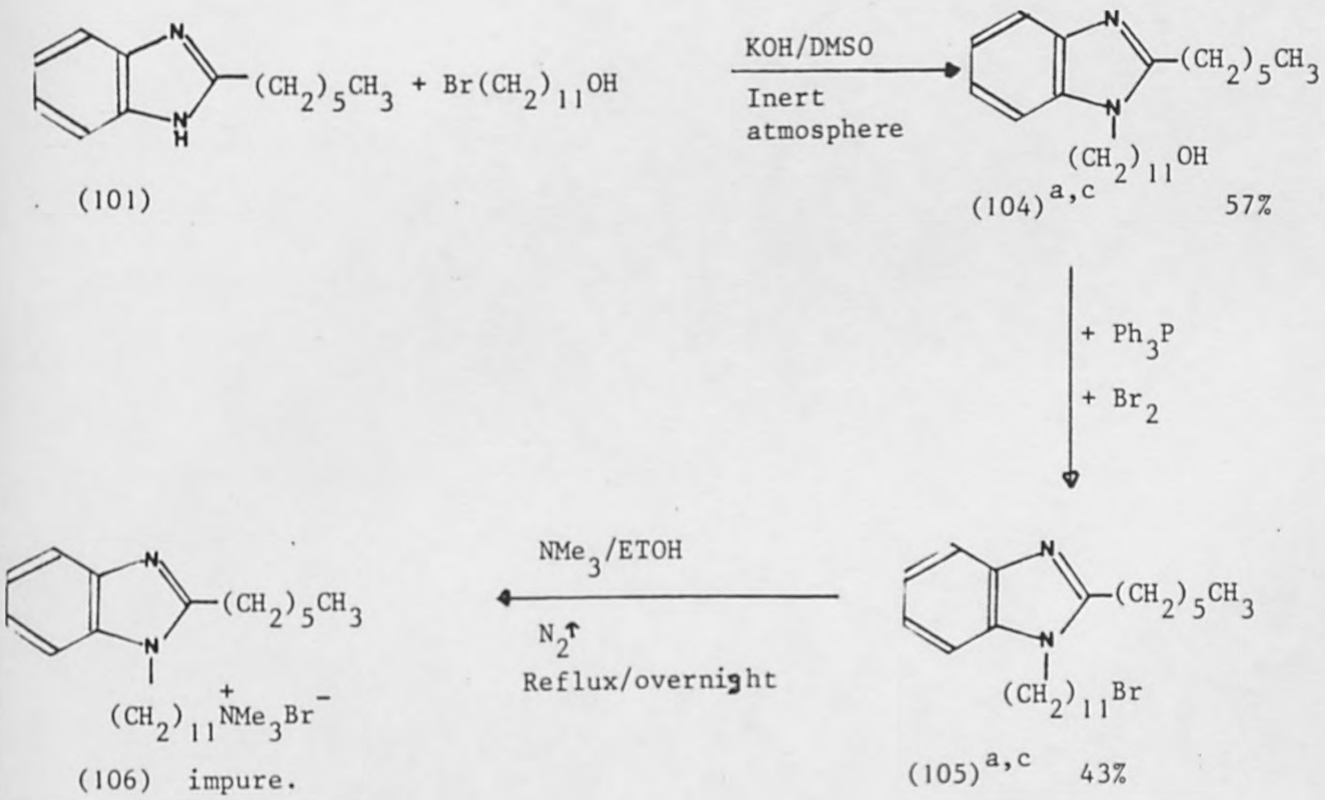
refluxed for 3 hrs. The expected product 1-(10-bromodecyl)-2-hexyl-benzimidazole (103) could not be obtained (NMR) as shown in Scheme N.

SCHEME N



The reaction of n-hexanoic acid with yellow mercuric oxide and bromine was carried out to obtain n-bromopentane in 10% yield. This low yield did not encourage us to try and prepare bromo-compounds e.g. (105), via the acids. Instead reaction Scheme P was followed.

SCHEME P



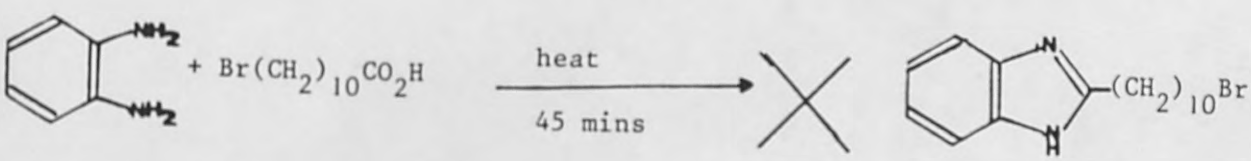
2-Hexyl benzimidazole (101) was reacted with 11-bromo-1-undecanol in the presence of potassium hydroxide and dimethyl sulphoxide to obtain 1-(11-hydroxyundecyl)2-hexyl benzimidazole (104) in 57% yield. This was then reacted with triphenyl phosphine and bromine in the presence of dry diethyl ether and dry pyridine. The expected product 1-(11-bromoundecyl)-2-hexyl benzimidazole (105) was obtained in 42% yield. Triphenyl phosphine oxide was removed, by flash column chromatography, from the product (105). The presence of a very small amount of triphenyl phosphine oxide could not be removed. The 1,2-dialkyl benzimidazole bromide (105) was finally reacted with tri-

methylamine in the presence of absolute ethanol and nitrogen to obtain the 1-(11-bromoundecyl)-2-hexyl benzimidazole trimethyl ammonium bromide (106). Attempts to purify the product (106) by washing it with dry ether and freeze-drying were not successful. Its behaviour as a fluorescent probe was not therefore studied. The product (106) was hygroscopic and soluble in water. An impurity in (106) is thought to be triphenyl phosphine oxide. These reactions are shown in Scheme P.

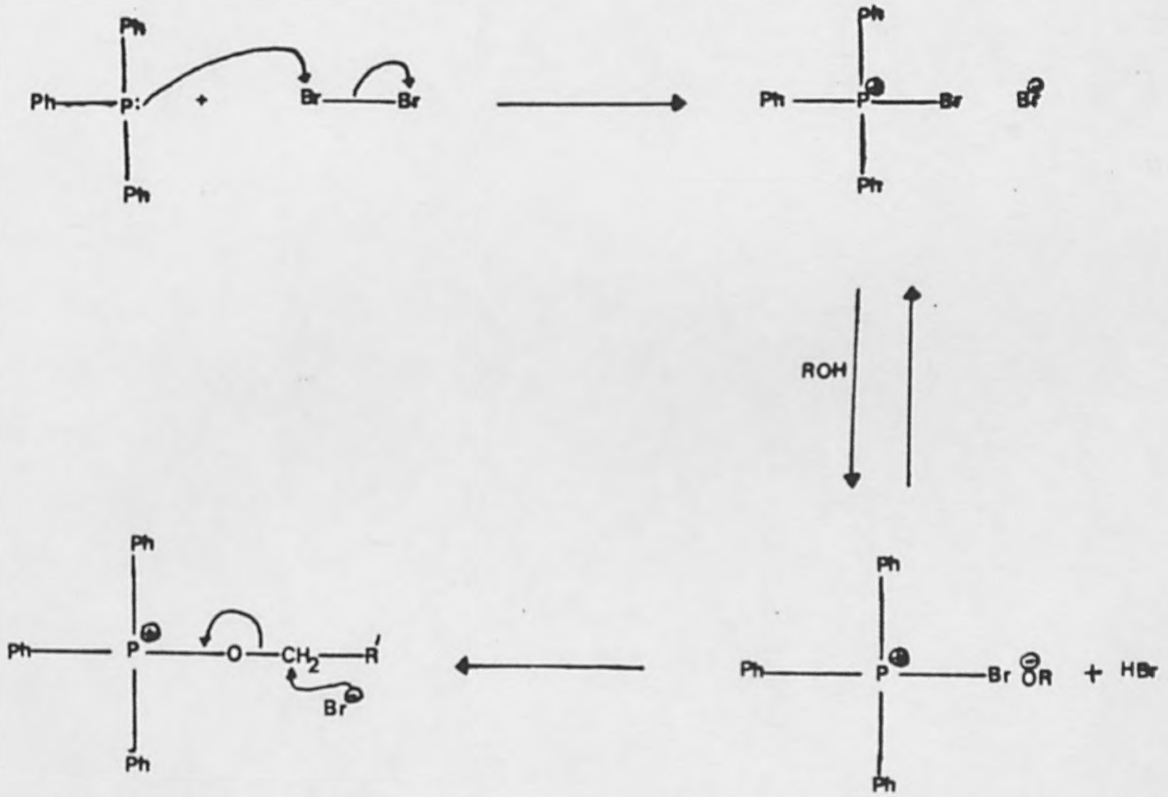
The purpose of doing these reactions (Scheme N and P) was to obtain the expected 1,2-dialkyl benzimidazole bromides (103) and (105), avoiding the formation of dimers like (95) and (100), when 1,10-dibromodecane was used as an alkylating agent (Scheme M).

An attempt was made to synthesise 2-(10-bromo)-decyl-benzimidazole (112) by reacting o-phenylene diamine with 11-bromoundecanoic acid for 45 minutes as shown in Scheme Q. A dark brown viscous solid was formed which could not be identified by ^{1}H NMR, which also confirmed the absence of the expected product (112).

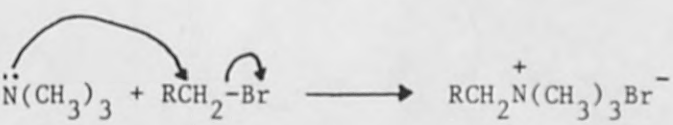
SCHEME Q



(1)



(2)



(1) Mechanism for reaction Scheme P.

(2) Mechanism for quaternisation of alkyl halides by trimethylamine (Scheme P).

2.3 Fluorescence study of micellar systems:

2.3.1 Fluorescence spectroscopy for the determination of critical micelle concentration (CMC):

It is possible to synthesise detergents that possess a luminescent probe as an integral part of their structure. The indole lumophore has shown significant solvent sensitivity, for example 1,3-dimethyl indole shows fluorescence maxima at 305 nm and 370 nm in cyclohexane and water respectively. Its fluorescence lifetime is also strongly solvent dependent (4×10^{-9} s and 16×10^{-9} s in cyclohexane and water respectively).[82] 11-(3-Hexyl-1-indolyl)undecyl trimethyl ammonium bromide also shows a dramatic shift in its fluorescence maxima and fluorescence lifetime as it passes from micellar environment to bulk aqueous solution. This is described in more detail under Section 1.2.7 (page 65). The quaternised salts of 1,3-dialkyl indoles were prepared as described earlier (Scheme A,B,F and H). The CMC values of these newly prepared indole surfactants (fluorescent probes) were determined using the fluorescent properties of the indole nucleus attributable to the indole group. Fluorescence wavelength maxima (λ_F max) are plotted as a function of concentration. Most of these 1,3-dialkyl indolyl trimethyl ammonium bromides show shifts in specific λmax values as the concentration is altered. The λ_F max shifts from 370 ± 1 nm to 352 ± 1 nm on changing from an aqueous to a micellar environment. The objective of this study was (a) to investigate whether a variation in the length of the alkyl chains at positions 1 and 3 of the indole nucleus significantly affects the CMC value, and (b) to obtain information on the structure of micelles and the position of the chromophore (lumophore) of the surfactant in the micellar environment.

The results of these studies are shown in Table III (see fig. 37-41). 10(3-Methyl-1-indolyl)-decyl trimethyl ammonium bromide (52) did not show any fluorescence wavelength shifts over the concentration range 1×10^{-2} M to 1×10^{-5} M. This indicates that, either this indole does not form a micellar structure or if the micelle is formed, the indole group is at the surface of the micelle. The fact that the fluorescence maximum is at 370 ± 1 nm indicates that the indole nucleus is in aqueous environment. It was confirmed by a microscopic study of liquid crystalline phases that the above indole (52) does form micelles. This study showed that indole (52) formed a hexagonal structure (at R.T. which melts at 45°C) and a lamellar structure (at R.T. which melts at 88°C) as shown in Table XXIX.

It can be concluded from Table III that as the hydrocarbon chain on either position of indole (3 or 1), is lengthened the changes in fluorescence wavelength maxima occur at lower and lower concentrations. When the hydrocarbon chain on the 3-position of indole is octadecyl (e.g. 10(3-octadecyl-1-indolyl)-decyl trimethyl ammonium bromide (86)) the CMC values are lower than 10^{-6} M. The fluorescence could not be detected at lower than 10^{-6} M and hence the CMCs could not be determined with these 1,3-dialkyl indolyl trimethyl ammonium bromides. However, more sophisticated laser fluorescence spectroscopy could be employed for the study of solutions having concentrations lower than 10^{-6} M and hence the CMC values could be obtained. One has to be very careful about the purity of the surfactants because of the sensitivity of the technique. Any impurity could be detected by this laser fluorescence technique. These indolyl surfactants ((69),

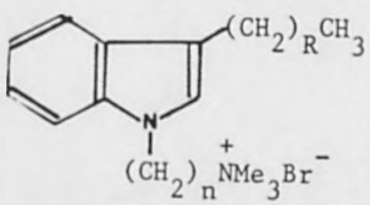
(84) and (86)) with long alkyl chains were weakly soluble in water, compared with other shorter chain indolic surfactants.

It can be concluded from the above investigations that fluorescence spectroscopy is a good technique for the determination of the CMCs of 1,3-dialkyl indolyl surfactants. However, it could not be used with indolyl compounds having very large (e.g. indole (84) and (86)) or very short alkyl chains (e.g. indole (52)). Excellent results can be obtained by employing the fluorescent probe molecule indole having 6 to 9 carbon atom chains on the 3-position and 6 to 10 carbon atom chains on the one position.

2.3.2 Fluorescence of cationic aqueous indole surfactants in a solution of micelle-forming host surfactant (CTAB):

The 1,3-dialkyl indolyl trimethyl ammonium bromides show identical behaviour in dilute aqueous solutions having fluorescence wavelength maxima (λ_F max) at 367 ± 2 nm. Addition of hexadecyl trimethyl ammonium bromide (CTAB, CMC 9.2×10^{-4} M) has no effect on the fluorescence spectra of these compounds until the CMC is reached, then the fluorescence λmax shifts to shorter wavelength. The indolic trimethyl ammonium bromide surfactants (61), (69), (70) and (84) were used as fluorescent probes for the determination of the CMC of CTAB. The CMC values of 9×10^{-4} M and 7.5×10^{-4} were in agreement with the literature CMC value (9.2×10^{-4} M)[82] when compounds (61) and (70) were employed as fluorescent probes respectively. See Table IX (Fig. 42) and Table X, (Fig. 43).

However, the data in Table X, Fig. 43; Table XI, Fig. 44 and Table XII show that when the hydrocarbon chain length on the 3-position of indole is increased (from 6 to 9, 11 or 17 carbon atoms) the shift in λmax of the fluorescence becomes less predictable and hence the CMC value is difficult to determine. From Fig. 42 and 44, it also appears that the CMC value may be determined to some extent by the size of the probe molecule. The larger probe molecules seem to be incorporated into the micelles and hence, lower the CMC value of the host surfactant.



(52) R = 0; n = 10.

(61) R = 5; n = 10.

(69) R = 11; n = 6.

(70) R = 8; n = 10.

(84) R = 17; n = 6.

(86) R = 17; n = 10.

The probe molecules (84) and (86) are weakly soluble in water and hence exhibit poor quality fluorescence spectra (in terms of signal to noise ratio). However, these molecules were solubilised in CTAB micelles at 5×10^{-3} M concentration and hence higher quality fluorescence spectra were obtained, but the CMC values could not be determined using these compounds.

The possibility of determining the CMC of host surfactant CTAB by using fluorescent probes of indolic surfactant (52) was also investigated. The results are shown in Table XIII.

The indole (52) shows a smaller shift in fluorescence wavelength maximum (368-362 nm) than the other indoles (61) and (70), (367-352 nm). This could be due to the fact that the indole nucleus of (52) is not being forced as deep into the micelles as the indoles having longer alkyl chains ((61) and (70)) at the three position. The indole group of (52) seems to lie close to the ionic head group of a micelle. Also, in the monomeric or aggregated form of the CTAB surfactant the indole group of the probe molecule (52) is apparently in an aqueous like environment and consequently there is little shift in λ_F max. Therefore, the critical micelle concentration of the host surfactant (cetyl trimethyl ammonium bromide) cannot be determined using this probe (52).

A plot of the wavelength maximum of the fluorescence of (52) against the concentration of CTAB gives a curve having a sigmoid shape. The inflection point occurs at 4.5×10^{-3} M concentration of CTAB (Fig. 45). Thus, this probe is indicating that the CMC of CTAB is 4.5×10^{-3} M, which is higher than the known CMC value of 9.2×10^{-4} M. This result together with others suggest that the use of fluorescent probes for CMC determinations must be employed with caution. It can also be concluded, from the above results, that the ideal probe for the determination of the CMC value of the host surfactant should contain neither very large (e.g. compounds (69), (84) or (86)) nor very short (e.g. compound (52)) hydrocarbon chains on the one or three positions of the indole nucleus. The indole surfactant compound having a 6-carbon atom straight hydrocarbon chain on the 3-position and a

10-carbon atom straight hydrocarbon chain on the 1-position is the most suitable probe for the determination of the CMC of the host surfactant.

A similar type of result was obtained by Turro[82] in a survey of the fluorescence wavelength maximum of 1,3-dialkyl indoles in the micelle forming host surfactants cetyl trimethyl ammonium bromide (CTAB) and cetyl trimethyl ammonium chloride (CTAC) (Table II, Figure 46). They indicated that these compounds are associated with micelles from CTAB and CTAC, but that they tend to remain close to the ionic interface. This is why a second hydrocarbon chain was attached to this indole aromatic system (at the 3-position) and improved micellar incorporation tremendously.

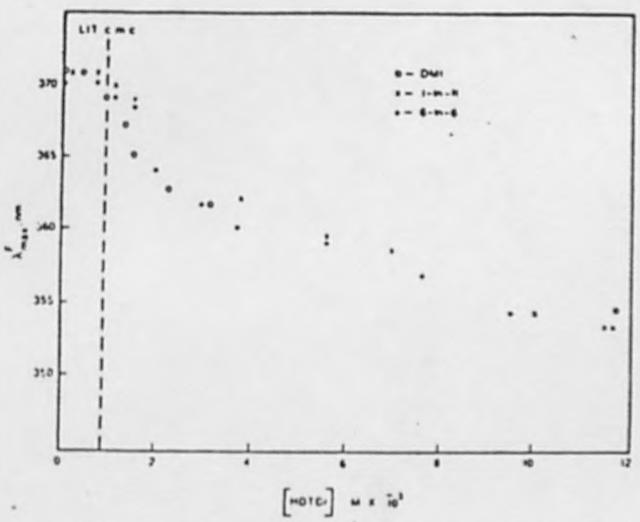
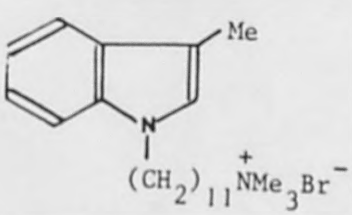


Figure 46: Fluorescence λmax for compounds DMI, I-In-II and 6-In-6 in aqueous solution as a function of added HDTBr.

DMI = 1,3-dimethyl indole.

I-In-II = 

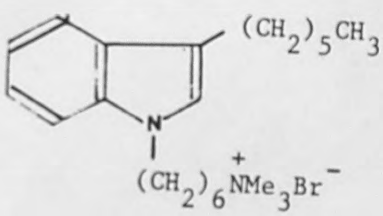
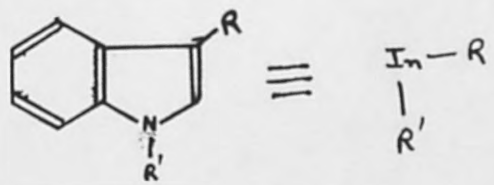
6-In-6 = 

TABLE III

Fluorescence probe for indolic cationic surfactants



Compound	CMC M	λmax shift ± 1 nm	Concentration Range M
In-Me $(CH_2)_{10}\overset{+}{N}Me_3\ Br^-$ (52)	-	370 nm	1×10^{-2} M to 1×10^{-5} M
In-$(CH_2)_5CH_3$ $(CH_2)_{10}\overset{+}{N}Me_3Br^-$ (61)	4×10^{-4} M see Fig. 38	369 to 356 nm	1×10^{-4} M to 1×10^{-3} M
In-$(CH_2)_8CH_3$ $(CH_2)_{10}\overset{+}{N}Me_3Br^-$ (70)	6.5×10^{-5} M see Fig. 40	366 to 353 nm	1×10^{-5} M to 2×10^{-3} M
In-$(CH_2)_{11}CH_3$ $(CH_2)_{10}\overset{+}{N}Me_3Br^-$ (78)	-	365 nm	1×10^{-2} M to 1×10^{-6} M
In-$(CH_2)_{17}CH_3$ $(CH_2)_{10}\overset{+}{N}Me_3Br^-$ (86)	-	350 nm	1×10^{-2} M to 1×10^{-6} M Compound poorly soluble in H_2O.
In-$(CH_2)_5CH_3$ $(CH_2)_6\overset{+}{N}Me_3Br^-$ (58)	3.25×10^{-3} M see Fig. 37	368 to 356 nm	1×10^{-3} M to 1×10^{-2} M

TABLE III (Continued)

Compound	CMC M	λmax shift ± 1 nm	Concentration Range M
In-$(CH_2)_8CH_3$ $(CH_2)_6\overset{+}{N}Me_3Br^-$ (68)	3.75×10^{-4} M see Fig. 39	368 to 355 nm	1×10^{-4} M to 1×10^{-3} M
In-$(CH_2)_{11}CH_3$ $(CH_2)_6\overset{+}{N}Me_3Br^-$ (69)	7.0×10^{-5} M see Fig. 41	362 to 352.5 nm	7×10^{-4} M to 1×10^{-5} M
In-$(CH_2)_{17}CH_3$ $(CH_2)_6\overset{+}{N}Me_3Br^-$ (84)	-	350 nm Weakly soluble in H_2O.	1×10^{-2} M to 1×10^{-6} M

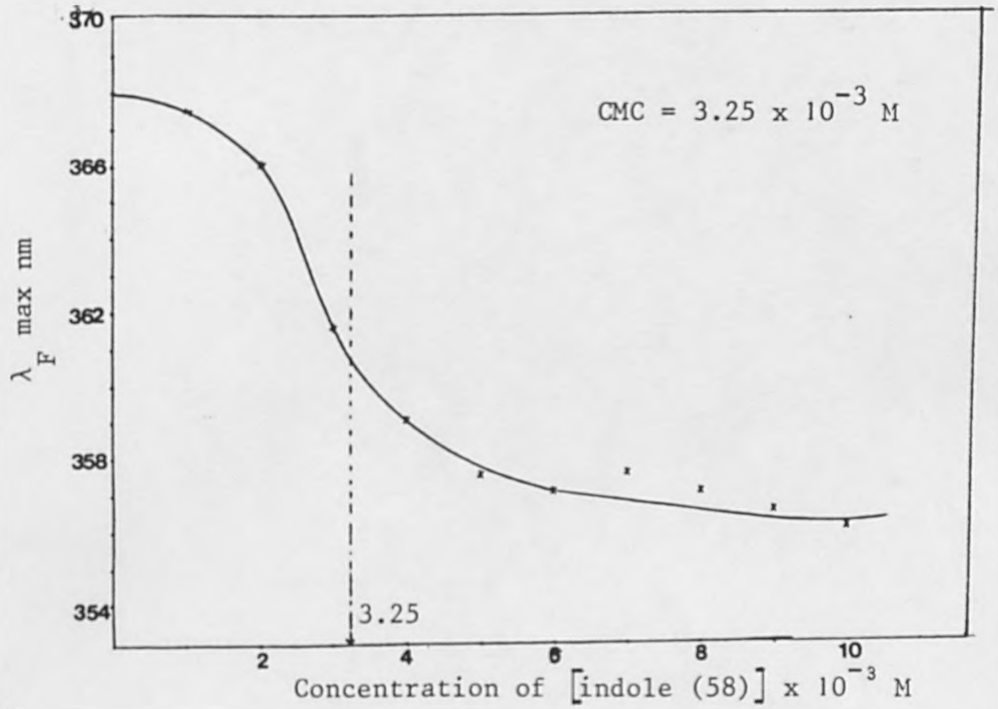


Figure 37

Fluorescence λmax of aqueous indole (58) as a function of concentration.

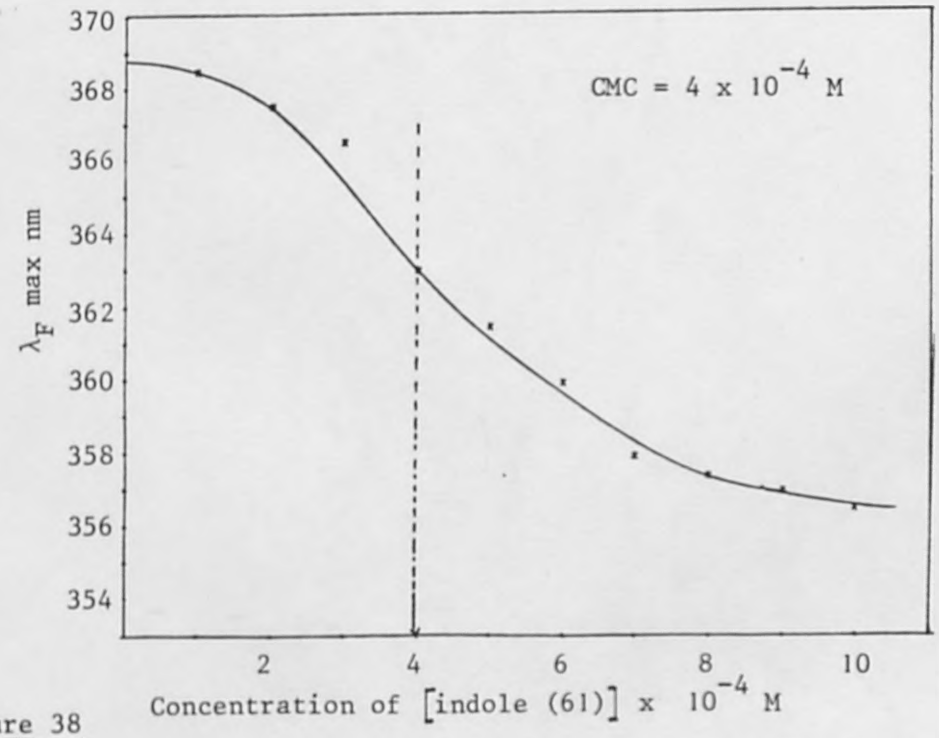


Figure 38

Fluorescence λmax of indole (61) as a function of concentration

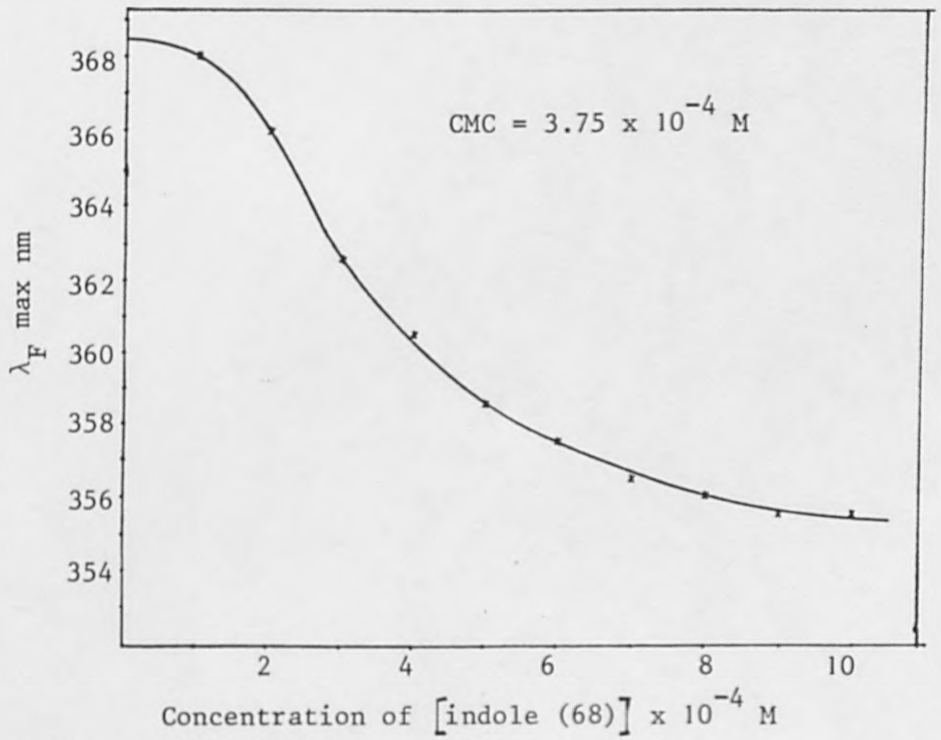


Figure 39

Fluorescence λmax of aqueous indole (68) as a function of concentration

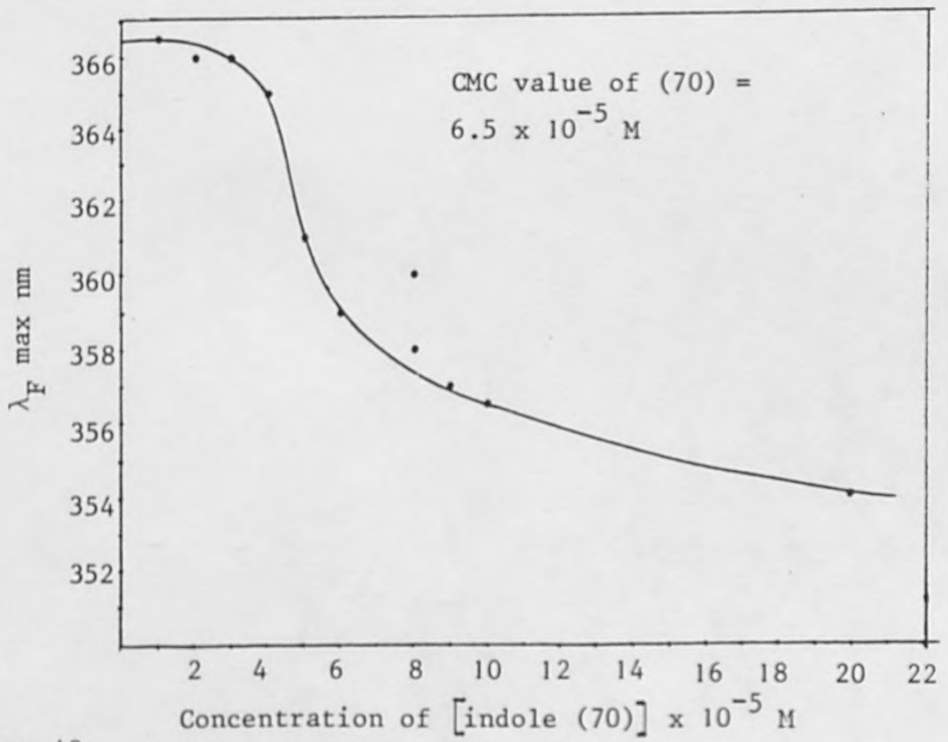


Figure 40

Fluorescence λmax of indole (70) as a function of concentration.

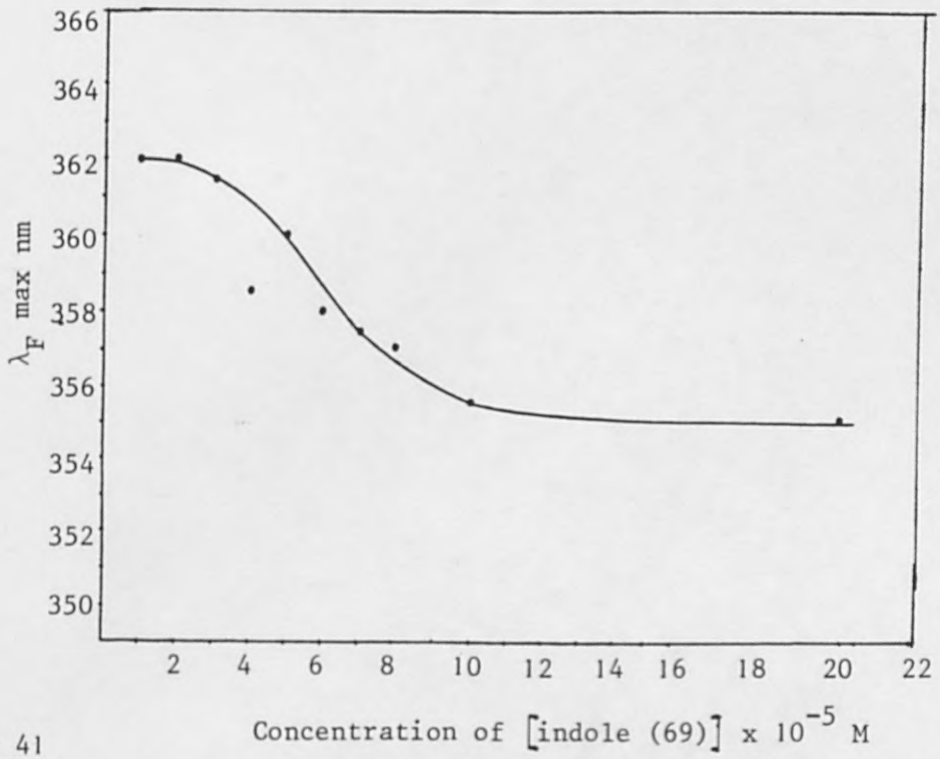


Figure 41

Fluorescence λmax of aqueous indole (69) as a function of concentration.

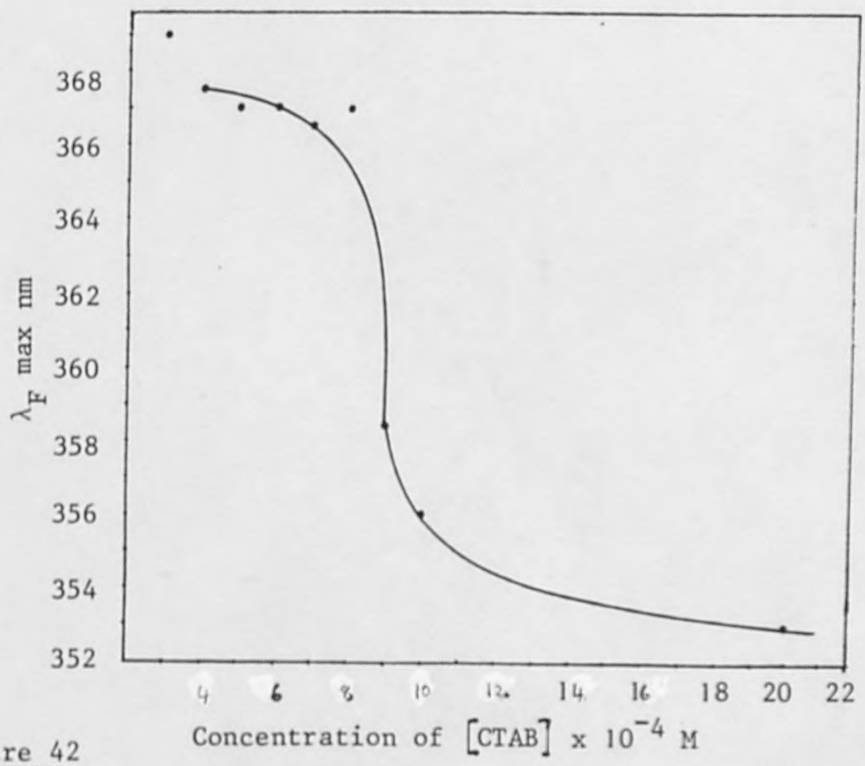


Figure 42

Fluorescence λmax of aqueous indole (61) as a function of added CTAB.

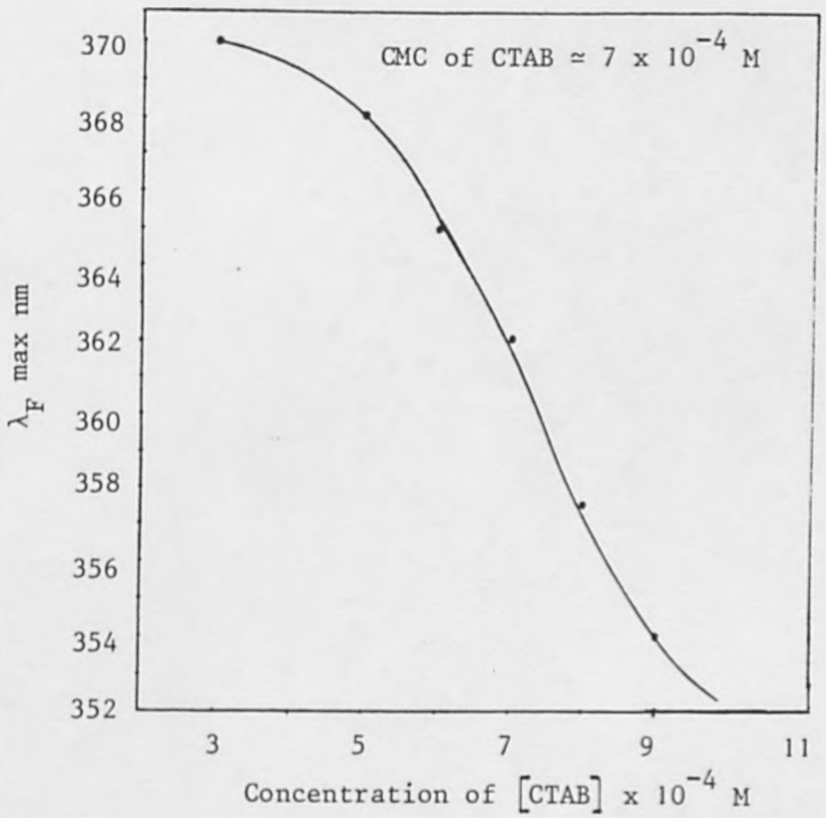


Figure 43

Fluorescence λmax of aqueous indole (70) as a function of added CTAB

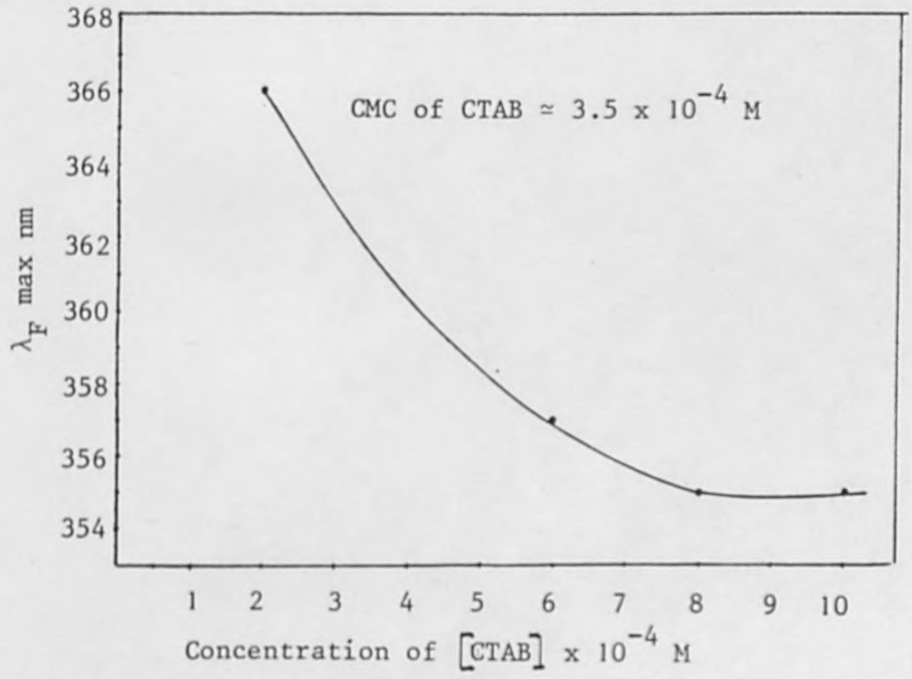


Figure 44

Fluorescence λmax of indole (69) as a function of added CTAB

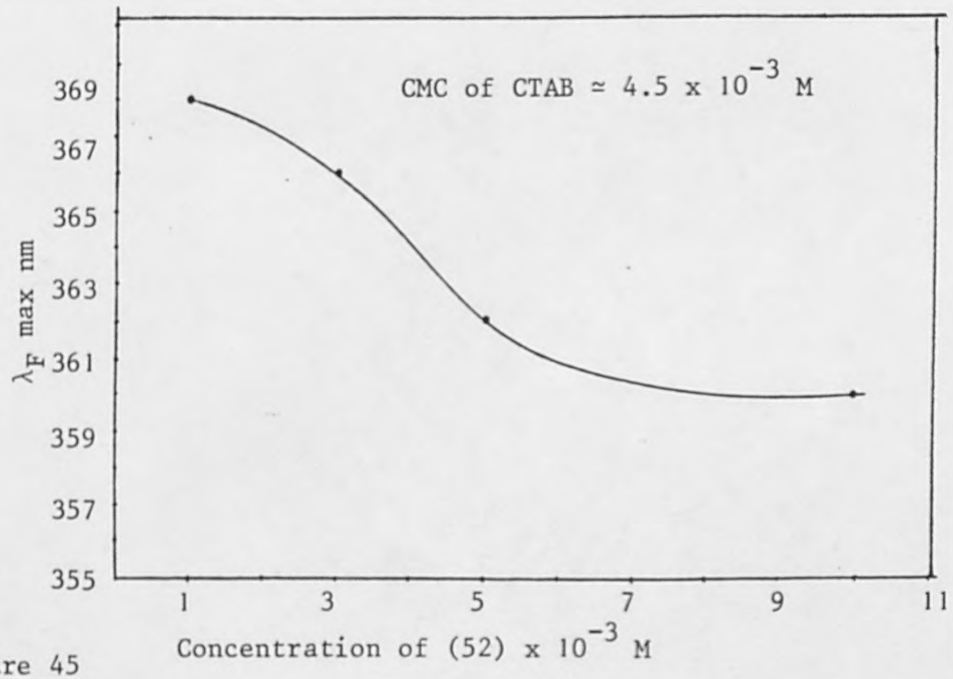


Figure 45

Fluorescence λmax of aqueous indole (52) as a function of added CTAB.

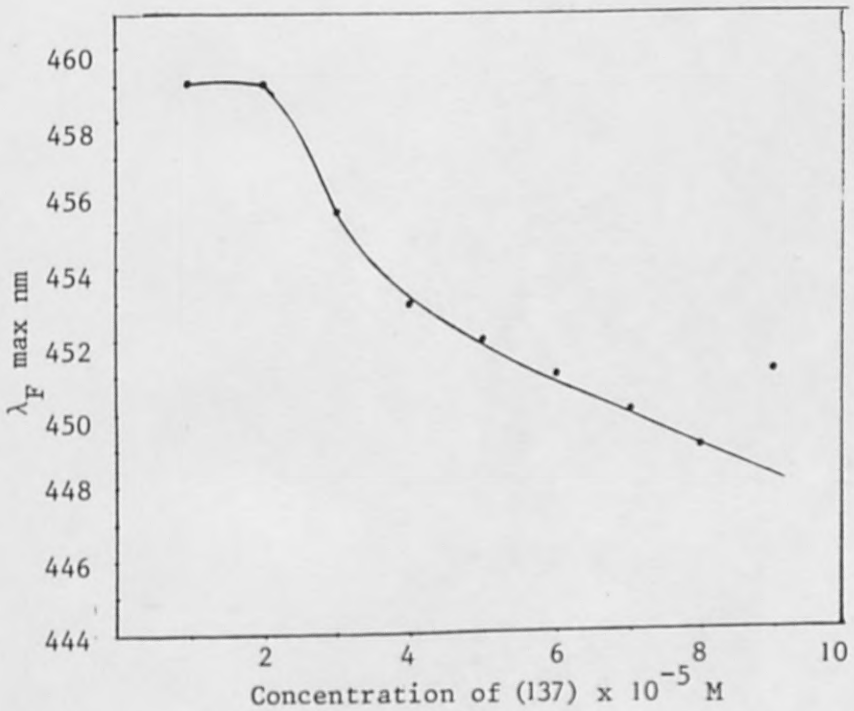


Figure 45a

Fluorescence λmax of aqueous pyrazoline surfactant (137) as a function of concentration

TABLE IV

Data for the fluorescence λmax of indole (58) as a function of its concentration

Concentration M	λ_F max nm ± 1
1×10^{-3}	367.5
2×10^{-3}	366.0
3×10^{-3}	361.0
4×10^{-3}	359.0
5×10^{-3}	357.5
6×10^{-3}	357.0
7×10^{-3}	357.5
8×10^{-3}	357.0
9×10^{-3}	356.5
1×10^{-2}	356.0

TABLE V

Data for λ_F max of indole (61) as a function of its concentration

Concentration M	λ_F max nm ± 1
1×10^{-4}	368.5
2×10^{-4}	367.5
3×10^{-4}	366.5
4×10^{-4}	363.0
5×10^{-4}	361.5
6×10^{-4}	360.0
7×10^{-4}	358.0
8×10^{-4}	357.5
9×10^{-4}	357.0
1×10^{-3}	356.5

TABLE VI

Data for λ_F max of indole (68) as a function of its concentration

Concentration M	λ_F max nm ± 1
1×10^{-4}	368.0
2×10^{-4}	366.0
3×10^{-4}	362.5
4×10^{-4}	360.5
5×10^{-4}	358.5
6×10^{-4}	357.5
7×10^{-4}	356.5
8×10^{-4}	356.0
9×10^{-4}	355.5
1×10^{-3}	355.5

TABLE VII

Data for λ_F max of indole (70) as a function of its concentration

Concentration M	λ_F max ± 1 nm
1×10^{-5}	366.5
2×10^{-5}	366.0
3×10^{-5}	366.0
4×10^{-5}	365.0
5×10^{-5}	361.0
6×10^{-5}	359.0
7×10^{-5}	360.0
8×10^{-5}	358.0
9×10^{-5}	357.0
1×10^{-4}	356.5
2×10^{-4}	354.0

TABLE VIII

Data for λ_F max of indole (69) as a function of its concentration

Concentration M	λ_F max ± 1 nm
1×10^{-5}	362.0
2×10^{-5}	362.0
3×10^{-5}	361.5
4×10^{-5}	358.5
5×10^{-5}	360.0
6×10^{-5}	358.0
7×10^{-5}	357.5
8×10^{-5}	357.0
9×10^{-5}	356.5
1×10^{-4}	355.5
2×10^{-4}	355.0

TABLE IX

Fluorescence λmax of aqueous indole (61) as a function of added CTAB

Concentration of (61) = 1×10^{-5} m.

Concentration of aq. CTAB	λmax of (61) ± 1 nm
1×10^{-2} M	352 nm
1×10^{-3} M	353 nm
1×10^{-4} M	368 nm
2×10^{-3} M	353 nm
2×10^{-4} M	369 nm
3×10^{-4} M	369 nm
4×10^{-4} M	367.5nm
5×10^{-4} M	367 nm
6×10^{-4} M	367 nm
7×10^{-4} M	366.5 nm
8×10^{-4} M	367 nm
9×10^{-4} M	358.5 nm
1×10^{-3} M	353 nm

TABLE X

Fluorescence λmax of aqueous indole (70) as a function of added CTAB

Concentration of (70) = 1×10^{-6} m.

Concentration of aq. CTAB	λmax of (70) ± 1 nm
3×10^{-4} M	370 nm
4×10^{-4} M	365 nm
5×10^{-4} M	368 nm
6×10^{-4} M	365 nm
7×10^{-4} M	362 nm
8×10^{-4} M	357.5 nm
9×10^{-4} M	354 nm
1×10^{-3} M	352 nm

TABLE XI

Fluorescence λmax of indole (69) as a function of added CTAB

O.D. ≃ 0.025 - 0.05 at 300 nm

Concentration of aq. CTAB	λmax of fluorescence of indole (69) ± 1 nm
2×10^{-4} M	366 nm
6×10^{-4} M	357 nm
8×10^{-4} M	355 nm
1×10^{-3} M	355 nm
5×10^{-3} M	355 nm

TABLE XII

Fluorescence λmax of indole (84) as a function of added CTAB*

O.D. ≃ 0.025-0.05 at 300 nm

Concentration of aq. CTAB	λmax of fluorescence of indole (84) ± 1 nm
2×10^{-4} M	very poor quality of spectrum (in terms of signal to noise ratio).
6×10^{-4}	≃ 355
5×10^{-3}	351

*Indole (84) is weakly soluble in the above solution.

TABLE XIII

Fluorescence λmax of aqueous indole (52) as a function of added CTAB

O.D. of indole (52) ≃ 0.05-0.06 at 300 nm

Concentration of CTAB in H_2O	λmax of fluorescence of indole (52) ± 1 nm
Water only	369 nm
5×10^{-4} M	368 nm
6×10^{-4} M	369 nm
7×10^{-4} M	368 nm
8×10^{-4} M	368 nm
1×10^{-3} M	368 nm
3×10^{-3} M	366 nm
5×10^{-3} M	362 nm
1×10^{-2} M	360 nm

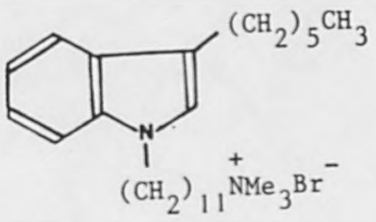
2.3.3 Fluorescent probes for sodium salts of indolic acids in water as a function of concentration:

The fluorescence studies of trimethyl ammonium salts of indolic surfactants containing different lengths of hydrocarbon chains at the 3- and one-positions of the indole ring provided information about the effect of the length of hydrocarbon chain on the fluorescence wavelength maximum and the CMC of these compounds. Sodium salts of indolic acids, prepared as described previously (Scheme F and I), and their use as fluorescence probes were investigated to find out whether the anionic indolic surfactants behave in the same way as the cationic surfactants (indolyl trimethyl ammonium bromides). The fluorescent probes were examined using different concentrations of aqueous solutions of these indolic surfactants ((55), (65), (75), (82)and(89)). These surfactants behave in a totally different way to the corresponding indolyl trimethyl ammonium bromides. The indole anionic surfactants do not show the gradual shift of the fluorescence to the shorter wavelength when the concentration is increased. The shift in the λmax value of the fluorescence for these anionic compounds does not decrease regularly when their concentration is increased, but shifts to higher wavelength instead. The data are presented in Table XIV.

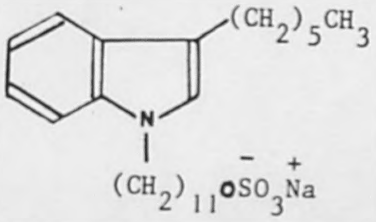
The anionic indole sulphate surfactants show smaller shifts in their fluorescence wavelength maximum compared with the cationic indolic surfactants, as found by Turro.[117] The fluorescence wavelength maximum shift for 6-In-II^{+} in HDTBr micelles is 19 nm compared to that in water, while that of 6-In-II^{-} in SDS micelles is 13 nm.

The lifetime of 6-In-II$^+$ in HDTBr micelles is 7 ns and that of 6-In-II$^-$ in SDS micelles is 12 ns compared to those in water (17 and 16 ns respectively) as shown in Table XV.

6-In-II$^+$ ≡



6-In-II$^-$ ≡



The data suggest that the environment of the chromophore of 6-In-II$^+$ is highly hydrophobic in HDTBr micelles, whereas that of the chromophore 6-In-II$^-$ in SDS is less hydrophobic compared to 6-In-II$^+$ in HDTBr micelles. The interior of HDTBr micelles is more hydrophobic because the surface of the HDTBr is covered with $-\overset{+}{N}(CH_3)_3-$ groups. The HDTBr molecules in the micelles are tightly packed to prevent the penetration of water into the interior of the micelle because this head group is hydrophobic. On the other hand, in SDS micelles the $-OSO_3^-$ group is highly hydrophilic, and hence water may penetrate easily into the interior of micelles. This is the reason why there is a smaller shift in both the λmax of fluorescence and fluorescence lifetime of the 6-In-II$^-$ (anionic) surfactant.

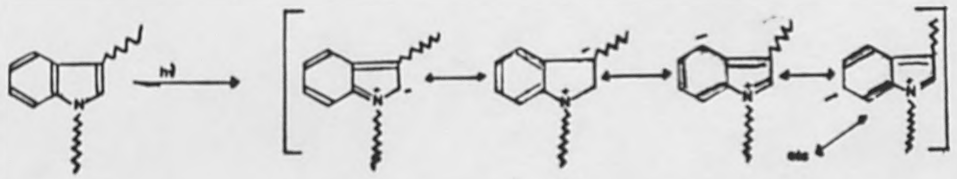
Muller and Birkhan[158] investigated the micelle structure of 10,10, 10-trifluorocaprate and related compounds ($CF_3(CH_2)_nCO_2Na$, n = 8, 10, 11) by fluorine magnetic resonance. Comparison of the chemical shift for the CF_3 group when it is in a micellar environment with chemical shifts, observed for the 10,10,10-trifluorocaprate soaps and for $CF_3(CH_2)_8CH_3$, in other solvents showed that the medium surrounding the CF_3 group when it is in the micelle has characteristics midway between that of water and that of a hydrocarbon. This suggested that there is considerable penetration of water into the interior of these micelles.

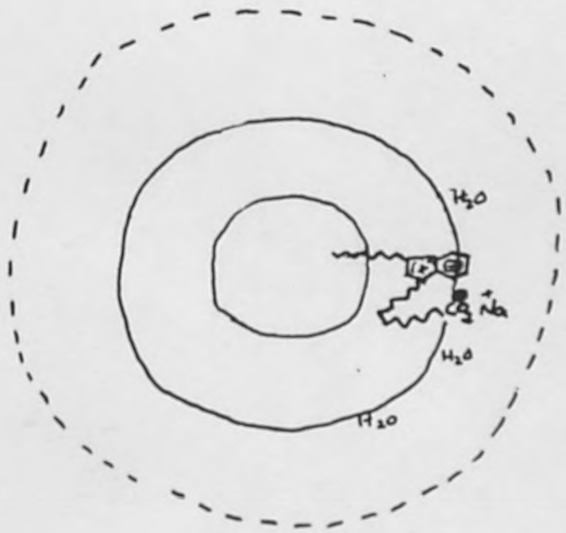
Svens and Rosenholm[129] have measured micellar radii and electron densities of the polar and non-polar regions in micelles of sodium-octanoate by using small angle x-ray scattering techniques. These results have indicated considerable hydration of the micelles and penetration of water between the hydrocarbon chains of sodium octanoate.

The above results suggest that the structure of the anionic micelles is similar to those of cationic micelles.[190] However, the penetration of water is greater in the interior of the anionic surfactant micelles due to the hydrophilic character of their head groups.

The indole carboxylate surfactant shows opposite behaviour in its fluorescence wavelength maximum shift to that of indolyl sulphate and indolyl trimethyl ammonium surfactants. When the indole carboxylate surfactant is in its initially aggregated form (dimer or trimers)[191]

the indole group seems to be located in the hydrocarbon environment. The initially formed aggregates are not as well organised and packed with hydrocarbon chains as their micelles. At higher concentration, they form a close packed hydrocarbon chain structure and the indole group comes out from the interior of the micelle into the aqueous environment. The indole group is not comicellising with its own micelles. This behaviour is also supported by the observation that this probe does not comicellise with the host micellar solutions such as SDS and sodium laurate (see Section 2.3.4). In the micellar solution of indole carboxylate the excited dipolar indole group (particularly $\overset{+}{N}$) may be interacting with a negatively charged carboxylic group, thus pulling the indole chromophore into the polar environment.

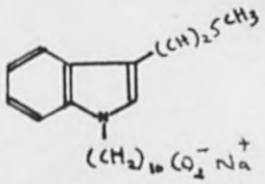




Possible position of indole group in indole carboxylate micelle.

TABLE XIV

Fluorescence λmax of aqueous sodium salts of indolic acids as a function of concentration

Indolic surfactant	Concentration	λmax
 (65)	1×10^{-2} M	360 nm
	1×10^{-3} M	360 nm
	1×10^{-4} M	360 nm
	1×10^{-5} M	350 nm
	2×10^{-5} M	345 nm
	3×10^{-5} M	345 nm
	4×10^{-5} M	345 nm
	5×10^{-5} M	345 nm
	6×10^{-5} M	347 nm
	7×10^{-5} M	347 nm
	8×10^{-5} M	345 nm
	9×10^{-5} M	349 nm
	1×10^{-4} M	348 nm
	1×10^{-3} M	358 nm
	2×10^{-4} M	359 nm
	3×10^{-4} M	365 nm
	4×10^{-4} M	365 nm
	5×10^{-4} M	364 nm
	6×10^{-4} M	361 nm
	7×10^{-4} M	361 nm
	8×10^{-4} M	357.5 nm
	9×10^{-4} M	357 nm

Continued.....

TABLE XIV Continued....

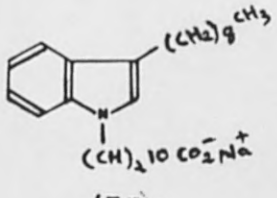
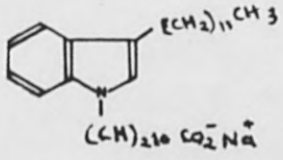
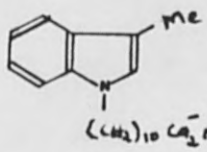
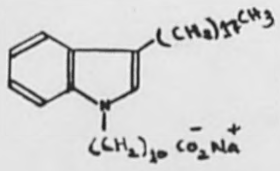
Indolic surfactant	Concentration	λmax
 (75).	1×10^{-3} M	352 nm
	1×10^{-4} M	351 nm
	1×10^{-5} M	352 nm
	1×10^{-2} M	360 nm
	2×10^{-3} M	354 nm
	3×10^{-3} M	356 nm
	4×10^{-3} M	356 nm
	5×10^{-3} M	357.5 nm
	6×10^{-3} M	358 nm
	7×10^{-3} M	359 nm
 (82).	1×10^{-2} M	357 nm
	1×10^{-3} M	348 nm
	1×10^{-4} M	345 nm
	1×10^{-5} M	345 nm
 (55).	1×10^{-2} M	366 nm
	1×10^{-3} M	369 nm
	1×10^{-4} M	368 nm
	1×10^{-5} M	369 nm
 (89).	1×10^{-2} M	370 nm
	1×10^{-3} M	366 nm
	1×10^{-4} M	357.5 nm
	1×10^{-5} M	357.5 nm
	1×10^{-6} M	360 nm
	1×10^{-7} M	363 nm

TABLE XV

Fluorescence λmax and lifetimes of indoles in aqueous micellar solution

Compound	Fluorescence λmax (nm) Water	Micelle	Fluorescence lifetime Water	Micelle
6-In-II$^+$	373 nm	354 (HDTBr) 355 (self)*	17 ns	7 ns (HDTBr) 6 ns (self)*
6-In-II$^-$	370 nm	357 nm (SDS) 360 nm (self)*	16 ns	12 ns (SDS) 7 ns (self)*

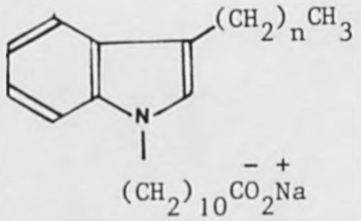
*Self means its own micelles.

2.3.4 Fluorescence study of aqueous indole acid surfactants in the micelle forming host surfactants sodium laurate and sodium lauryl sulphate:

Turro[117] has synthesised sodium II-(3-hexyl-1-indolyl)undecyl sulphate (63) to investigate the use of this detergent (63) as a fluorescent probe for the location of chromophoric groups in ionic micelles (e.g. sodium lauryl sulphate). The chromophore of the indole detergent (63) was found to be located in the interior of the hydrophobic environment of sodium lauryl sulphate micelles. We have decided to investigate the use of indole acid detergents (55),(65) and (75) as fluorescent probes for the determination of the CMC of sodium laurate and sodium dodecyl sulphate (SDS).

When sodium laurate forms micelles in the presence of aqueous indole (75) (1×10^{-4} M) the maximum wavelength of the fluorescence is

expected to be shifted towards lower wavelengths and thus the CMC could be determined. This is by analogy with the behaviour of cationic and anionic indolic surfactants, e.g. 11-(3-hexyl-1-indolyl) undecyl trimethyl ammonium bromide.[117] The fluorescence wavelength maximum (340 nm) however, does not shift even though the concentration of sodium laurate is increased from 1×10^{-4} M to 1×10^{-2} M. Indole acid salt (55) was also used as a fluorescent probe for sodium laurate. The wavelength maximum of the fluorescence (368 nm) of indole (55) did not change when the concentration of sodium laurate was increased from 1×10^{-5} M to 1×10^{-2} M as shown in the Table XVI.



(55) n = 0; (65) n = 5;
(75) n = 8; (82) n = 11;
(89) n = 17.

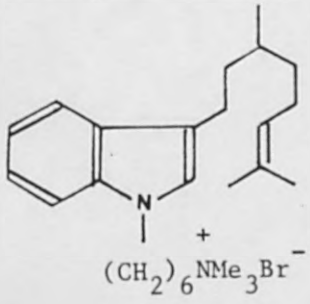
The indole (75) has a fluorescence λmax at 340 nm, whereas indole (55) has a fluorescence λmax at 368 nm. Indole (75) has a hydrocarbon chain of nine carbon atoms on the 3-position of the indole ring. Indole (55) seems to be in a more aqueous environment than the indole (75). There is also the possibility that comicelles are not being formed and that the emission is coming from aggregates of the indolic surfactants.

The fluorescence of the salts of indolic acids (65) and (75) was also studied as a function of added sodium dodecyl sulphate (SDS) in water. Addition of SDS has no noticeable effect on the

fluorescence wavelength maxima of the indole acid detergents (65) and (75) as shown in Tables XVII and XVIII respectively.

It was noted that when the concentration of the SDS solution was 1×10^{-2} M or 1×10^{-1} M (CMC value, i.e. 7.4×10^{-3} M), the indolic compound seemed to be dissolved in micelles and very much higher quality spectra (in terms of signal to noise ratio) were obtained compared to lower concentrations of SDS.

2.3.5 Fluorescence study of 6-(3-citronellyl-1-indolyl)hexyl trimethyl amminium bromide (47):



(47)

The purpose of investigating the fluorescence behaviour of indolic surfactant (47) was to find out how this type of surfactant behaves in micellar environments when it is used as a fluorescent probe. This should show whether the presence of methyl groups and a double bond in the chain affects the way chains pack in the micelles. This type of surfactant, with a double bond and methyl groups in the hydrocarbon chain of the indole nucleus (position-3), has not been used as a fluorescent probe previously.

The indolic surfactant (47) (aqueous) does not show any shift in the fluorescence wavelength maximum (λ_F max) as its concentration is altered from 1 x 10^{-5} to 1 x 10^{-2} M, and hence it was not possible to determine the CMC of this surfactant using fluorescence spectroscopy.[187] The results are shown in Table XIX. However, the analogous straight chain indole (68) (with no methyl groups) shows a shift in fluorescence λmax when the concentration is altered and has a CMC of 3.7 x 10^{-4} M. The absence of a shift in the fluorescence λmax for indolic surfactant (47) could be due to the rigidity of the hydrocarbon chain (on the three position of the indole ring) because of the double bond present and the way the methyl groups affect the available methods of packing in the micelle. Therefore, the indolic chromophore is located close to the surface of the micelle.

2.3.6 Fluorescence of different indolic alcohols in solutions of micelle forming host surfactants (cationic, anionic and nonionic surfactants):

It was thought that 1,3-dialkyl indolyl alcohols may be incorporated into cationic, anionic and nonionic host surfactants since the alcohol group is itself nonionic. Thus such compounds should enable us to determine the CMC of the host surfactants. A variety of the indolic alcohols, whose synthesis has been previously described (Scheme F), were used as fluorescent probes. Three types of host surfactants were used (i) cetyl trimethyl ammonium bromide (CTAB), (ii) sodium dodecyl sulphate (SDS) and (iii) synpronic E07 (PEG derivatives).

The fluorescence of these alcohols in water do not show any regular shift in fluorescence wavelength maxima when the concentrations of the above mentioned host surfactants are increased above their CMC values. These indolic alcohols are not very soluble in water.

The fluorescence spectra of indolic alcohols are more smooth and of higher quality (in terms of signal to noise ratio) when they are used with higher concentrations of host surfactants (above the CMC values) Fig.53-56. This could be due to the indolic alcohol dissolved in the micelles of the host surfactants.

Table XX illustrates the behaviour of these indolic alcohols in terms of wavelength maximum in water and different micelle forming host surfactants.

The inability to obtain good fluorescence spectra (in terms of signal-to-noise ratio) could be attributed to the fact that these indoles were weakly soluble in water and hence the signals may have been distorted due to light scattering. Self aggregation of indolic alcohols (dimers etc) may also have taken place.

TABLE XVI

Fluorescence λmax of aqueous indole (55) as a function of added sodium laurate

Concentration of sodium laurate	Fluorescence λmax of (55) ± 1 nm
1×10^{-2} M	368 nm
1×10^{-3} M	368 nm
1×10^{-4} M	368 nm
1×10^{-5} M	369 nm

Concentration of indole (55) = 1×10^{-5} M.

TABLE XVII

Fluorescence λmax of aqueous indole (65) as a function of added sodium lauryl sulphate

Optical density of indole (65) ≃ 0.04 to 0.055 at 300 nm

Concentration of SDS in H_2O	Fluorescence λmax of (65) ± 1 nm
1×10^{-4} M	355 nm
1×10^{-3} M	355 nm
1×10^{-2} M	375 nm
1×10^{-1} M	354 nm
Water only	360 nm

TABLE XVIII

Fluorescence λmax of aqueous indole (75) as a function of added sodium lauryl sulphate

Optical density of indole (75) ≃ 0.04 to 0.06 at 300 nm

Concentration of SDS in H_2O	Fluorescence λmax of (75) ± 1 nm
1×10^{-4} M	332 and 350 nm
1×10^{-3} M	332 and 350 nm
1×10^{-2} M	355 nm
1×10^{-1} M	350 nm
Water only	332 and 350 nm

TABLE XIX

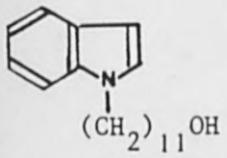
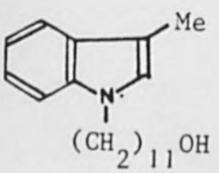
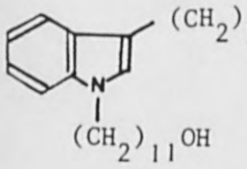
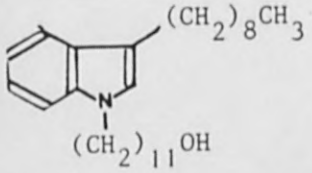
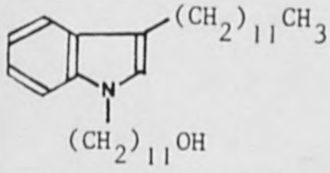
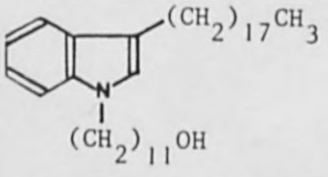
Fluorescence λmax of aqueous indole (47) as a function of concentration

Concentration of indole (47) M, in water	λmax of indole (47) ± 1 nm
1×10^{-5} M	368 nm
1×10^{-4} M	368 nm
1×10^{-3} M	367 nm
1×10^{-2} M	366 nm

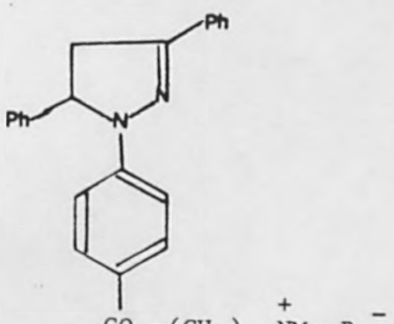
TABLE XX

Fluorescence behaviour of indolic alcohols in micelle forming host surfactants

Optical density indolic alcohols = 0.04 - 0.055 at 300 nm.

Compound	Fluorescence λmax in water nm	Fluorescence in aqueous CTAB		Fluorescence in aqueous SDS		Fluorescence in aqueous synpronic E07	
		Concn. of CTAB M	λmax nm	Concn. of SDS M	λmax nm	Concn. of E07 M	λmax nm
	Two peaks 335 & 353 nm Poor spectrum in terms of noise	9×10^{-4} M	335 nm 350 nm smooth	-	-	-	-
		1×10^{-4} M	355 nm	-	-	-	-
	357 nm	9×10^{-4} M	355 nm smooth	-	-	-	-
		5×10^{-4} M	355 nm				
		1×10^{-4} M	364 nm (noise)				
	333 nm & 348 nm noise	1×10^{-4} M	Insoluble No spectrum	1×10^{-5} M	332 nm 345 nm noise	1×10^{-8} M	Two peaks 334 & 356 nm noise
		1×10^{-3} M	351 nm smooth	1×10^{-3} M	334 nm 345 nm noise	1×10^{-6} M	334 nm 347 nm noise
		5×10^{-3} M	350 nm smooth				
				1×10^{-2} M	356 nm smooth	1×10^{-4} M	335 nm smooth
				1×10^{-1} M	353 nm smooth		
	Insoluble	9×10^{-4} M	Insoluble	-	-	-	-
	Insoluble	9×10^{-4} M	Insoluble	-	-	-	-
	Insoluble	9×10^{-4} M	Insoluble	-	-	-	-

2.3.7 Fluorescence behaviour of pyrazoline surfactant (137) in water solutions:



(137)

Some pyrazoline derivatives are optical brighteners[192] and can be attached to fibres (wool). Since pyrazoline (137) contains trimethyl ammonium bromide groups it should behave as a surfactant. It was proposed to investigate whether the fluorescence of this compound behaves in a similar way to that of indolic surfactants. Its fluorescence shows a gradual shift (459 to 448 nm) when the concentration is increased from 1×10^{-5} M to 1×10^{-4} M. These results are shown in Table XXI.

The CMC value of this pyrazoline compound (137) was found to be (4×10^{-5} M). A new fluorescence band appeared at 535 $\pm$ 1 nm, this was at the expense of the 445 nm band, when the concentration of (137) was increased from 1×10^{-3} M to 1×10^{-2} M. This may be due to intermolecular charge transfer excited complex formation. The fluorescence spectra were taken at different concentrations as shown in Table XXII. However, it should be kept in mind that the solution of (137) was not completely optically clear at 1×10^{-2} M concentration.

Fluorescence behaviour of pyrazoline (137) was also investigated as a function of added cationic surfactant CTAB. The expected shift in fluorescence wavelength maxima occurred (456 nm to 428 nm) as shown in Table XXIII. The structure of the fluorescence is more smooth and featureless (broad) when the pyrazoline (137) is incorporated in the CTAB micelles.

2.3.8 Determination of sites of indolic cationic detergents in wool:

Pyrazoline surfactant (137) could be applied to wool via the quaternary ammonium group. Since the fluorescence of (137) is concentration dependent and the fluorescence wavelength maximum is determined by the solvent environment, it should be useful in determining the sites where cationic detergents bind to wool. In a related study the indoles (52), (58), (70) and (69) were applied to wool and the wavelength of fluorescence indicated that the indole nucleus is located in a hydrophobic environment, as shown in Table XXIV.

2.3.9 Measurement of quantum yields of fluorescence (ϕ_F) of indolic surfactants and indolic alcohols:

The cationic indole surfactants display fluorescence in aqueous solution. When these compounds were incorporated into a micellar solution of CTAB (5×10^{-3} M), a marked increase in the fluorescence quantum yield was observed (see Table XXV and XXVI). Consequently the measurement of the fluorescence quantum yields of cationic indolic surfactants as a function of the concentration of the cationic host surfactant may possibly provide a useful method

for determining the CMCs of the host surfactants. Wolf has already investigated the possibility of determining the CMC of different ionic host surfactants using Acridine as the fluorescent probe. In this study the quantum yield of the fluorescence decreased drastically when the concentration of the host surfactant was above its CMC.[84,85]

It can be seen from Table XXV and XXVI that the quantum yield of the fluorescence of indolic trimethyl ammonium bromides is approximately 0.9 when they are in micellar environments (e.g. in 5×10^{-3} M aqueous CTAB solution), but the quantum yield value is greatly reduced to approximately 0.1, when they are in monomeric form (in water). A possible reason for this decrease in quantum yield for the indole probes could be the fluorescence quenching by bromide ions as a consequence of either internal heavy atom effects or electron transfer. This process cannot occur if the indole detergent is comicellised and hence located in a hydrocarbon environment, away from the bromide ions. Indoles (84) and (86) (Table XXVI) display fluorescence, λmax at 353 and 350 nm respectively, in aqueous solution and the fluorescence quantum yields are lower compared with other indole detergents. This could be due to poor solubility of these compounds in water and they may be forming their own aggregates.

The value of the fluorescence quantum yield of indolic alcohols in cyclohexane is approximately 0.7. For those indole alcohols which could be dissolved in a micellar solution of CTAB, a change in the

fluorescence quantum yield was observed. However, it appears that these compounds are only poorly solubilised in the solution of CTAB and hence a variable change is observed, possibly due to self-aggregation. The fluorescence quantum yield of these compounds appeared to be increasing (slightly) in cyclohexane when the length of the hydrocarbon chain, on the 3-position of the indole ring, was increased (see Table XXVII).

TABLE XXI

Fluorescence λmax of aqueous pyrazoline (137) as a function of concentration

Concentration of aqueous (137)	Fluorescence λmax
1×10^{-5} M	459 nm
2×10^{-5} M	459 nm
3×10^{-5} M	455.5 nm
4×10^{-5} M	453 nm
5×10^{-5} M	452 nm
6×10^{-5} M	451 nm
7×10^{-5} M	450 nm
8×10^{-5} M	449 nm
9×10^{-5} M	451 nm
1×10^{-4} M	448 nm
1×10^{-3} M	445 nm

TABLE XXII

Excited charge transfer complex of pyrazoline (137) in water

Concentration of Pyrazoline (137)	Shift in λmax (fluorescence)	
	Height of fluorescence band at ≃ 445 nm %	Height of fluorescence band at ≃ 535 nm %
2×10^{-3} M	58.2 %	41.97%
3×10^{-3} M	52.3 %	47.7 %
4×10^{-3} M	36.23%	63.76%
5×10^{-3} M	25.46%	74.53%
6×10^{-3} M	16.08%	83.91%
7×10^{-3} M	23.07%	76.92%
8×10^{-3} M	22.5 %	77.5 %
1×10^{-2} M	14.78%	85.21%

TABLE XXIII

Fluorescence λmax of aqueous pyrazoline (137) as a function of added CTAB

Concentration of added CTAB in aqueous 1×10^{-6} (137)	λmax fluorescence nm
1×10^{-4} M	456 nm
5×10^{-3} M	428 nm

TABLE XXIV

Fluorescence of indolic cationic detergents in wool

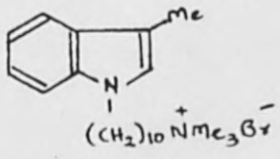
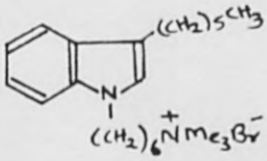
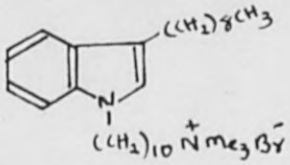
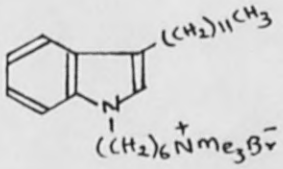
Indole structure	Fluorescence emission λmax nm in water (monomeric)	Fluorescence emission λmax in wool	Environment in wool
 (52)	370 nm (± 2)	354 nm	Hydrophobic
 (58)	369 nm (± 2)	352 nm	Hydrophobic
 (70)	366 nm (± 1)	350 nm	Hydrophobic
 (69)	362 nm (at 1 x 10^{-5} M)	354 nm	Hydrophobic

TABLE XXV

Quantum yields of indoles in 5×10^{-3} M aqueous CTAB

Optical Density of indole = 0.1 at 300 nm

Temperature 25-27°C.

Standard: 1-methyl naphthalene in 5×10^{-3} M CTAB.

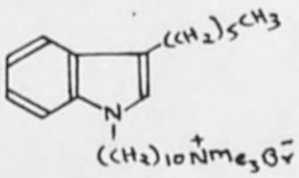
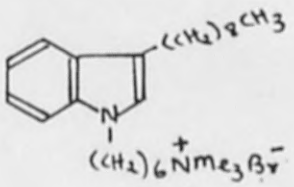
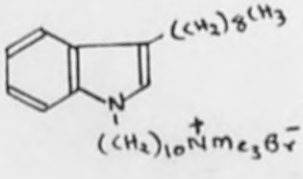
Compound	ϕ_F	λmax (fluorescence)
1-methyl naphthalene	Found 0.08 found by experimental value. Known 0.21 in Cyclohexane by literature value.	
 (61)	0.90	352 nm
 (68)	0.91	355 nm
 (70)	0.94	352 nm

TABLE XXV (Continued)

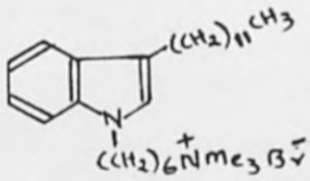
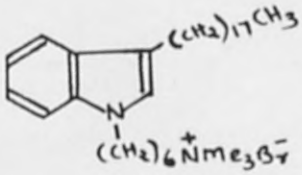
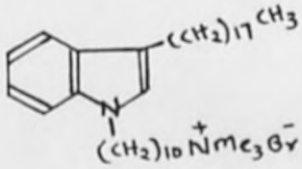
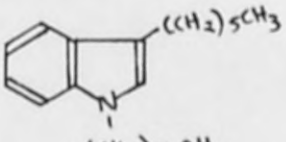
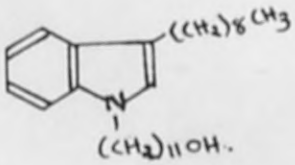
Compound	ϕ_F	λmax (fluorescence)
 (69)	1.00	354 nm
 (84)	1.00	352 nm
 (86)	0.76	348 nm
 (62)	0.85	350 nm
 (72)	0.19	325 nm

TABLE XXV (Continued)

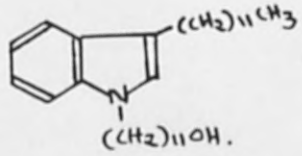
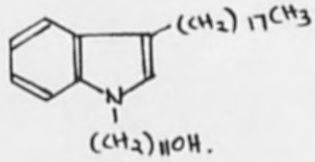
Compound	ϕ_F	λmax (fluorescence)
 (79)	0.23	351 nm
 (87)	0.47	351 nm

TABLE XXVI

Quantum yields of indolic surfactants in water

Optical Density of indole = 0.1 at 300 nm

Temperature 25-27°C

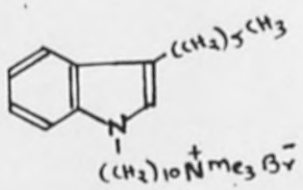
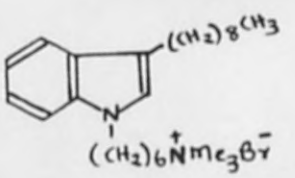
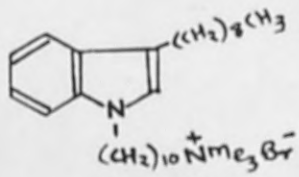
Compound	ϕ_F	λmax (fluorescence)
Standard: 1-methyl naphthalene	0.1 found by experimental (H_2O) value. Standard 0.21 in cyclohexane by literature value.	332 nm
 (61)	0.19	369 nm
 (68)	0.17	367 nm
 (70)	0.15	365 nm

TABLE XXVI (Continued)

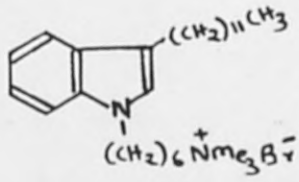
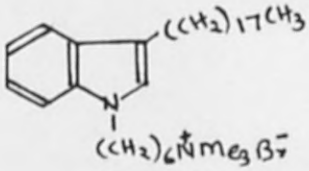
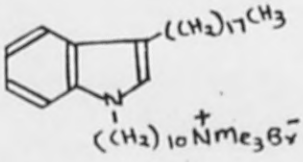
Compound	ϕ_F	λ max (fluorescence)
 (69)	0.06	367 nm
 (84)	0.08	353 nm
 (86)	0.06	≈ 350 nm

TABLE XXVII

Fluorescence quantum yields of indolic alcohols in cyclohexane

Optical Density of indole alcohol = 0.1 at 300 nm

Temperature 25-27°C

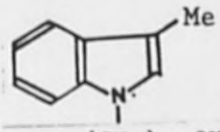
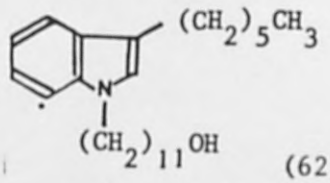
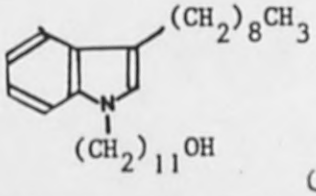
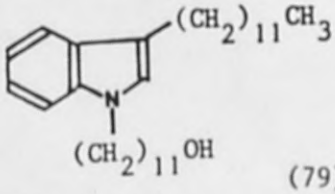
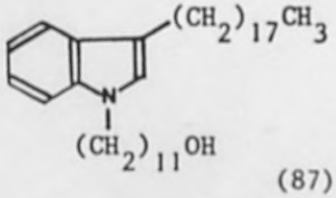
Compound	ϕ_F	λmax (fluorescence)
Standard 1-methyl naphthalene	0.21 (known) by literature value	325 nm
 (7a)	0.69	322 nm
 (62)	0.75	322 nm
 (72)	0.79	322 nm
 (79)	0.78	322 nm
 (87)	0.77	322 nm

TABLE XXVIII

Fluorescence quantum yield of 1-methyl indole in cyclohexane and in 5×10^{-3} M aqueous CTAB

Optical Density of indole = 0.1 at 300 nm.

Temperature $\simeq 25^{\circ}C$

Compound	ϕ_F	Solvent
1-Methyl naphthalene	0.21 (known) by literature value	Cyclohexane
1-Methyl indole	0.67	Cyclohexane
1-Methyl naphthalene	0.20 (calculated) by experimental value	5×10^{-3} M aqueous CTAB
1-Methyl indole	0.51	5×10^{-3} M aqueous CTAB

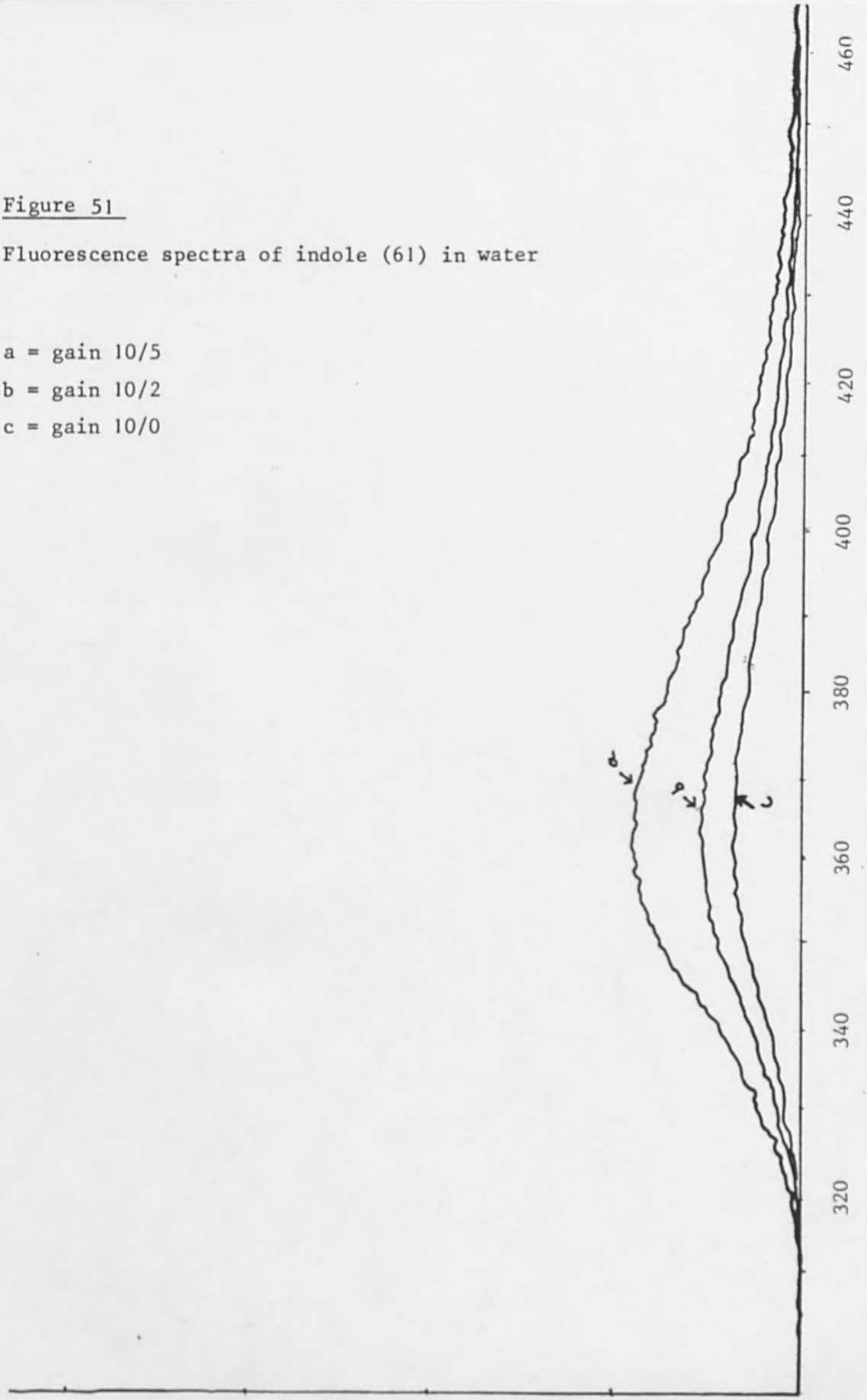
Figure 51

Fluorescence spectra of indole (61) in water

a = gain 10/5

b = gain 10/2

c = gain 10/0

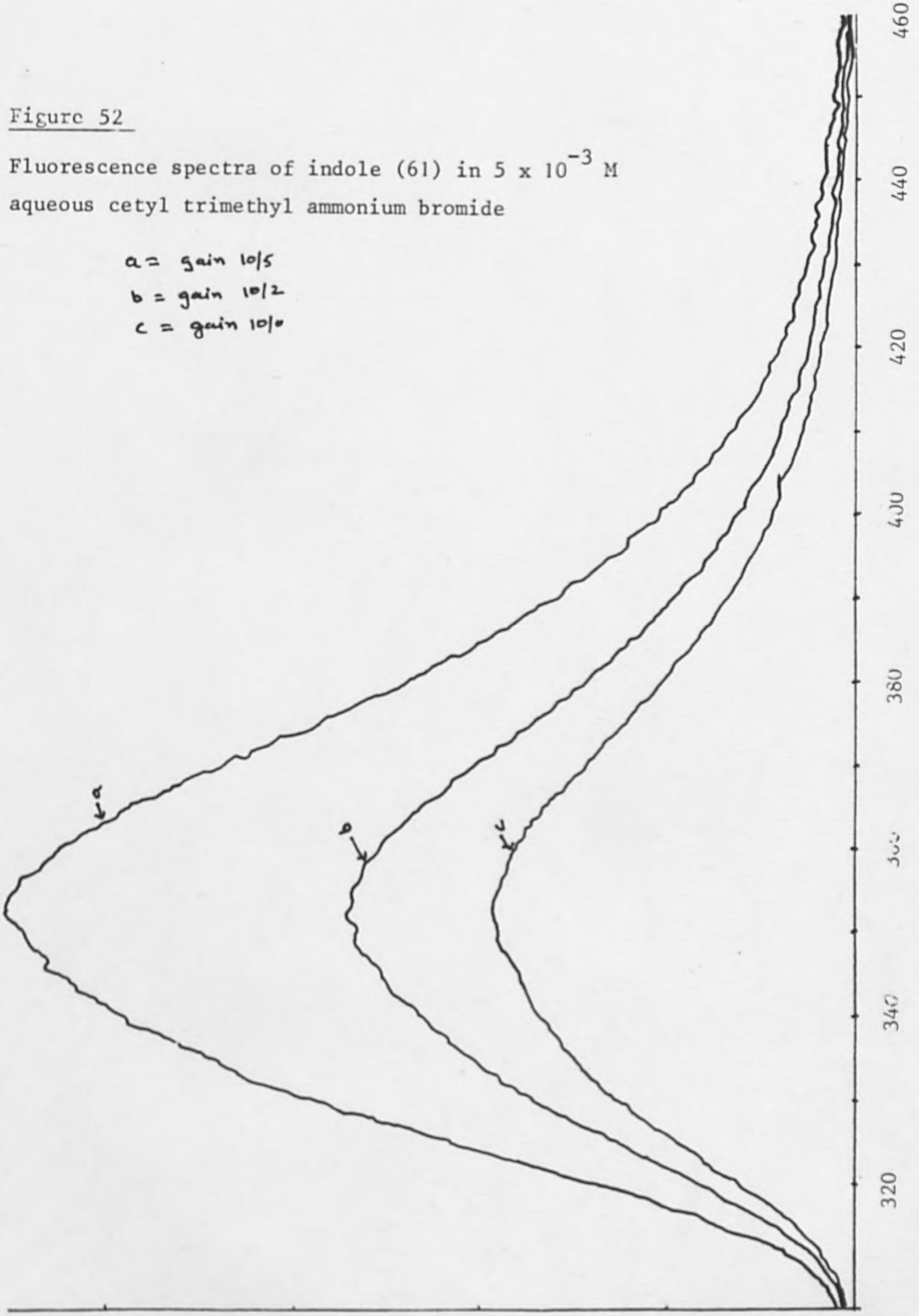


Intensity (Arbitrary units)

Figure 52

Fluorescence spectra of indole (61) in 5 x 10^{-3} M aqueous cetyl trimethyl ammonium bromide

a = gain 10/5
b = gain 10/2
c = gain 10/0



Intensity (Arbitrary units)

Figure 53

Fluorescence spectrum of indole (62) in water.

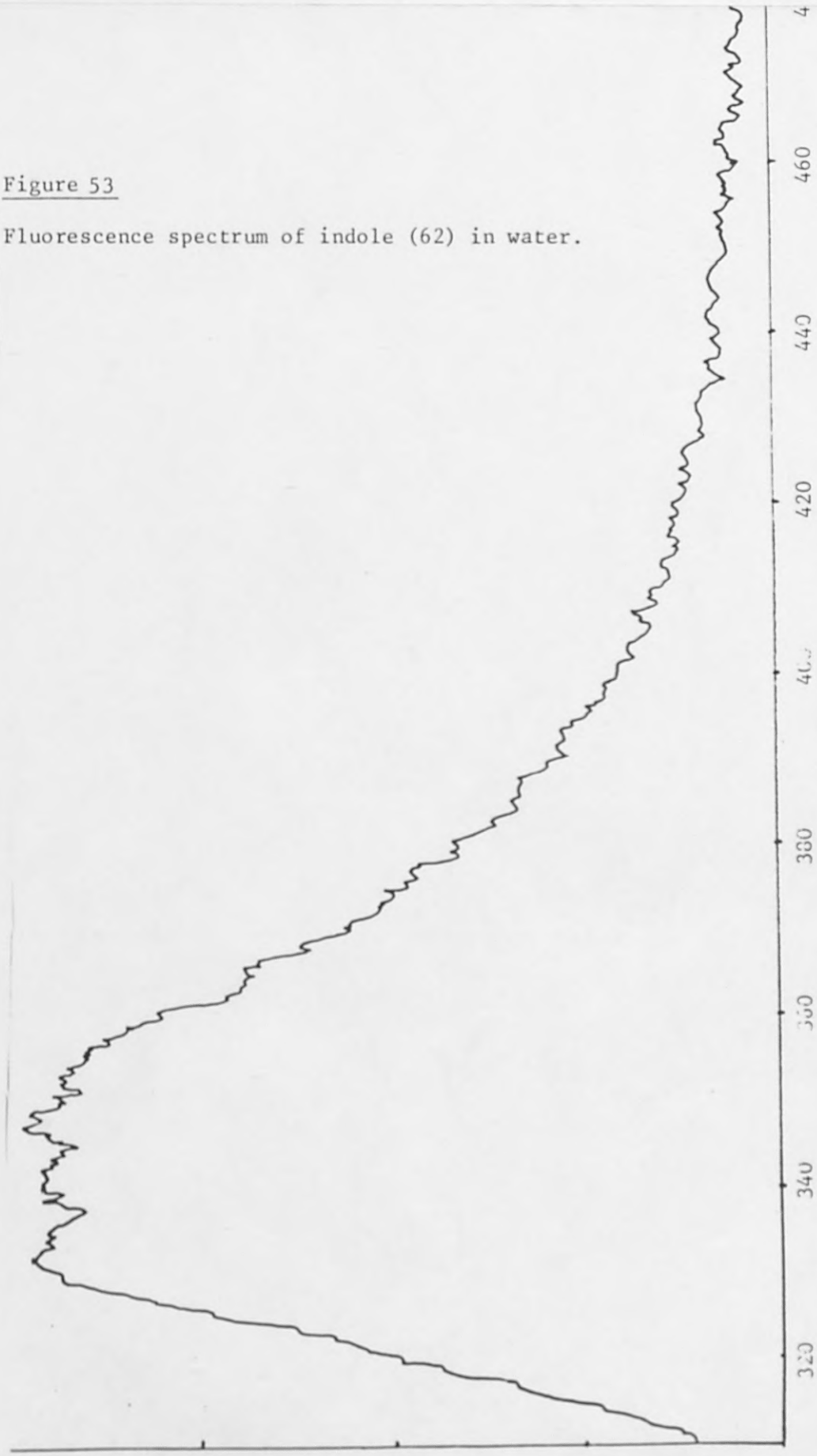


Figure 54

Fluroescence spectrum of indole (62) in 5×10^{-3} M aqueous CTAB.

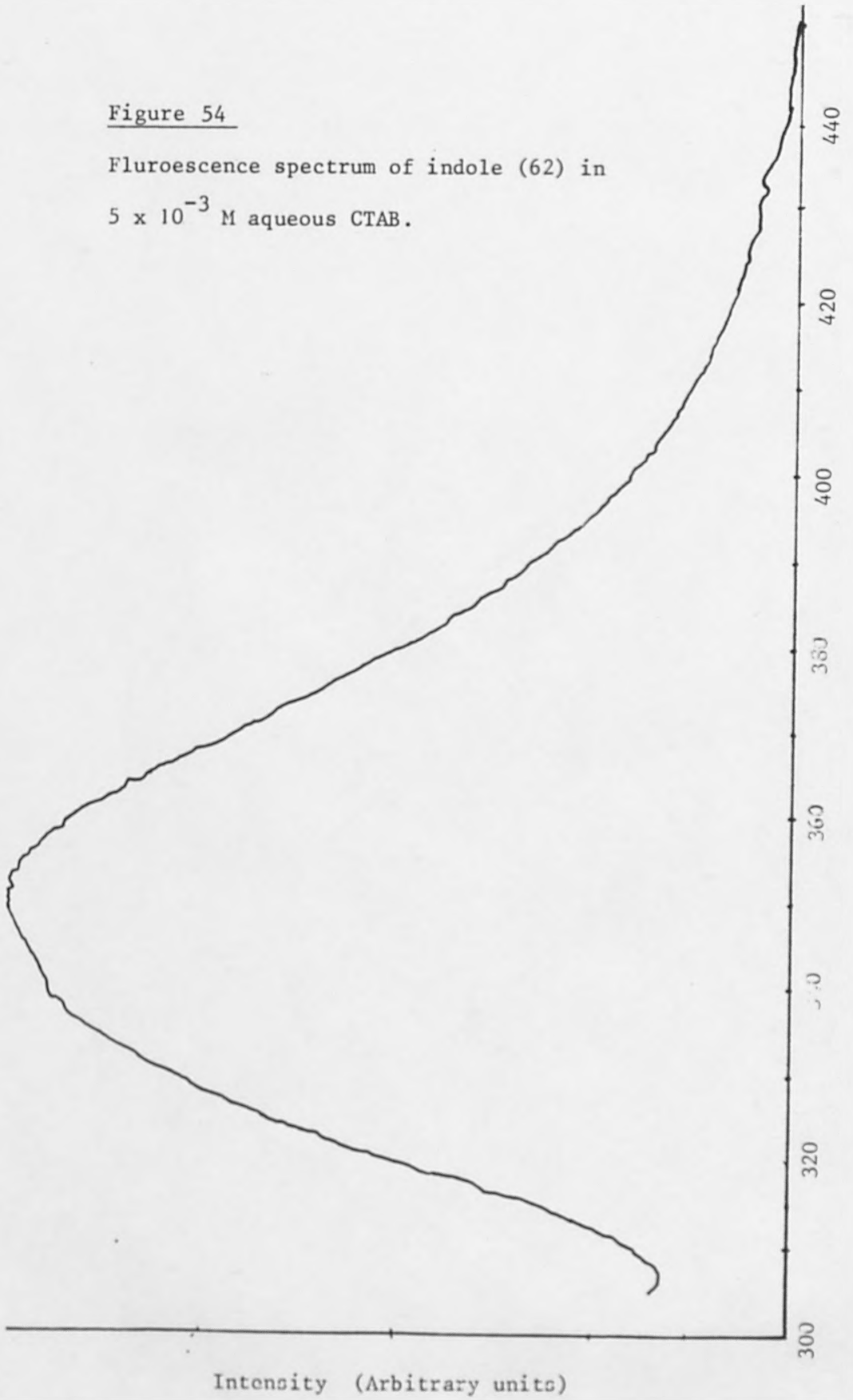


Figure 55

Fluorescence spectrum of indole (62) in 1×10^{-1} M aqueous sodium dodecyl sulphate

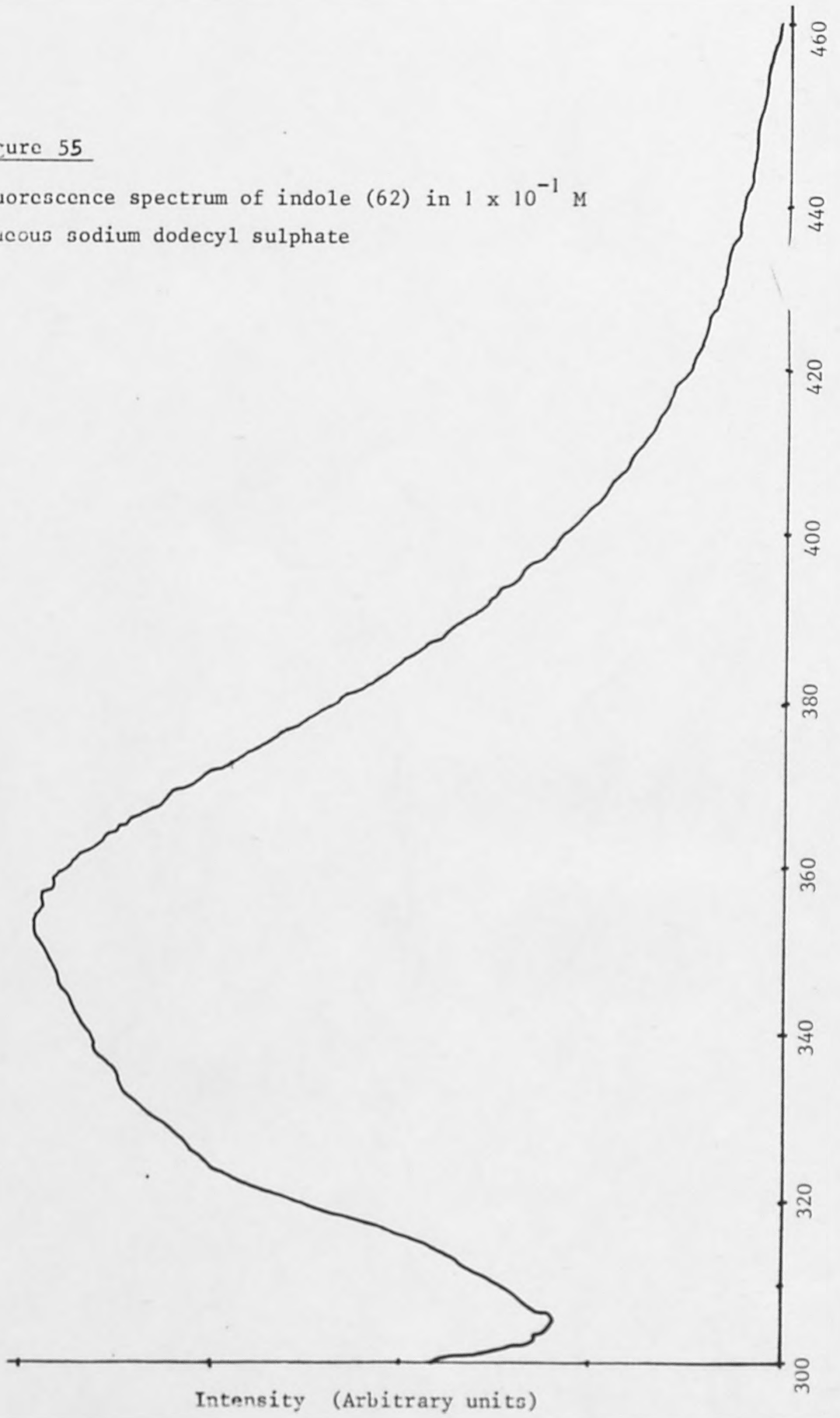


Figure 56

Fluorescence spectrum of indole (62) in 1 x 10^{-4} aqueous synpronic E07

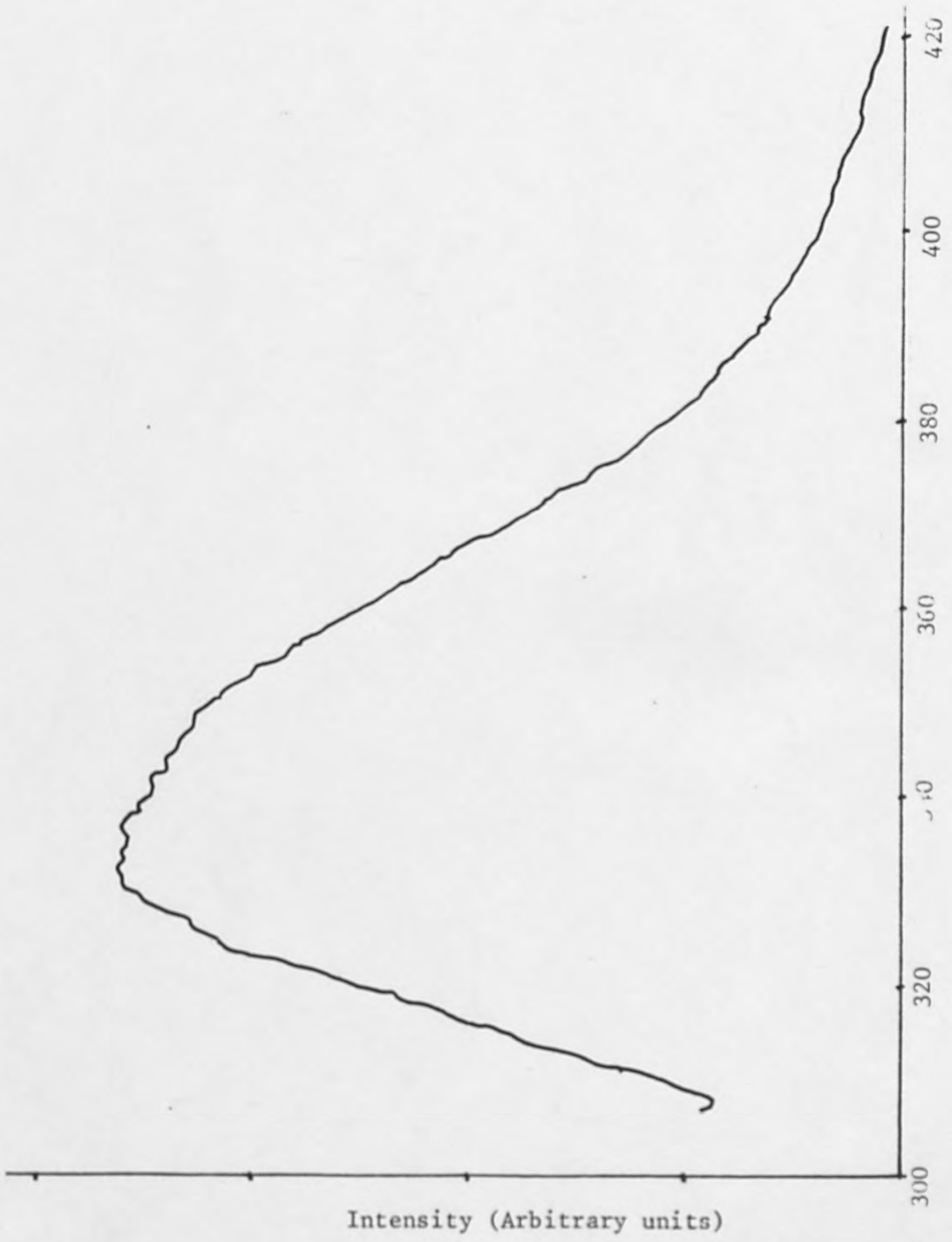
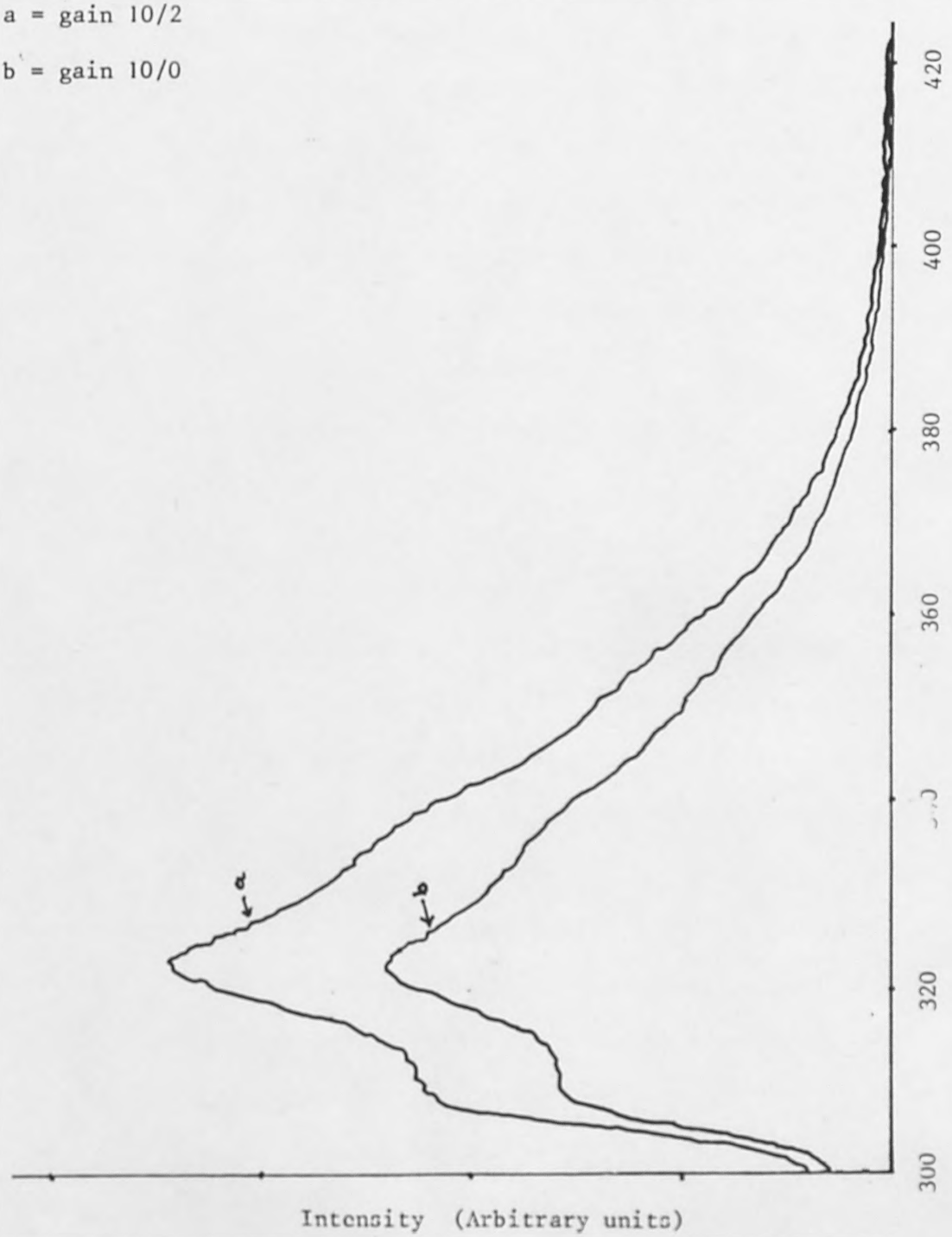


Figure 57

Fluorescence spectra of indole (62) in cyclohexane

a = gain 10/2

b = gain 10/0



2.4 Liquid crystal phases:

Liquid crystals (LC) are also known as mesophases. LC phase is an intermediate stage between the solid phase and a melt liquid phase. Within a crystal the molecules are positioned in a regular lattice and have little or no mobility, whereas liquids have no long range structure and little short-range order but molecular movement is very rapid. Liquid crystals have long range order and fast molecular motion. There are two main types of liquid crystals, thermotropic and lyotropic. Thermotropic mesophases are formed by heating polar, rod-shaped molecules.[193] Formation of thermotropic LC phase is due to the occurrence of strong short range intermolecular interactions, such as those in solids.

Lyotropic liquid crystals occur when some substances are dispersed in a solvent. The most common are those formed by surfactants, where the solvent is usually water. When water is added to solid surfactants three types of behaviour can occur. (i) The surfactant is practically insoluble and remains as solid crystals together with an aqueous solution of monomers. (ii) Some of the surfactant dissolves to form an aqueous micellar solution. (iii) A lyotropic liquid crystal is formed, which may dissolve in more water to form an aqueous micellar solution. The lyotropic liquid crystal can be regarded as arising from the interactions between micelles which occur at high surfactant concentrations.[194]

There are three well established classes of lyotropic LC phases, (i) Lamellar (Lα); (ii) Hexagonal (H_1, H_2) and (iii) Cubic (I_1, I_2, V_1, V_2). The classification is based on the type of low angle X-ray diffraction patterns obtained from each phase.[195-198]

(i) Lamellar LC phase (Lα):

This is the most common mesophase and consists of surfactant bi-layers separated by water layers (Fig. 47). The surfactant head-groups are restricted to the chain/water interface. These layers can extend over large distances. The phase is optically anisotropic when viewed by a microscope between crossed polarisers, with the birefringence being positive in most cases. The observed 'textures' can be used to identify phase structures.[199] The lamellar phase can be identified by the 'mosaic' or 'oily streak' textures.

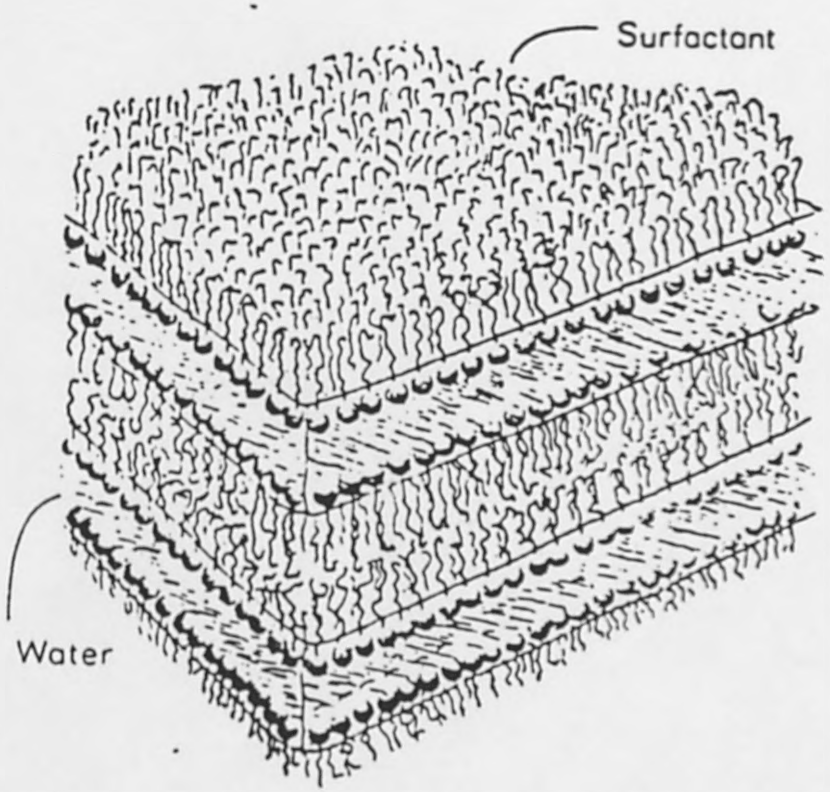


Figure 47 Schematic diagram of the lamellar (Lα) phase

(ii) Hexagonal phases (H_1, H_2):

Hexagonal structures are the second most common class of lyotropic phases. There are two types, 'normal' and 'reversed' hexagonal phase. The normal hexagonal phase (H_1) is composed of long cylindrical micelles packed in a hexagonal array, where the polar groups occupy the cylinder surfaces, these cylinders are separated by a continuous water region (Figure 48). In the reverse hexagonal phase (H_2), the hydrocarbon chains occupy the spaces between the hexagonally packed water cylinders (Figure 49).

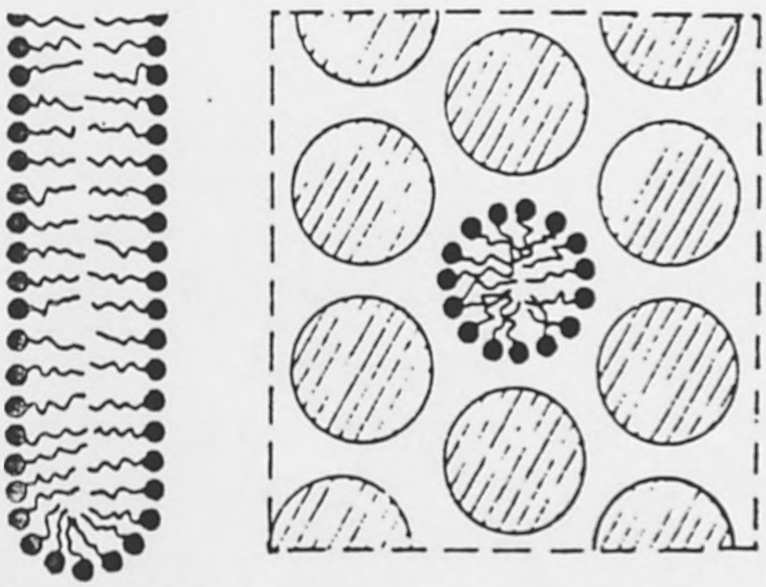


Figure 48 Schematic diagram of 'normal' hexagonal (H_1) phase

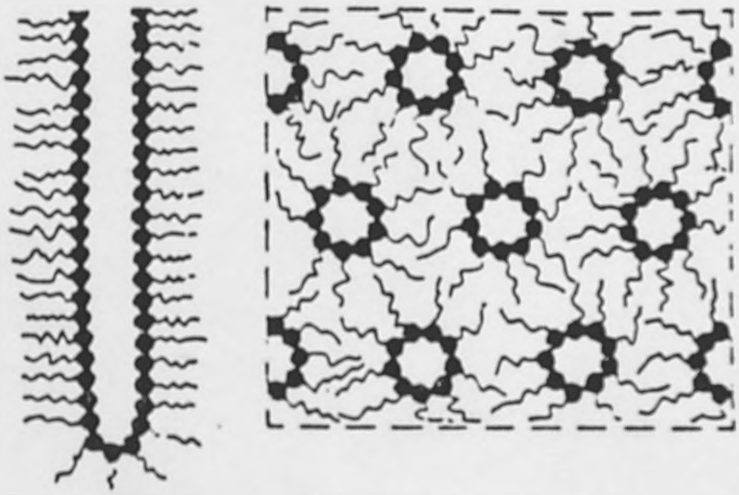


Figure 49 Schematic diagram of 'reverse' hexagonal (H_2) phase

These hexagonal phases are optically anisotropic when viewed between crossed polarisers and are best identified by the 'fan-like' or 'non-geometric' textures.[199]

(iii) Cubic phases:

Face centred cubic packing of (a) normal micelles and (b) reversed micelles (Figure 50)

There are two main classes of cubic phases, each further sub-divided into 'normal' and 'reversed' structures. The first group designated 'I_1' or 'I_2' consists of close packed spherical micelles. The second group of cubic phases (V_1, V_2) consist of interspersed, three dimensional networks of water and surfactant. They are termed 'bicontinuous' because both water and surfactant form continuous zones.[199,200-202]

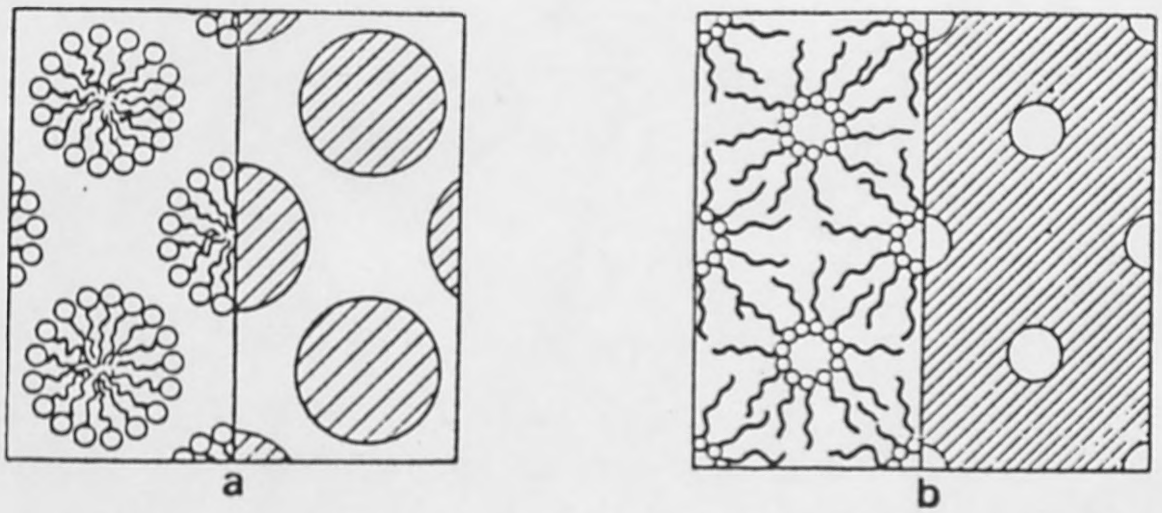


Figure 50 Schematic diagrams of face centred cubic packing of (a) normal micelles and (b) reversed micelles.

There are a few more LC phases known, e.g. 'Nematic phases' ('Nematic' lyotropic phases are formed by material with a low viscosity and they can be 'aligned' by strong magnetic field, e.g. when placed in a magnetic field the micelles alter their position so that the local axes take the same orientation with respect to the fixed direction[203]), surfactant water gels, equivocal phases etc.

2.4.1 Microscopic study of liquid crystal phases of 1,3-dialkyl indole surfactants in water:

The microscopic studies of 1,3-dialkyl indole detergents were carried out using a microscope and hot plate. The samples were prepared using water as a solvent. One or two drops of water (40%) were enough for making the liquid crystal phase. Different temperature ranges were used to identify the liquid crystal phases as shown in Table XXIX.

This study was carried out to investigate whether these detergents form liquid crystal phases or not, and to prove that all of these surfactants can form micelles if these liquid crystals are diluted in water.

2.5 Phase transfer catalysis:

2.5.1 Introduction:

The basic principle of phase transfer catalysis (PTC) is that a reaction is carried out in a system of two phases. Using a phase transfer agent, which in catalytic quantities can bring one reactant from its 'normal' phase into the phase of the second reagent,

TABLE XXIX

Microscopic study of liquid crystal phases of indolic surfactants

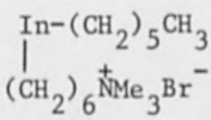
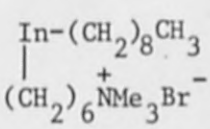
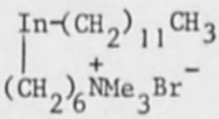
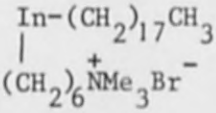
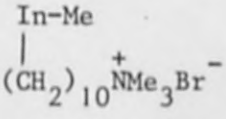
Compound	Liquid Crystal Phase
S.D.S.	Hexagonal 25°C, Lamellar 50°C Intermediate 47°C, Cubic 87°C
Na-octanoate	Cubic 62°C, Lamellar 78°C Hexagonal R.T.
3-phenyl penta decane sulphonate	Hexagonal 40°C Lamellar 48.5°C
2-phenyl penta decane sulphonate	Hexagonal 50°C Lamellar 65°C
	Hexagonal and Lamellar at R.T.
	Hexagonal Lamellar } at R.T.
	Hexagonal and Lamellar at R.T.
	Hexagonal and Lamellar at R.T.
	Hexagonal at R.T. melts at 45°C Lamellar at R.T. melts at 88°C

TABLE XXIX (Continued)

Compound	Liquid Crystal Phase
$\begin{array}{l} In\text{-}(CH_2)_5CH_3 \\ \vert \\ (CH_2)_{10}\overset{+}{N}Me_3Br^- \end{array}$	Hexagonal at R.T. $\longrightarrow$ all Lamellar Lamellar at R.T. at 70°C
$\begin{array}{l} In\text{-}(CH_2)_8CH_3 \\ \vert \\ (CH_2)_{10}\overset{+}{N}Me_3Br^- \end{array}$	Hexagonal and Lamellar at R.T.
$\begin{array}{l} In\text{-}(CH_2)_{17}CH_3 \\ \vert \\ (CH_2)_{10}\overset{+}{N}Me_3Br^- \end{array}$	Hexagonal at 32°C Lamellar at 45°C

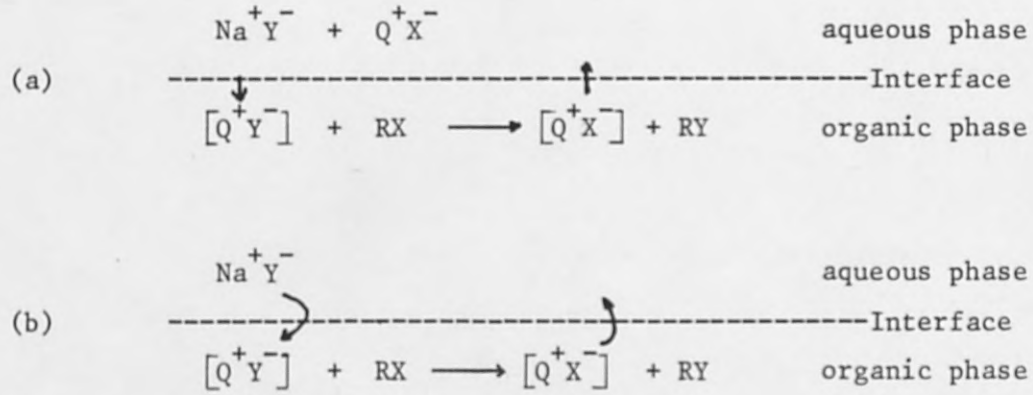
enables a reaction to occur between the two with reasonable speed. The mobile species may be any chemical reagent, but generally the work is concentrated on the transfer of anions from aqueous (or solid inorganic) phases to organic phases. Most of the catalysts in use are either quaternary ammonium[204-207] or phosphonium salts[208] (onium salts) or highly organised organic reagents, particularly crown ethers[209,179] and cryptates.[176]

Phase transfer catalysis often has the following advantages over conventional methods.

Savings can be made on expensive anhydrous aprotic solvents. The reaction time can be shortened and less vigorous reaction conditions are often suitable. In some cases the aqueous potassium hydroxide can be used in place of alkyl metal alkoxides, which makes for simpler work up procedures. Side reactions are also less likely to occur (e.g. C/O-alkylation) and so greater yields are obtained.

The mechanism of PTC in the case of displacement reactions, in particular nucleophilic substitution[210,211] where the transfer of anions from the aqueous (or solid inorganic phases) to the organic phase occurs, is shown in Scheme R.[208]

SCHEME R PTC in nucleophilic substitution
(ion pairs in square brackets)



Q^+X^- = Phase transfer catalyst.

RX = Electrophile (R = alkyl, X = leaving group).

Y^- = Nucleophile.

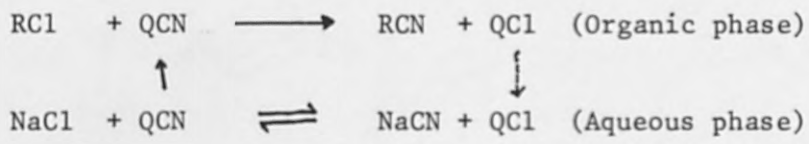
Q^+Y^- = Nucleophile complexed with cation of phase transfer catalyst.

Generally highly lipophilic catalyst cations (Q^+) are used so that Q^+ is not present in the aqueous phase to any appreciable extent. Landini et al.[212] have shown that Q^+ stays in the organic phase and only the anions are exchanged across the interface as shown in Scheme R(b).

In the reaction between aqueous sodium cyanide and 1-chloro octane, the addition of an organic-soluble quaternary ammonium or phosphonium salt catalyses the chloride displacement by the cyanide anion as shown in Scheme S. The function of the quaternary salt (QX) is to transfer the cyanide ion into the organic phase in a form suitable

for it to react with 1-chlorooctane (RCl) and return the displaced chloride ion to the aqueous phase where QCN can be regenerated.[211]

SCHEME S Chloride displacement on 1-chlorooctane by cyanide using PTC. RCl = 1-chlorooctane.



2.5.2 Crown ether as phase transfer catalyst:

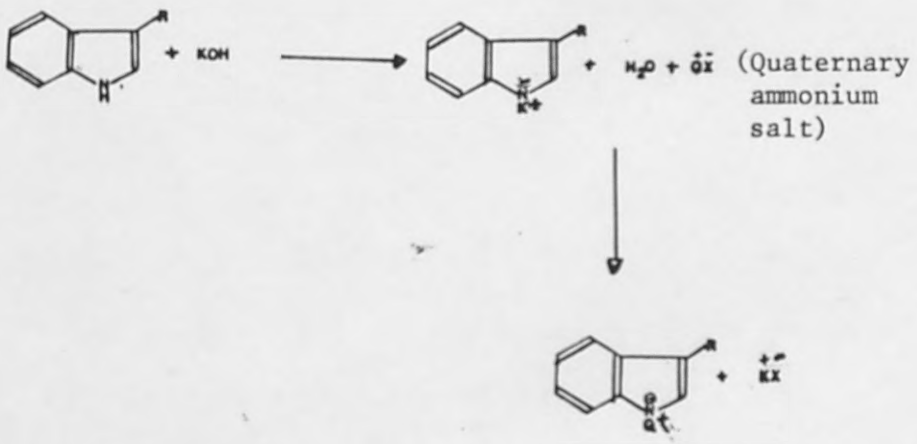
Crown ethers have previously been used as phase transfer catalysts.[179,209] They can form a complex with alkali metals (notably the potassium cation) and transfer the resulting complex salt into the organic phase. Hence the $Q^{(+)}$ need not necessarily be an ammonium or phosphonium salt but can also be an alkali metal ion complexed with a crown ether. For example, 18-crown-6 and potassium hydroxide.

Crown ethers are both expensive and toxic, hence their use in PTC is limited compared to the quaternary ammonium salts. 18-Crown-6 ether has been used as a PTC in many reactions[176,177] and its use in the N-alkylation of indoles has also been reported.[178,179]

2.5.3 The alkylation of different heterocyclic compounds using phase transfer catalysis:

Alkylation of indole or pyrroles is effected by simply stirring a solution containing the alkylating agent, heterocycle and phase transfer catalyst in the presence of concentrated aqueous sodium or potassium hydroxide. When a quaternary ammonium salt is used as a PTC exclusive N-alkylation is usually observed, since the counter ion is a quaternary ammonium ion and therefore is only loosely associated with the heterocyclic pyrrole or indolyl anion as shown in Scheme T.

SCHEME T



The N-alkylation of heterocyclic compounds has been carried out by many authors using the phase transfer catalysis method. For example, Guida and Mathre have found that N-alkylation of heterocyclic compounds bearing an acidic hydrogen atom attached to nitrogen can be accomplished, in diethyl ether, via a phase transfer process where 18-crown-6 is employed as the catalyst and potassium tert-butoxide

is the base. In this manner pyrrole, indole, pyrazole, imidazole, benzimidazole, benzotriazole, carbazole and methyl indole,3-acetate have been successfully alkylated. The procedure is convenient and mild and it generally gives rise to exclusive N-alkylation.[179]

The pyrrollyl and indolyl anions are poor nucleophiles and consequently alkylation can occur at carbon as well as at nitrogen. The amount of alkylation at nitrogen relative to carbon is dependent upon a number of factors. These include the base for the deprotonation of the heterocycle, the solvent and the alkylating agent. Nitrogen alkylation generally predominates when the cation is sodium or potassium. Carbon alkylation usually predominates with harder[215] cations like lithium or magnesium which are tightly bound to nitrogen.[216] The solvent can dramatically influence the rate of nitrogen to carbon alkylation[21,204,217-221] and dipolar aprotic solvents can give rise to predominant N-alkylation of salts derived from pyrrole or indole even when magnesium is the counter ion.[204,217,218] The alkylating agent can also influence the ratio of N to C alkylation. For example, when compared with other alkylating agents allylic or benzylic halides generally afford a greater proportion of carbon alkylated material.[204,217,221,207]

An increasing number of useful procedures for the alkylation of indole have been proposed and a wide variety of base systems have been utilised for the generation of the indolyl anion, e.g. sodium amide in liquid ammonia,[222] sodium hydride in either hexamethyl

phosphoramide[221] or dimethyl sulphoxide[223] and potassium hydroxide in dimethyl sulphoxide.[21] All the above reported methods require strictly anhydrous conditions and the use of strongly ionising solvents. Baraldi and co-workers[205] reported that N-alkylation can also be accomplished by adding the indole to a two phase system consisting of 50% aqueous sodium hydroxide solution and a benzene solution of alkylating agent, containing a catalytic amount of tetrabutyl ammonium hydrogen sulphate. The alkylating agents used included dimethyl sulphate (Me_2SO_4), methyl iodide, diethyl sulphate (Et_2SO_4), ethyl iodide, benzyl bromide and bromopentane. Santaniello and others,[209] have successfully N-alkylated pyrrole and indole in good yields ($\simeq$ 75%) using potassium hydroxide in the presence of 3-5 mol% of crown ether and dry benzene as solvent. Benzyl bromide, benzyl chloride, ethyl iodide and butyl iodide were used as the alkylating agents.

Alkylation of anionic nucleophiles such as potassium acetates, potassium benzyl, allyl, n-butyl and cetyl acetates as well as potassium indole has been achieved in good yield ($<$ 93%) in the presence of aliquat 337 ($Oct_3\overset{+}{M}e\overset{-}{N}Cl$) or tetrabutyl ammonium bromide (NBu_4Br) as the phase transfer catalyst and a small amount of titanium dioxide (TiO_2). Ethyl iodide and n-octyl bromide were used as alkylating agents.[224]

In spite of the many advantages that the phase transfer procedure offers several disadvantages decrease the general applicability of this procedure. For example, when alkyl iodides are used as alkylating agents respectable yields of products are usually

obtained only when a stoichiometric amount of catalyst is employed.[204-206] In addition there are a number of solvents in which the commonly employed quaternary ammonium salts are insoluble.[208] Consequently the phase transfer procedure using these salts as catalysts would be expected to fail when such solvents are used. For example, diethyl ether cannot be effectively utilised as a solvent for the quaternary ammonium salt catalysed phase transfer alkylation of pyrrole.[179]

2.5.4 Results and Discussion:
N-alkylation of aromatic amines and related compounds using polyethylene glycols and other compounds as phase transfer catalysts:

The N-alkylation of aromatic amines, particularly indoles, has been carried out by reacting the amine with an alkyl halide in dimethyl sulphoxide solution in the presence of crushed potassium hydroxide. This method has proved one of the most efficient, in terms of yields, in the N-alkylation of indoles (see 2.1.3). However, a problem often arose at the product isolation and purification stage due to difficulties encountered with the removal of dimethyl sulphoxide. This could be overcome by the use of phase transfer catalysis. However, it was necessary to find out the most suitable phase-transfer catalyst and to investigate the efficiency of the method. Both 18-crown-6 and quaternary ammonium salts were used to catalyse the N-alkylation of some amines using different reaction conditions. Investigations were also carried out to determine whether PEG (1540) and PEG methyl ether (350) function as phase transfer catalysts.

Neither of these polyethylene glycols have previously been used as phase transfer catalysts. The results shown in Table XXX indicate that both PEG (1540) and PEG methyl ether (350) can be used as phase transfer catalysts for N-alkylation reactions using methyl iodide, primary alkyl bromides and benzyl bromides as alkylating agents.

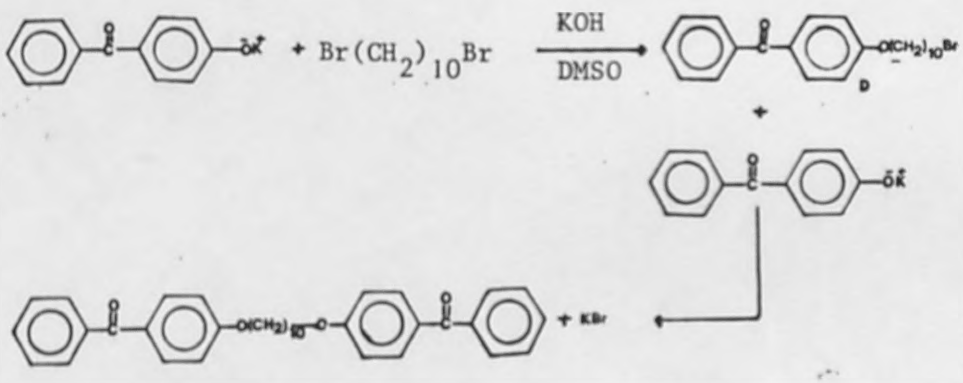
Clearly PEG can complex with alkali ions (notably K^+) and transfer the complex salt into the organic phase with an efficiency comparable to that of 18-crown-6. Additionally PEG has the advantage of being less expensive than 18-crown-6 and non-toxic.

2.5.5 Reaction of p-hydroxy benzophenone with alkyl halides:

o-Alkylation of p-hydroxy benzophenone was carried out using the 18-crown-6 and PEG (1540) as phase transfer catalysts as well as crushed potassium hydroxide in the presence of dimethyl sulphoxide (DMSO). These reactions were carried out to investigate whether the PEG (1540) works as a phase transfer catalyst when oxygen is alkylated rather than nitrogen. A comparison of yields obtained by different methods has also been made. 1-Bromododecane and 1,10-dibromodecane were used as alkylating agents. PEG (1540) worked successfully as phase transfer catalyst in these reactions. Reaction of p-hydroxy benzophenone with 1-bromododecane gave 30% yield (product isolated and purified) when PEG (1540) was used as PTC. 1,10-bis(4-benzophenyloxy)decane (10a) was formed in 4% yield when the p-hydroxy benzophenone was reacted with 1,10-dibromodecane

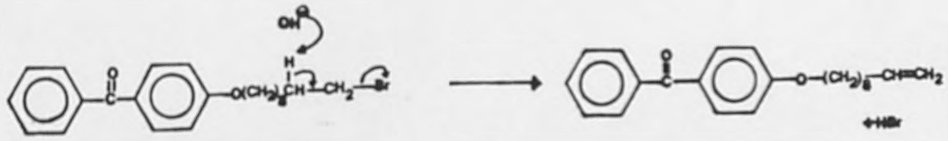
in the presence of PEG as phase transfer catalyst. 18-Crown-6 was not a very successful phase transfer catalyst in these reactions. Yields of 5% and 31% were obtained when p-hydroxy benzophenone was reacted with 1-bromododecane and 1,10-dibromodecane respectively in the presence of 18-crown-6 as phase transfer catalyst. The dimer (10) was also obtained along with the monomer (9) in the reaction of 1,10-dibromodecane and p-hydroxybenzophenone using 18-crown-6 as phase transfer catalyst.

When p-hydroxy benzophenone was reacted with 1-bromododecane in the presence of crushed potassium hydroxide and DMSO the product (8b) was obtained in 66% yield, but when 1,10-dibromodecane reacted with p-hydroxybenzophenone in the presence of KOH/DMSO only 3% monomer (9b) and 10% dimer (10b) were obtained. Most of the monomer (9b) could not be separated from the dimer (10b) and 4-(dec-9-enyloxy)-benzophenone (25). The purification was carried out by silica gel column chromatography. Dimer (10b) was formed even though the benzophenone anions were added to an excess of 1,10-dibromodecane and DMSO solution.



Dimer (10b).

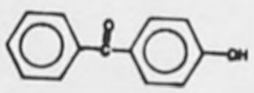
The product (25) was identified by ^{1}H NMR and obtained in a minor amount. This could be due to dehydrohalogenation when excess base was used.



(25)

These products were recrystallised from ethanol and CHN analysis was also carried out. These reactions are represented in Scheme U.

SCHEME U

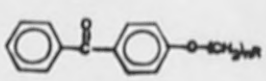


+ $Br(CH_2)_nR$

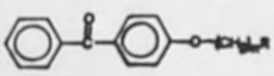
n = 11, R = Me

n = 10, R = Br

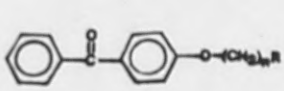
18-crown-6	PEG (1540)	KOH/DMSO
KOH/H_2O	KOH/H_2O	
CCl_4	CCl_4	



n = 11, R = CH_3 (8)
(5% isolated pure).
n = 10, R = Br
(monomer (9) 31%)
(dimer (10) 9%)



n = 11, R = CH_3
(8a) (30% pure)
n = 10, R = Br
(monomer (9a), 36%)
(dimer (10a) 4%)



n = 11, R = Me
(8b) (66% pure)
n = 10, R = Br
(monomer (9b) 31%)
(dimer (10b) 10%)
enyloxy product (25) minor.

TABLE XXX

N-alkylation of amines using different phase transfer catalysts

a = Yield determined by ^{1}H NMR; d = Purity determined by ^{1}H NMR;
b = Yield determined by GLC; e = Purity determined by GLC.
c = No reaction in the absence of catalyst;

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction time hrs	% yield of alkylated products	Purity (%)
Indole	Methyl iodide	18-Crown-6	KOH + H_2O + CCl_4 stirred at R.T.	40 hrs	26[a,b]	98[d]
"	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 stirred at R.T.	20 hrs	40[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	6 hrs	60[a,b,c]	99[d]
"	Benzyl bromide	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	8 hrs	78[a,b,c]	98[d]
"	2-Bromopropane	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	72 hrs	No product[a]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	72 hrs	No product[a]	
"	1-Bromododecane	18-Crown-6	KOH + H_2O + CCl_4 refluxed	50 hrs	64[a,c]	95[d]
"	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	40 hrs	No product[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	72 hrs	45[a]	85[e]
3-Methyl indole	Methyl iodide	18-Crown-6	KOH + H_2O + CCl_4 refluxed	48 hrs	59[a]	
" "	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	20[a]	
" "	1-Bromododecane	18-Crown-6	KOH + H_2O + CCl_4 refluxed	88 hrs	89[a]	
" "	1,10-Dibromodecane	" " "	KOH + H_2O + CCl_4 refluxed	40 hrs	54[a]	

TABLE XXX (Continued)

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction time hrs	% yield of alkylated products	Purity (%)
3-Methyl indole	1,10-Dibromodecane	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	Minute amount[a]	
" " "	11-Bromo-1-undecanol	18-Crown-6	KOH + H_2O + CCl_4 refluxed	15 hrs	56[a]	
Carbazole	Methyl iodide	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	< 5[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	8 hrs	20[a]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	8 hrs	30[b,c]	
"	Benzyl bromide	18-Crown-6	KOH + H_2O + CCl_4 refluxed	48 hrs	< 5[a]	99[e]
"	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	< 5[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	8 hrs	40[a,b]	95[e]
"	2-Bromopropane	18-Crown-6	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a,b]	
"	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	72 hrs	No product[a,b]	
"	1-Bromododecane	18-Crown-6	KOH + H_2O + CCl_4 refluxed	48 hrs	8[a]	95[e]
"	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a]	

TABLE XXX (Continued)

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction Time hrs	% yield of alkylated products	Purity (%)
Carbazole	1-Bromododecane	PEG methyl ether (MW 350)	KOH + dry toluene stirred at R.T.	12 hrs	74[b]	99
"	" "	None	KOH + dry toluene stirred at R.T.	72 hrs	16[b]	98
Imidazole	Methyl iodide	PEG methyl ether (MW 350)	KOH + dry toluene stirred at R.T.	5 hrs	25[a]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	6 hrs	40[a,b]	
"	" "		KOH + H_2O + CCl_4 refluxed	6 hrs	18[a]	
"	Benzyl bromide	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	8 hrs	94[a,b]	
"	2-Bromopropane	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	48 hrs	14[a,c] mixture of two compounds (i) N-isopropyl-imidazole (70%)[b] (ii) 4-isopropyl-imidazole (30%)[b]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	48 hrs	No product[a]	
"	1-Bromododecane	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	48 hrs	26[a,c] isolated	100[d]
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 Stirred at R.T.	48 hrs	74[a,b,c]	55[d]
Diphenylamine	Methyl iodide	18-Crown-6	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a,c]	

TABLE XXX (Continued)

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction Time hrs	% yield of alkylated products	Purity (%)
Diphenylamine	Methyl iodide	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	24 hrs	50[a,b]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	24 hrs	52[a,b,c]	
"	Benzyl bromide	18-Crown-6	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a,c]	
"	" "	PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	48 hrs	58[a,b]	95[e]
"	2-Bromopropane	PEG methyl ether (MW 350)/PEG (MW 1540)/18-Crown-6	KOH + H_2O + CCl_4 refluxed/ KOH + dry toluene stirred at R.T.	24/48 hrs respectively	No product[a,b]	
"	1-Bromododecane	18-Crown-6/ PEG (MW 1540)	KOH + H_2O + CCl_4 refluxed	48 hrs	No product[a]	
"	" "	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	48 hrs	37[b,c]	
N-Methyl aniline	Methyl iodide	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	8 hrs	40[a,b]	
" " "	" "	No catalyst	KOH + H_2O + CCl_4 refluxed	72 hrs	10[b]	
" " "	Benzyl bromide	PEG methyl ether (MW 350)	KOH + H_2O + CCl_4 refluxed	16 hrs	70[a,c]	

TABLE XXX (Continued)

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction Time hrs	% yield of alkylated products	Purity (%)
N-Methyl aniline	2-Bromopropane	PEG methyl ether (MW 350)	$KOH + H_2O + CCl_4$ refluxed/ KOH + dry toluene stirred at R.T.	48 hrs	No product[a,b]	
" " "	1-Bromododecane	18-Crown-6	$KOH + H_2O + CCl_4$ refluxed	88 hrs	81[a,b,c]	90[d]
" " "	" "	PEG (MW 1540)	$KOH + H_2O + CCl_4$ refluxed	90 hrs	86[a]	90[d,e]
" " "	" "	PEG methyl ether (MW 350)	$KOH + H_2O + CCl_4$ refluxed	48 hrs	70[b]	86[d,e]
" " "	" "	No catalyst	$KOH + H_2O + CCl_4$ refluxed	72 hrs	18[a]	
p-Hydroxybenzo-phenone	1-Bromododecane	18-Crown-6	$KOH + H_2O + CCl_4$ refluxed	36 hrs	23[a] (isolated) recrystallised yield (5%) no. (8) (100% pure)	
p-Hydroxybenzo phenone	" "	PEG (MW 1540)	$KOH + H_2O + CCl_4$ refluxed	70 hrs	43[a] (isolated) recrystallised yield, no. (8a) (30%), CHN 100%.	
p-Hydroxybenzo-phenone	1,10-Dibromodecane	18-Crown-6	$KOH + H_2O + CCl_4$ refluxed	70 hrs	(i) 4-(10-Bromodecyl-oxy) benzophenone (31%)[a] (9)[c] (ii) 1,10-bis (4-benzo-phenonyloxy)decane (9%)[a] Isolated and analytically pure products (10)	
p-Hydroxybenzo-phenone	" " "	PEG (MW 1540)	$KOH + H_2O + CCl_4$ refluxed	70 hrs	(i) 4-(10-Bromodecyl-oxy)benzophenone (36%)[a] (9a)[c]. (ii) 1,10-bis(4-benzophe-nonyloxy)decane (4%)[a] (10a). Both products isolated and analytically purified.	

2.5.6 The application of ultrasound to the N-alkylation of amines using phase transfer catalysis:

The application of ultrasound to organic reactions is new, and its uses are steadily growing.[225-231] Examples include the liberation of halogen atoms from aliphatic and aromatic halides by ultrasonic waves,[225] promotion of the debromination of α-bromoketones by ultrasonically dispersed mercury,[226] formation of grignard reagents[227] and coupling of aryl and alkyl chlorosilanes using lithium and sonic waves to form disilanes was also reported.[228] The use of ultrasound was also found to accelerate the catalysis of two-phase ester saponification (basic hydrolysis) to such an extent that reactions requiring 90 minutes of reflux could be completed after approximately 10 minutes of sonication.[229] Similar types of acceleration in the N-alkylation reactions of amines was found by the application of ultrasound techniques.[230] Ultrasound was found to change the reaction course completely from a Friedel-Crafts reaction to nucleophilic substitution. For example, benzyl bromide treated with potassium cyanide and alumina in toluene, under mechanical agitation at 50°C, gives only a mixture of o- and p-benzyl toluenes. In contrast, when the above reaction mixture was irradiated by ultrasound the substitution took place to afford benzyl cyanide.[231]

In all these heterogeneous reactions a factor of key importance is keeping the surface of the catalysing metal clean. The known ability of ultrasound to clean the surfaces of metals immersed in

suitable fluids is attributed to the ultrasound causing the fluids to cavitate and therefore causing very efficient mixing.

We have applied the ultrasound technique to a phase transfer catalysis system. The amines can be N-alkylated under phase transfer conditions[232] which employ a solid/liquid reaction mixture as shown in Table XXX. Many of these reactions take place at room temperature but, if high yields are to be obtained, long reaction times are required. When ultrasound is applied to these reactions high yields of products have been obtained using reasonable reaction times. The results are shown in the Table XXXI. For these, the reactions were monitored by G.L.C. in order to determine the optimal conditions. Ultrasound is known to cause rapid agitation, so to ensure that the reactions are truly examples of phase transfer catalysed processes, they were repeated in the absence of a catalyst. Under these conditions, no reaction occured. This showed that the application of ultrasound accelerated the phase transfer reactions.

During the process of sonication the temperature of the reaction gradually increased over a period of an hour to 50°C and consequently some of the observed acceleration may, in part, be due to the effect of temperature. However, temperatures far in excess of 50°C would be required to cause the observed degree of acceleration, as shown in Table XXX.

TABLE XXXI

Application of ultrasound to the N-alkylation of amines using phase transfer catalysis

KOH + dry toluene + N_2 stirred at R.T. = T.

a = ^{1}H NMR; d = Purity determined by ^{1}H NMR;

b = GLC/MS; e = Purity determined by GLC.

c = No reaction observed in absence of catalyst.

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction Time hrs	% yield of alkylated products	Purity (%)
Indole	Methyl iodide	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at 20°C (T)	5 hrs	60[b,c]	
"	" "	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 ultrasound	0.5 hrs	65[b]	
"	Benzyl bromide	PEG methyl ether (MW 350)	KOH + dry toluene + N_2 stirred at R.T.	8 hrs	80[a,b,c]	
"	" "	PEG methyl ether (MW 350)	T and ultrasound	2 hrs	95[b,c]	
"	1-Bromododecane	PEG methyl ether (MW 350)	T stirred at R.T.	72 hrs	48[a,c,b]	80[d]
"	" "	PEG methyl ether (MW 350)	T ultrasound	1.3 hrs	60[b,c]	
"	" "	Tetrahexyl ammonium chloride	T ultrasound	1 hrs	92[b,c]	
"	" "	Tetrabutyl ammonium nitrate	T stirred at R.T.	3 hrs	19[b,c]	
"	" "	Tetrabutyl ammonium nitrate	T ultrasound	1.3 hrs	90[b,c]	
"	" "	Tetrabutyl ammonium iodide	T ultrasound	0.8 hrs	73[b,c]	
Carbazole	Benzyl bromide	PEG methyl ether	T stirred at R.T.	8 hrs	50[b,c]	99[e]
"	" "	None	T stirred at R.T.	48 hrs	16[a,b]	
"	" "	PEG methyl ether	T ultrasound	1 hrs	96[b]	
"	" "	None	T ultrasound	1 hrs	20[b]	
"	1-Bromododecane	Tetrabutyl ammonium iodide	T ultrasound	3 hrs	84[b,c]	

TABLE XXXI (Continued)

Compound	Alkylating Agent	Catalyst	Reaction conditions	Reaction Time hr	% yield of alkylated product	Purity (%)
Imidazole	Benzyl bromide	PEG methyl ether (MW 350)	T stirred at R.T.	8 hrs	95[b]	
"	" "	No catalyst	T stirred at R.T.	8 hrs	15[b]	
"	" "	PEG methyl ether (MW 350)	T ultrasound	0.6 hrs	97[b]	
Diphenylamine	1-Bromododecane	Tetrabutyl ammonium iodide	T ultrasound	0.8 hrs	58[b,c]	
"	Benzyl bromide	PEG methyl ether (MW 350)	T heated under reflux	48 hrs	70[a,b,c]	90[e]
"	" "	PEG methyl ether (MW 350)	T ultrasound	1 hrs	98[b,c]	
N-Methyl aniline	Methyl iodide	PEG methyl ether (MW 350)	T stirred at R.T.	8 hrs	52[b]	
" " "	" "	No catalyst	T stirred at R.T.	72 hrs	15[b]	
" " "	" "	PEG methyl ether (MW 350)	T ultrasound	1 hrs	89[b]	
" " "	Benzyl bromide	PEG methyl ether (MW 350)	T stirred at R.T.	16 hrs	80[b,c]	
" " "	" "	PEG methyl ether (MW 350)	T ultrasound	1 hrs	95[b]	
" " "	1-Bromododecane	PEG methyl ether (MW 350)	T stirred at R.T.	48 hrs	74[a,b,c]	
" " "	" "	PEG methyl ether (MW 350)	T ultrasound	1.17 hrs	80[b]	

CHAPTER THREE
EXPERIMENTAL

3.1 Instrumentation:

The experimental work presented in this thesis was carried out in the Department of Chemistry, The City University, London (TCU), between January 1980 and December 1982.

3.1.1 IR spectra:

The IR spectra were recorded either as nujol mulls or as neat films using a Perkin-Elmer 157G grating spectrophotometer. All ν max values are quoted in cm^{-1} units.

3.1.2 U/V-visible spectra:

Perkin-Elmer 402 U/V-visible spectrophotometer was used when the spectra were recorded on chart paper. On occasions where solutions of known optical density at a specific wavelength were required, but their absorption spectra were not needed, the solutions were prepared using a Cecil Instruments CE 272 Linear Readout Ultraviolet Spectrophotometer.

3.1.3 ^{1}H NMR spectra:

The ^{1}H NMR spectra were measured using a Jeol JNM-MH 100 NMR spectrometer operated at 100 MHz, utilising an external lock. Tetramethyl silane (TMS) was used as the internal standard and deuterochloroform ($CDCl_3$) used as the solvent. All spectral chemical shifts are quoted in δ units (PPM), together with integrated signal intensities. The following abbreviations are used in spectral interpretations:

s - singlet, d - doublet, t - triplet, q - quartet,
m - multiplet, br - broad.

Coupling constants are recorded where necessary in Hz.

3.1.4 Accurate mass spectrometry (AMS):

Measurements were carried out by Mr. C. Whitehead, using a Kratos MS 30 Double Beam Double Focussing mass spectrometer, using Electron Impact Ionisation. The spectrometer was linked to a data system (DS 50). All measurements were taken at 70 eV. Where possible the mass peak (M^+) and the base peak (100%) are given.

3.1.5 Elemental analysis:

C,H,N, Analyses are quoted in weight percentages. Analyses were performed by Mr. P. Hemming using a Carlo Erba Model 1106 Elemental Analyser.

3.1.6 Melting points/Boiling points:

Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected. All compounds prepared as oils, were distilled under reduced pressure using a Büchi Kugel oven. Boiling points are not corrected.

3.1.7 Solvents:

Benzene and diethyl ether were dried over sodium wire.

3.1.8 G.L.C.

The instrument used for the GLC analysis was a Perkin Elmer Sigma 3 model. I would like to thank Mr. A. Safdar for carrying out the analysis on the compounds obtained using the phase transfer catalysis method (see Table XXX and XXXI).

3.1.9. H.P.L.C.

The M6000A model (Waters Associates Inc.) was used for analysis of some of the indolic compounds. The u.v. detector used was a CE2012, Cecil Instruments.

3.1.10 Sources of materials used:

The following chemicals were used as supplied unless otherwise stated.

Aldrich Chemical Co. Ltd: Indole (Gold label), 3-Methyl indole, Oxalyl chloride, Methyl iodide, 1-Bromododecane, 1,10-Dibromo decane, 11-Bromo,1-undecanol, p-Hydroxy benzophenone, Diphenyl amine, Benzyl bromide, 2-Bromopropane, Carbazole, Imidazole, N-Methyl aniline, Lithium aluminium hydride, Bromoethane, Oxalyl chloride, N,N-Dimethyl acetamide, Hexanoic acid, Nonoic acid, Lauric acid, Stearic acid, o-chlorophenyl acetic acid, Pyridine, Chromoium trioxide, Citronellol, n-Bromopropane, 11-Bromoundecanol, 11-Bromoundecanoic acid, Trimethyl ammonium sulphur trioxide complex, 1,2-Dichloroethane, 3-Bromopropyl alcohol, Sodium iodide, Sodium thiosulphate, o-Phenylene diamine, Haptoic acid, n-Hexanol, Methane sulphonyl chloride, Polyethylene glycol methyl ether (300), Cetyltrimethyl ammonium bromide, 18-Crown-6-ether.

B.D.H. Chemicals Ltd: Dimethyl sulphoxide, Magnesium sulphate, Phosphorous oxychloride, Polyethylene glycol (1540), Sodium hydroxide, Potassium hydroxide, Sodium acetate, Sodium nitrite, Sodium bicarbonate, Chloroform.

FLUKA AG, Fluorochem Ltd: Sodium dodecyl sulphate, Dimethyl amine (anhydrous), Trimethyl amine (anhydrous).

Fisons Ltd: Triethylene glycol, Pyridine, Diethyl ether, Hydrochloric acid, Benzene, Acetone.

May and Baker Ltd: Dichloromethane, Carbon tetrachloride, Petroleum ether (60-80^{o}C), Ethyl acetate.

James Burrough Ltd: Absolute Ethanol.

3.2 Experimental:

3.2.1 Preparation of N-methyl indole (1):

To indole (0.5 g, 0.0042 mol), stirred in an aqueous potassium hydroxide solution (3-6 N, 2.4 g, in 10 ml water), iodomethane (0.65 g, 1.1 eq. molar) in carbon tetrachloride (10 ml) was added. To this, 18-crown-6 ether (0.11 g, 0.1 eq. molar) was then added and the reaction mixture left stirring for 40 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Distillation of the crude product gave a pale yellow oil (b.p. 110°C at 2.15 mm, 0.17 g, Lit. b.p. pure N-methylindole, 133°C at 26 mm).[165] After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the distillate was a mixture of N-methylindole (1) (26%) and indole (74%).

3.2.2 Preparation of 1,3-dimethyl indole (2):

3-methyl indole (0.65 g, 0.005 mol) was stirred in an aqueous potassium hydroxide solution (6 N, 5 ml). After addition of methyl iodide (1.42 g, 0.01 mol) in carbon tetrachloride (5 ml), 18-crown-6-ether (0.132 g, 0.1 eq. mol) was also added. The reaction mixture was refluxed, with stirring, for 48 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. Distillation of the red-brown liquid gave 1,3-dimethyl indole (2) (b.p. 95°C at 2.75 mm, lit. b.p. 119-20°C, at 7 mm, 0.44 g, 59%).[233] NMR ($CDCl_3$) δ 2.32 (s, 3H), 3.70 (s, 3H), 6.71 (m, 1H, Indole H-2), 6.8-7.32 (m,3H), 7.44-7.64 (m, 1H, Indole H-4).

3.2.3 Preparation of 1,3-dimethyl indole (2a) using PEG (1540) as PTC:

To a solution of aqueous potassium hydroxide (6 N, 5 ml), 3-methyl indole (0.65 g, 0.005 mol) and polyethylene glycol 1540 (0.77 g, 0.1 eq. molar) were added. The mixture was stirred while methyl iodide (1.42 g, 0.01 M) in carbon tetrachloride (5 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 48 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. Distillation of the red brown liquid gave 1,3-dimethyl indole (2a) in 20% yield (b.p. 90-100°C/3.0 mm, Lit. b.p. 119-20°C/7 mm).[233]

NMR ($CDCl_3$) δ 2.32 (s, 3H), 3.68 (s, 3H), 6.74 (br. s, 1H, Indole H-2), 6.9-7.3 (m, 3H), 7.4-7.6 (m, 1H, Indole H-4).

3.2.4 Preparation of N-methyl indole (1a) using PEG 1540 as PTC:

To a solution of aqueous potassium hydroxide (4.2 N, 5 ml), indole (0.5 g, 0.0042 mol) and polyethylene glycol 1540 (0.64 g, 0.1 eq. molar) were added. The mixture was stirred while methyl iodide (1.2 g, 2 eq. molar) in carbon tetrachloride (5 ml) was introduced. The reaction mixture was stirred overnight (20 hrs). The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness.

After analysis of this material by ^1H NMR spectroscopy and on consideration of the respective integrals it was apparent that the final product was a mixture of N-methyl indole (1a) (40%), indole (60%) and polyethylene glycol 1540 as an additional contaminant.

3.2.5 Preparation of N-dodecyl indole (3) using 18-crown-6-ether as PTC:

To a solution of aqueous potassium hydroxide (6N, 10 ml), indole (1.17 g, 0.01 mol) with 18-crown-6-ether (0.264 g, 0.1 eq. molar) was added. The mixture was stirred while 1-bromododecane (5.96 g, 0.024 mol) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 50 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the crude product isolated was a mixture of N-dodecyl indole (3) (64%), indole (36%) and 1-bromododecane as an additional contaminant.

3.2.6 Attempted preparation of N-dodecyl indole (3a) using PEG 1540 as PTC:

To a solution of aqueous potassium hydroxide (6 N, 10 ml), indole (1.17 g, 0.01 mol) and polyethylene glycol 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromododecane (2.98 g, 1.2 eq. molar) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 40 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Analysis of this material by ^{1}H NMR spectroscopy showed only a very minute amount of N-dodecyl indole to be present. The major contents were shown to be indole, 1-bromododecane and PEG 1540.

3.2.7 Preparation of 1-(10-bromodecyl)-3-methyl indole (4) using 18-crown-6- ether as PTC:

To a solution of aqueous potassium hydroxide (6 N, 10 ml), 3-methyl indole (1.31 g, 0.01 mol) and 18-crown-6- ether (0.264 g, 0.1 eq. molar) were added. The mixture was stirred while 1,10-dibromodecane in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 40 hrs. After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the product isolated was a mixture of 1-(10-bromodecyl)-3-methyl indole (4) (83%) and 3-methyl indole (17%) with 1,10-dibromodecane present as an additional contaminant. Distillation of the crude product gave pure 1-(10-bromodecyl)-3-methyl indole (4) (b.p. 120-135°C at approx. 0.001 mm, 1.9 g, 54% yield).

NMR ($CDCl_3$) δ 1.2-2.00 (m, 16H), 2.30 (s, 3H), 3.32 (t, J = 6.5 Hz, 2H, $Br-CH_2$), 4.00 (t, J = 7.0 Hz, 2H, $N-CH_2$), 6.80 (m, 1H, Indole H-2), 7.0-7.24 (m, 3H), 7.5-7.64 (m, 1H, Indole H-4). Anal. calcd. for $C_{19}H_{28}NBr$: C, 65.14; H, 8.06; N, 4.00. Found: C, 64.99; H, 8.27; N, 4.27.

3.2.8 Attempted preparation of 1-(10-bromodecyl)-3-methyl indole (4a) using PEG 1540 as PTC:

To a solution of aqueous potassium hydroxide (6 N, 10 ml), 3-methyl indole (1.31 g, 0.01 mol) and polyethylene glycol 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1,10-dibromodecane (6.0 g, 2 eq. molar) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with

stirring, for 48 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. Analysis of this material by ^{1}H NMR spectroscopy showed only a very minute amount 1-(10-bromodecyl)-3-methyl indole to be present (< 5%). The major constituents were shown to be 3-methyl indole, 1,10-dibromodecane and PEG 1540.

3.2.9 Preparation of 1-dodecyl-3-methyl indole (5) using 18-crown-6-ether as PTC:

To a solution of aqueous potassium hydroxide (6 N, 10 ml), 3-methyl indole (1.31 g, 0.01 mol) and 18-crown-6-ether (0.264 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromododecane (4.98 g, 2 eq. molar) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 88 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the product isolated was a mixture of 1-dodecyl-3-methyl indole (5) (89%) and 3-methyl indole (11%) with 1-bromododecane as an additional contaminant.

3.2.10 Preparation of N-methyl-N-dodecyl aniline (6) using 18-crown-6-ether as PTC:

To an aqueous solution of potassium hydroxide (6 N, 10 ml), N-methyl aniline (1.07 g, 0.01 mol) and 18-crown-6 ether (0.264 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromododecane (4.98 g, 2 eq. molar) in carbon tetrachloride (10 ml)

was introduced. The reaction mixture was heated under reflux, with stirring, for 88 hrs.

The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. Hydrochloric acid (2 M, 10 ml) was added to the crude product and then extracted with diethyl ether (3 x 20 ml). The aqueous (acidic) layer was separated and treated with aqueous potassium hydroxide solution to pH 7. This solution was then extracted with diethyl ether (3 x 25 ml). The diethyl ether extracts were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a brown oil (0.24 g, 9% yield). After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the product isolated was a mixture of N-methyl, N-dodecyl aniline (6) (81%) and 1-bromododecane (19%). ^{1}H NMR see Table XXXII.

3.2.11 Preparation of N-methyl,N-dodecyl aniline (6a) using PEG as PTC:

To an aqueous solution of potassium hydroxide (6N, 10 ml), N-methyl aniline (1.07 g, 0.01 mol) and polyethylene glycol 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromo-dodecane (4.98 g, 2 eq. molar) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 90 hrs.

The carbon tetrachloride layer could not be separated since the reaction mixture became an emulsion. However, the solution was evaporated to dryness leaving a solid oil mixture. This mixture was treated with excess hydrochloric acid (2 M) and extracted with diethyl ether (20 ml x 3). The acidic layer was separated and treated with potassium hydroxide solution to pH 7. This solution was then extracted with dichloromethane (25 ml x 3). The dichloromethane extracts were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a brown oil. After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the product isolated was a mixture of N-methyl,N-dodecyl aniline (6a) (86%) and 1-bromododecane (14%) with PEG as an additional contaminant. ^{1}H NMR see Table XXXII.

3.2.12 Preparation of 1-(11-hydroxyundecyl)-3-methyl indole (7):

To an aqueous solution of potassium hydroxide (6 N, 10 ml), 3-methyl indole (1.31 g, 0.01 mol) and 18-crown-6-ether (0.264 g, 0.1 eq. molar) were added. The mixture was stirred while 11-bromo-1-undecanol in carbon tetrachloride (10 ml) was introduced. The mixture was heated under reflux, with stirring, overnight (15 hrs).

The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. Distillation of the crude product gave a pale yellow oil (b.p. 150-170°C/0.1 mm, 1.46 g). After analysis of this material by NMR spectroscopy and on consideration

of the respective integrals it was apparent that the distillate was a mixture of 1-(11-hydroxyundecyl)-3-methyl indole (7) (56%) and 11-bromo-1-undecanol (44%). ^{1}H NMR see Table XXXII.

3.2.13 Preparation of 4-(dodecyloxy)-benzophenone (8) using 18-crown-6-ether as PTC:

To an aqueous solution of potassium hydroxide (6 N, 10 ml), p-hydroxy benzophenone (1.98 g, 0.01 mol) and 18-crown-6-ether (0.264 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromodecane (3.23 g, 0.013 mol) in carbon tetrachloride (10 ml) was introduced and then heated under reflux for 36 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. After analysis of the crude product by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the isolated solid was a mixture of 4-(dodecyloxy)benzophenone (8) (23%) and 1-bromododecane (77%). This material was recrystallised from ethanol to give the desired product as colourless crystals. (m.p. 55-58^{o}C, 0.19 g, 5% yield). ^{1}H NMR, see Table XXXII.

3.2.14 Preparation of 4-(dodecyloxy)benzophenone (8a) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (6 N, 10 ml), p-hydroxy benzophenone (1.98, 0.01 mol) and polyethylene glycol 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromododecane (3.23 g, 1.3 eq. molar) in carbon tetrachloride was introduced. The mixture was heated under reflux and stirred for

70 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. After analysis of this crude product by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the isolated solid was a mixture of 4-(dodecyloxy)-benzophenone (8a) (43%) and 1-bromododecane (54%). This material was recrystallised from ethanol to give colourless crystals of the desired product (m.p. 61-62°C, 1.11 g, 30% yield). For NMR see Table XXXII.

Anal. calcd. for $C_{25}H_{34}O_2$, C, 81.92; H, 9.35. Found C, 81.77; H, 9.53.

3.2.15 Preparation of 4-(10-bromodecyloxy)benzophenone (9) and 1,10-bis-(4-benzophenonyloxy)-decane using 18-crown-6-ether as PTC:

To an aqueous solution of potassium hydroxide (6 N, 10 ml), p-hydroxy benzophenone (1.98 g, 0.01 mol) and 18-crown-6-ether (0.264 g, 0.1 eq. molar) were added. The mixture was stirred while 1,10-dibromodecane (3.9 g, 1.3 eq. molar) in carbon tetrachloride (10 ml) was introduced, and heated under reflux for 70 hrs. The solution was then cooled to room temperature. A solid material precipitated out from the solution which was filtered and washed with carbon tetrachloride and water. Recrystallisation of this product from benzene gave 1,10-bis-(4-benzophenonyloxy)-decane (10). (m.p. 131°C, 0.5 g, 9% yield). NMR ($CDCl_3$) δ 1.28-2.0 (m, 16H), 4.08 (t, J = 6 Hz, 4H, $O-CH_2$), 7.04 (d, J = 8 Hz, 4H), 7.6-7.8 (m, 6H), 7.88-8.08 (m, 8H).

After filtration of the precipitated solid the carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. This gave a solid material which was distilled (b.p. 227°C/0.85 mm) and then recrystallised from ethanol to give 4-(10-bromodecyl-oxy)-benzophenone (9) as colourless crystals. (m.p. 63.5-64°C, 1.28 g, 31% yield). NMR ($CDCl_3$), δ 1.2-2.0 (m, 16H), 3.32 (t, J = 6Hz, 2H, $Br-CH_2$), 3.96 (t, J = 7 Hz, 2H, $O-CH_2$), 6.88 (d, J = 8 Hz, 2H), 7.40-7.60 (m, 3H), 7.66-7.90 (m, 4H).

3.2.16 Preparation of 4-(10-bromodecyl-oxy)benzophenone (9a) and 1,10-bis-(4-benzophenonyl-oxy)-decane (10a) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (6 N, 10 ml), p-hydroxybenzophenone (1.98 g, 0.01 mol) and polyethylene glycol 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1,10-bromododecane in carbon tetrachloride (10 ml) was introduced, and heated under reflux for 70 hrs. The solution was then cooled at room temperature. A solid material precipitated out from the solution which formed an emulsion with CCl_4, water and PEG. The carbon tetrachloride layer (emulsion) was separated and evaporated to dryness. Semi-solid material was obtained which was washed with carbon tetrachloride. This washed solid was recrystallised from benzene to give 1,10-bis-(4-benzophenonyl-oxy)-decane (10a). (m.p. 134-135°C, 0.2 g, 4% yield). NMR ($CDCl_3$), δ 1.28-1.98 (m, 16H), 4.08 (t, J = 6 Hz, 2H, OCH_2), 7.04 (d, J = 9.0 Hz, 4H), 7.6-7.8 (m, 6H), 7.88-8.9 (m, 8H). Anal. calcd. for $C_{36}H_{38}O_4$: C, 80.86; H, 7.16. Found: C, 80.69; H, 7.13.

The carbon tetrachloride soluble material was then distilled (b.p. > 227°C at 0.8 mm, 1.49 g, 36% yield) and then recrystallised from ethanol to give 4-(10-bromodecyl-oxy)benzophenone (9a) as a colourless crystalline material (m.p. 58-60°C, 0.7 g). NMR ($CDCl_3$) δ 1.2-2.0 (m, 16H), 3.30 (t, J = 7 Hz, 2H, Br-CH_2), 3.96 (t, J = 6 HZ, 2H, O-CH_2), 6.84 (d, J = 8 Hz, 2H), 7.4-7.60 (m, 3H), 7.64-7.88 (m, 4H). Anal. calcd. for $C_{23}H_{29}O_2Br$: C, 66.19; H, 7.00. Found: C, 66.46; H, 7.04.

3.2.17 Attempted synthesis of 1-(10-bromodecyl)3-nonyl indole (11) using PEG as PTC:

To an aqueous solution of potassium hydroxide (6 N, 10 ml), 3-nonyl-indole (0.8 g, 0.0033 mol) and polyethylene glycol 1540 (0.508 g, 0.1 eq. molar) were added. The mixture was stirred while 1,10-di-bromodecane (1.98 g, 2 eq. molar) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 49 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Analysis of this material by ^1H NMR spectroscopy indicated none of the desired product to be present. The major constituents were shown to be 3-nonyl indole, 1,10-dibromodecane and PEG 1540.

3.2.18 Attempted preparation of N-methyl-diphenyl amine (12) using PEG as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), diphenyl-amine (1.6 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while methyl iodide (2.84 g, 0.02 mol)

in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux with stirring for 48 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Analysis of the crude product by ^{1}H NMR spectroscopy showed proton resonance for unreacted diphenyl amine and PEG (1540) but not for the desired product N-methyl-diphenyl amine.

3.2.19 Attempted preparation of N-benzyl-diphenyl amine (13) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), diphenyl amine (1.69 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were introduced. The mixture was stirred while benzyl bromide (1.8 g, 0.0105 mol) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 48 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Analysis of the crude material by ^{1}H NMR spectroscopy showed proton resonance for unreacted diphenyl amine, benzyl bromide and PEG 1540 but not for the desired product N-benzyl diphenyl amine (13).

3.2.20 Attempted synthesis of N-isopropyl diphenyl amine (14) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), diphenyl-amine (1.69 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 2-bromopropane (1.25 g, > 0.01 mol) in carbon tetrachloride (10 ml) was introduced. The reaction

mixture was heated under reflux, with stirring, for 48 hrs. The carbon tetrachloride layer was then separated from the aqueous layer and evaporated to dryness. Analysis of this material by ^{1}H NMR spectroscopy showed the presence of unreacted diphenyl amine and a minor amount of PEG 1540 but no evidence for the desired product.

3.2.21 Attempted synthesis of N-dodecyl-diphenyl amine (15) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), diphenyl-amine (1.69 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromododecane (2.5 g, > 0.01 mol) in carbon tetrachloride (10 ml) was introduced, and then heated under reflux for 48 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Analysis of the material by ^{1}H NMR spectroscopy showed the presence of unreacted diphenyl amine, PEG 1540 and 1-bromododecane. No evidence for the desired product, N-dodecyl-diphenyl amine (15), was found.

3.2.22 Preparation of N-methyl carbazole (16) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), carbazole (1.67 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while methyl iodide (2.84 g, 0.02 mol) in carbon tetrachloride (10 ml) was introduced. This was then heated under reflux, with stirring, for 48 hrs. The unreacted carbazole was filtered off and the carbon tetrachloride layer separated from the

aqueous layer. Evaporation to dryness of the organic layer gave a minor amount of N-methyl carbazole (16) (< 5%). NMR ($CDCl_3$): δ 3.8 (s, 3H, N-Me), 7.16-7.30 (m, 2H), 7.3-7.4 (m, 2H), 7.4-7.64 (m, 2H), 8.08 (br. d, J ≃ 8 Hz, 2H).

3.2.23 Preparation of N-benzyl carbazole (17) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), carbazole (1.67 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while benzyl bromide (1.8 g, > 0.01 mol) in carbon tetrachloride (10 ml) was introduced. This was then heated under reflux, with stirring, for 48 hrs. The unreacted carbazole was filtered off and the carbon tetrachloride layer separated from the aqueous layer. Evaporation to dryness of the organic layer gave a minor amount of the crude product (< 0.1 g). After analysis of this crude mixture by ^1H NMR spectroscopy and on consideration of the respective integrals it was apparent that the isolated material was a mixture of N-benzyl carbazole (17) (45%), benzyl bromide (26%) and carbazole (29%). ^1H NMR data - see Table XXXII.

3.2.24 Attempted preparation of N-isopropyl carbazole (18) using PEG 1540 as PTC:

To an aqueous solution of potassium hydroxide (4 N, 10 ml), carbazole (1.67 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 2-bromo propane (1.25 g, > 0.01 mol) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 48 hrs. The unreacted

carbazole was filtered off and the carbon tetrachloride layer separated from the aqueous layer and evaporated to dryness. Analysis of the crude material by ^{1}H NMR spectroscopy showed unreacted carbazole and no evidence for the desired product.

3.2.25 Attempted preparation of N-dodecyl carbazole (19) using PEG 1540 as PTC:

To potassium hydroxide (4 N, 10 ml), carbazole (1.67 g, 0.01 mol) and PEG 1540 (1.54 g, 0.1 eq. molar) were added. The mixture was stirred while 1-bromododecane (2.5 g, 0.01 mol) in carbon tetrachloride (10 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 48 hrs. The unreacted carbazole was filtered off and the carbon tetrachloride layer separated from the aqueous layer and evaporated to dryness to give a minor amount of crude product (0.1 g). After analysis of the crude mixture by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the isolated material was a mixture of the desired product, N-dodecyl carbazole (19) (8%) and 1-bromo-dodecane (89%). For ^{1}H NMR data, see Table XXXII.

3.2.26 Preparation of N-methyl imidazole (20) using PEG methyl ether 350 as PTC:

To an aqueous solution of potassium hydroxide (8 N, 10 ml), imidazole (1.36 g, 0.02 mol) and PEG methyl ether 350 (0.7 g, 0.002 M) were added. The mixture was stirred while methyl iodide (5.76 g, 0.04 mol) in carbon tetrachloride (20 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 5 hrs. The aqueous

layer was separated from the carbon tetrachloride layer and extracted with dichloromethane (5 x 5 ml). The carbon tetrachloride layer and dichloromethane extracts were combined and evaporated to dryness. The crude product was distilled to give a colourless oil (b.p. 40-50°C/approx. 0.5-1.0 mm, Lit. b.p. 94-95°C/14-15 mm;[234] 0.4 g, 25% yield). NMR ($CDCl_3$) δ 3.6 (s, 3H, N-Me), 6.7 (d, J = 1 Hz, 1H), 6.82 (d, J = 1 Hz, 1H), 7.2 (s, 1H).

3.2.27 Preparation of N-benzyl imidazole (21) using PEG methyl ether-350 as PTC:

To an aqueous solution of potassium hydroxide (8 N, 25 ml), imidazole (1.36 g, 0.02 mol) and PEG methyl ether-350 (0.7 g, 0.002 M) were added. The mixture was stirred while benzyl bromide (3.5 g, > 0.02 mol) in carbon tetrachloride (25 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 48 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. The crude product was distilled to give N-benzyl-imidazole (21) as a colourless oil (b.p. 110-112°C/approx. 0.5-1.0 mm; 1.26 g, 40% yield). NMR ($CDCl_3$): δ 5.3 (s, 2H, CH_2-Ph), 7.12 (s, 1H), 7.3-7.7 (m, 6H), 7.76 (s, 1H).

3.2.28 Preparation of N-isopropyl imidazole (22) using PEG methyl ether-350 as PTC:

To an aqueous solution of potassium hydroxide (8 N, 25 ml), imidazole (1.36 g, 0.02 mol) and PEG methyl ether-350 (0.7 g, 0.002 M) were added. The mixture was stirred while 2-bromopropane (2.5 g, > 0.02 M) in carbon tetrachloride (25 ml) was introduced. The

reaction mixture was heated under reflux with stirring for 48 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. The crude product was distilled to give a colourless liquid (b.p. 67-73°C, approx. 1.0 mm, 0.3 g, 14%). After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the distillate was a mixture of N-isopropyl imidazole (22) (70%) and 4-isopropyl imidazole (23) (30%). The infrared spectrum of the mixture was consistent with the assigned structure in that an N-H absorption was observed at ca. 3400 cm^{-1}. NMR data, see Table XXXII.

3.2.29 Preparation of N-dodecyl imidazole (24) using PEG methyl ether 350 as PTC:

To an aqueous solution of potassium hydroxide (8 N, 25 ml), imidazole (1.36 g, 0.02 mol) and PEG methyl ether-350 (0.7 g, 0.002 M) were added. The mixture was stirred while 1-bromododecane (4.98 g, > 0.02 mol) in carbon tetrachloride (25 ml) was introduced. The reaction mixture was heated under reflux, with stirring, for 48 hrs. The carbon tetrachloride layer was separated from the aqueous layer and evaporated to dryness. Distillation of the crude product gave N-dodecyl imidazole (24) as a colourless oil (b.p. 140-145°C/approx. 1.0 mm, 1.2 g, ≈ 26%). Analysis of this product by ^{1}H NMR spectroscopy showed the presence of a minor amount of PEG methyl ether 350 as an additional contaminant. NMR ($CDCl_3$) δ 0.76-2.2 (m, 23H), 4.32 (t, J = 6 Hz, 2H), 7.24 (br. s, 1H, 6 imidazole H-5), 7.4 (br. s, 1H, imidazole H-4), 7.5 (br. s, 1H, imidazole H-2).

3.2.30 Preparation of N-methyl,N-dodecyl aniline (6b) using sodium acetate:

N-methyl aniline (2.14 g, 0.02 mol), 1-bromo dodecane (5.2 g, ≃ 0.02 mol) and sodium acetate (3.70 g, > 0.025 mol) were heated under reflux for 2.5 hrs at 150°C with vigorous stirring. The mixture was allowed to cool, water (25 ml) was added, and the mixture stirred until all solid had dissolved. The solution was extracted with dichloromethane (3 x 25 ml) and the extracts combined, dried (magnesium sulphate) and evaporated to dryness giving the crude product as a dark brown oil (5.61 g).

Hydrochloric acid (20 ml, 2 M) was added to the crude product which was then extracted with diethyl ether (3 x 20 ml). The aqueous (acidic) layer was separated and treated with aqueous potassium hydroxide solution to pH 7.5. This solution was then extracted with diethyl ether (3 x 25 ml). The diethyl ether extracts were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a brown oil (2.26 g, 43% yield). After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the product isolated was a mixture of N-methyl, N-dodecyl aniline (6b) (78%) and N-methyl aniline (22%). For ^{1}H NMR data see Table XXXII.

3.2.31 Preparation of N-methyl, N-dodecyl aniline (6c) using sodium hydride:

N-methyl aniline (2.14 g, 0.02 mol), sodium hydride (0.89 g) and dry tetrahydrofuran were heated to reflux under a nitrogen atmosphere

(0.5 hr). 1-Bromododecane (5.47 g, 0.022 mol) in dry tetrahydrofuran (15 ml) was then added dropwise and the reaction mixture refluxed overnight. The excess sodium hydride and the inorganic salt formed in the reaction were filtered off using filter aid. The solvent was then evaporated to dryness. The product so isolated was taken up into dry diethyl ether (25 ml) and the insoluble material filtered off. The solvent was then removed under reduced pressure giving the crude product as a pale yellow oil (4.74 g).

After addition of hydrochloric acid (20 ml, 2 M) the product was extracted with diethyl ether (3 x 20 ml). The aqueous layer was separated and a sufficient volume of an aqueous potassium hydroxide solution added to bring the solution to pH 7.5. This solution was then extracted with diethyl ether (3 x 25 ml). The diethyl ether extracts were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give pure N-methyl, N-dodecyl aniline (6c) as a pale yellow oil (2.5 g, 46% yield). For NMR see Table XXXII.

3.2.32 Preparation of 4-(dodecyloxy)-benzophenone (8b) using potassium hydroxide and DMSO:

Crushed pellets of potassium hydroxide (5.6, 0.1 mol) were added to dimethyl sulphoxide (40 ml) and stirred for half an hour. p-Hydroxybenzophenone (3.96 g, 0.02 mol) was then added and the reaction mixture stirred for a further 1 hr. Under a nitrogen atmosphere, 1-bromododecane (7.47 g, 0.03 mol) in dimethyl sulphoxide (40 ml) was added dropwise over a period of one hr and the reaction mixture left

stirring overnight. Water (125-150 ml) was then added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each ether extract was backwashed with water (3 x 50 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness and the solid material obtained was crystallised firstly from diethyl ether, and then ethanol to give a colourless crystalline product (8b), (4.87 g, 66% yield, m.p. 55-58°C). For ^{1}H NMR see Table XXXII. Anal. calcd. for $C_{25}H_{34}O_2$. C, 81.92; H, 9.35. Found: C, 81.77; H, 9.53.

3.2.33 Preparation of 4-(10-bromodecyloxy)-benzophenone (9b) and 1,10-bis(4-benzophenonyloxy)-decane (10b) using potassium hydroxide and dimethyl sulphoxide:

Crushed pellets of potassium hydroxide (5.6 g, 0.1 mol) were stirred with dimethyl sulphoxide (40 ml) for half an hour. p-Hydroxybenzophenone (3.96 g, 0.02 mol) was then added and the reaction mixture stirred for a further 1 hr under an argon atmosphere. This mixture was then added dropwise to a stirred solution of 1,10-dibromodecane (9.0 g, 0.03 mol) and dimethyl sulphoxide (40 ml), over a period of one hr, and the reaction mixture left stirring overnight. The solid material which precipitated out from the solution was filtered and washed with diethyl ether and water. Recrystallisation of this product from benzene gave 1,10-bis(4-benzophenonyloxy)-decane (10b) (1.09 g, 10% yield, m.p. 131°C). For ^{1}H NMR see Table XXXII. Ms; m/e, (% dev. mmu), M^+, $C_{36}H_{38}O_4$, 534.2794 (4, + 2.5), $C_{36}H_{36}O_3$, 516.2752 (2, + 8.8), $C_7H_5O_2$, 121.0057 (100, -23.3).

After filtration of the precipitated solid, water (125-150 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each ether extract was backwashed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give an oil which solidified on standing at room temperature. A further attempt was made to purify this product by column chromatography. (Alumina column, Pet. ether/60-80^{o}C and ethyl acetate solvent systems).

Three main fractions were obtained after column chromatography. After analysis of the first fraction by ^{1}H NMR spectroscopy and on consideration of respective integrals it was apparent that the isolated material (0.47 g) was a mixture of 4-(dec-9-enyloxy)-benzophenone (25) (58%) and 1,10-dibromo decane (41%), ^{1}H NMR for (25) ($CDCl_3$) 1.2-2.0 (m, 14H), 4.06 (t, J = 6.5 Hz, 2H, O-CH_2), 4.98-5.30 (m, 2H), 5.76-6.2 (m, 1H), 7.04-7.24 (br.d, J = 8.5 Hz, 2H), 7.52-7.80 (m, 3H), 7.88-8.14 (m, 4H).

The second isolated material was mainly a mixture of 4-(10-bromodecyloxy)-benzophenone (9b) and 1,10-dibromodecane. The third fraction of the isolated material was crystallised from ethanol giving 4-(10-bromo-decyloxy)-benzophenone (9b) as colourless crystals (0.23 g, 3% yield, m.p. 72^{o}C). For ^{1}H NMR see Table XXXII.

TABLE XXXII

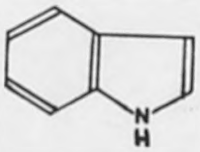
Table for ^{1}H NMR data

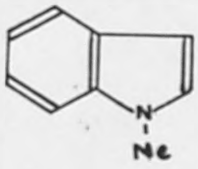
Compound	^{1}H NMR Chemical shift in δ
N-methyl indole (1) and (1a)	δ 3.72 (s, 3H, N-Me), 6.4-6.56 (m, 1H, indole H-2), 6.96-7.44 (m, 4H), 7.52-7.72 (br.d. J ≃ 7.0 Hz, 1H, indole H-4).
1,3-Dimethyl indole (2) and (2a)	δ 2.32 (s, 3H, indole Me-3), 3.70 (s, 3H, N-Me), 6.71-6.80 (m, 1H, indole H-2), 6.8-7.32 (m, 3H), 7.44-7.64 (br.d. 1H, indole H-4).
N-dodecyl indole (3) and (3a)	δ 0.7-1.00 (t, J ≃ 5.0 Hz, 3H, $-CH_2-CH_3$), 1.0-2.0 (m, 20H), 4.0 (t, J ≃ 7.0 Hz, 2H, $N-CH_2$), 6.4-6.5 (br.d. J = 3 Hz, 1H, indole H-2), 7.0-7.40 (m, 4H), 7.52-7.64 (br.d. J ≃ 7Hz, 1H, indole H-4).
1-(10-bromodecyl-3-methyl indole (4) and (4a)	δ 1.2-2.00 (m, 16H), 2.30 (s, 3H, indole Me-3), 3.32 (t, J ≃ 6.5 Hz, 2H, $Br-CH_2$), 4.00 (t, J ≃ 7.0 Hz, 2H, $N-CH_2$), 6.80 (m, 1H, indole H-2), 7.0-7.24 (m, 3H), 7.5-7.64 (m, 1H, indole H-4).
1-dodecyl,3-methyl indole (5)	δ 0.74-2.0 (m, 23H), 2.3 (s, 3H, indole Me-3), 3.94 (t, J ≃ 7 Hz, 2H, $N-CH_2$), 6.8 (br.s. 1H, indole H-2), 7.0-7.4 (m, 3H), 7.44-7.64 (br.d., J = 7 Hz, 1H, indole H-4).
N-methyl, N-dodecyl aniline. (6), (6a), (6b) and (6c)	δ 0.76-2.1 (m, 23H), 2.94 (s, 3H, N-Me), 3.24 (t, J ≃ 7 Hz, 2H, $Br-CH_2$), 6.64-6.94 (br.d., $J_{3,4}$ ≃ 7.29 Hz, and $J_{2,3}$ ≃ 8.4 Hz, 3H), 7.2-7.48 (m, 2H).

Table for ^{1}H NMR data (continued)

Compound	^{1}H NMR Chemical shift in δ
1-(11-hydroxyundecyl)-3-methyl indole (7)	δ 1.21-2.3 (m, 18H), 2.5 (s, 3H), 3.5 (t, J ≃ 6.5 Hz, 2H, HO-CH_2-), 4.1 (t, J ≃ 7.0 Hz, 2H, N-CH_2), 6.94 (br.s. 1H, indole H-2), 7.16-7.50 (m, 3H), 7.6-7.8 (m, 1H, indole H-4).
4-(dodecyloxy)-benzophenone (8), (8a) and (8b)	δ 0.8-2.0 (m, 23H), 4.04 (t, J ≃ 6.5 Hz, 2H, -O-CH_2), 7.04 (br.d, J ≃ 8.5 Hz, 2H), 7.56-7.74 (m, 3H), 7.8-8.04 (m, 4H).
N-benzyl carbazole (17)	δ 5.4 (s, 2H, N-CH_2-Ph), 7.0-7.5 (m, 6H), 8.04-8.20 (br.d, J ≃ 8.0 Hz, 2H).
N-dodecyl carbazole (19)	δ 0.7-2.0 (m, 23H), 4.24 (t, J ≃ 7 Hz, 2H, N-CH_2-), 7.2-7.6 (m, 6H), 8.04-8.2 (br.d, J ≃ 8.0 Hz, 2H).
N-isopropyl imidazole (22)	δ 1.4-1.68 (2s, 6H, N-$CHMe_2$), 4.2-4.7 (m, 1H, -CH-Me_2), 7.12 (br.s, 1H), 7.22-7.34 (br.s, 1H), 7.7-8.02 (br.s, 1H).
4-isopropyl imidazole (23)	δ 1.2-1.4 (2s, 6H), 2.8-3.2 (m, 1H, CH-Me_2), 6.8 (s, 1H), 7.64 (s, 1H).
4-(10-bromodecyloxy)-benzophenone (9), (9a) and (9b).	δ 1.2-2.0 (m, 16H), 3.32 (t, J ≃ 6 Hz, 2H, Br-CH_2), 3.96 (t, J ≃ 7.0 Hz, 2H, O-CH_2), 6.88 (d, J ≃ 8 Hz, 2H), 7.40-7.60 (m, 3H), 7.66-7.90 (m, 4H).
1,10-bis-(4-benzophenonyloxy)-decane. (10), (10a) and (10b).	δ 1.28-2.0 (m, 16H), 4.08 (t, J ≃ 6Hz, 4H, O-CH_2), 7.04 (d, J ≃ 8 Hz, 4H), 7.6-7.8 (m, 6H), 7.88-8.08 (m, 8H).

3.2.34 Product analysis of 1-methyl indole (1) by ^{1}H NMR spectroscopy:





(1)

Total number of protons in aromatic region = b = 85 (integral units)

No. of protons in N-Me region = a = 3H = 16 (integral units) see figure (58).

∴ No. of protons in aromatic region due to N-methyl indole = 6H = 2 X a.

∴ No. of protons in aromatic region due to indole = b-2a

$$\% \text{ of N-methyl indole} = \frac{2a}{b} \times 100$$

$$= \frac{32}{85} \times 100 = \underline{38\%}$$

$$\% \text{ of indole} = \frac{b-2a}{b} \times 100$$

$$= \frac{85-32}{85} \times 100 = \underline{62\%}$$

3.2.35 Preparation of 3-nonoyl indole (26):

This procedure was adapted from that of Schore and Turro.[82]

To a solution of nonoic acid (7.74 g, 0.045 mol) in dry benzene (10 ml), oxalyl chloride (19.05 g, 0.15 mol) was carefully added. The mixture was refluxed (0.5 hr) and allowed to stir at room temperature, under nitrogen, until used as outlined below.

A flask containing magnesium turnings (0.9 g, 0.0375 mol) was flame dried under nitrogen, cooled and charged with sodium dried diethyl ether (40 ml). Bromoethane (5.4 g, 0.05 mol) was added dropwise and the mixture stirred and refluxed until all the magnesium had reacted. Then sodium dried benzene (40 ml) was added and the mixture warmed under a stream of nitrogen to evaporate the diethyl ether and excess ethyl bromide. A solution of indole (4.38 g, 0.0375 mol) in dry benzene (15 ml) was added slowly and the mixture was refluxed (0.5 hr). Excess oxalyl chloride was evaporated from the nonoyl chloride solution, prepared previously, and this solution was then added dropwise to the well-cooled and vigorously stirred indole-magnesium bromide mixture.

A dark red solid formed which was thoroughly mixed with hydrochloric acid solution (40 ml, 2N) and warm ethyl acetate (125 ml). The ethyl acetate layer was separated and washed with water (40 ml), saturated aqueous sodium bicarbonate (2 x 40 ml), water (40 ml) and brine (25 ml) before being dried over magnesium sulphate. The solvent was removed and the residue recrystallised from acetone to give the product (26) as a tan powder (2.85 g, 28% yield, m.p. 138-141°C). ^{1}H NMR (DMSO-D_6), δ 0.70-1.80 (m, 15H), 2.70 (t, J $\simeq$ 6.5 Hz, 2H, CH_2-CO), 7.04-7.60 (m, 3H), 8.08-8.23 (m, 2H). IR (nujol mull) 3130 (NH), 1630 (C=O), 748 cm^{-1} (indole H-2). Analysis calcd. for: $C_{17}H_{23}NO$, C, 79.38; H, 8.95; N, 5.45. Found: C, 79.18; H, 8.93; N, 5.73.

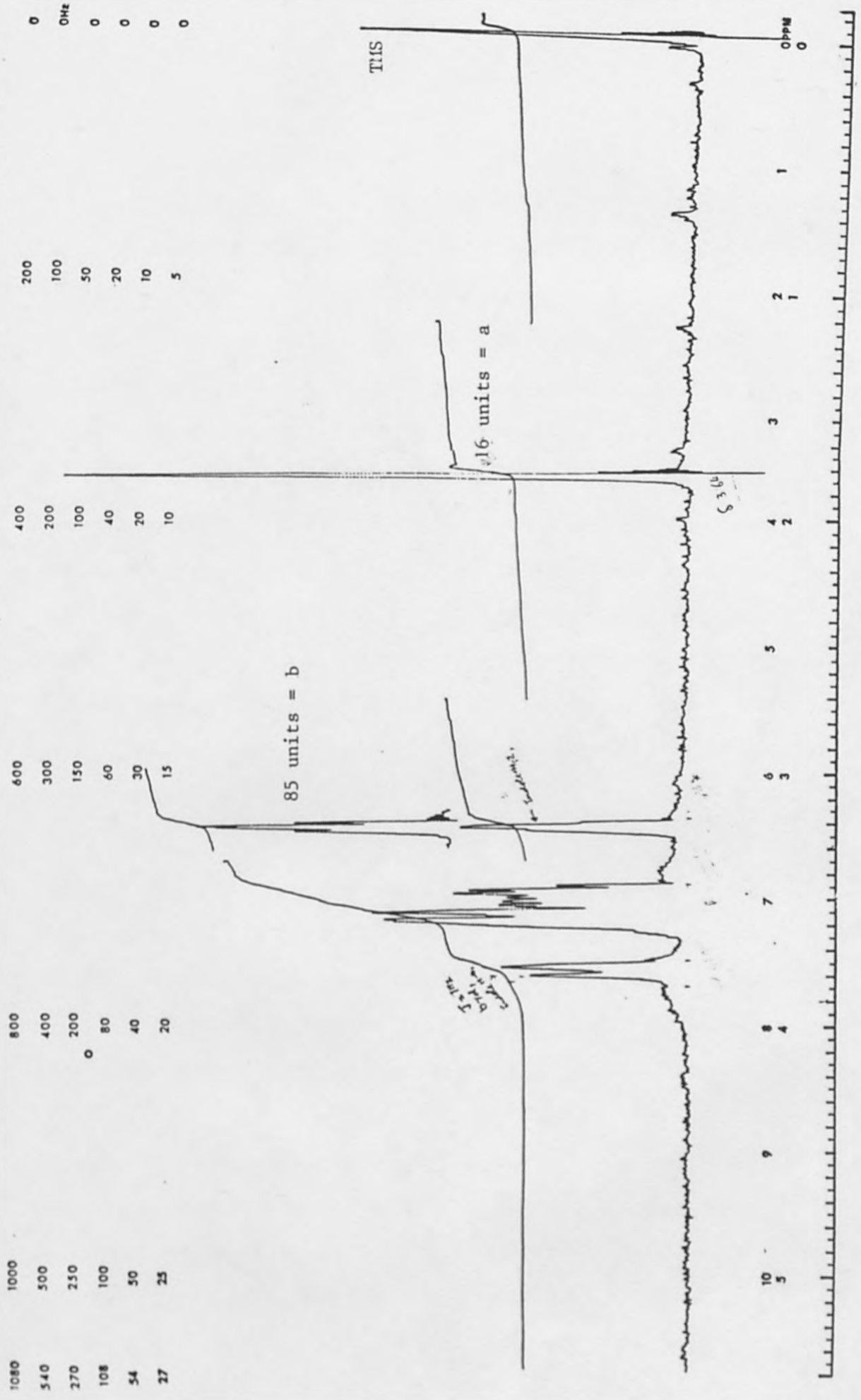


Figure 58 . Analysis of 1-methyl indole by ^{1}H NMR spectroscopy

3.2.36 Preparation of 3-nonyl indole (27):

To a suspension of 3-nonoyl indole (26) (3.39 g, 0.0139 mol) in sodium dried diethyl ether (100 ml), a suspension of lithium aluminium hydride (2.5 g, 0.06 mol) in dry diethyl ether (40 ml) was added dropwise. The solution was refluxed under nitrogen (18 hrs), cooled and treated with water (10 ml), 15% sodium hydroxide (10 ml) and water (10 ml). The diethyl ether was filtered through magnesium sulphate and evaporated to leave a solid product which was then recrystallised from petroleum ether (60-80°C), to give colourless needles (2.25 g, 65% yield, m.p. 64-64°C). ^{1}H NMR ($CDCl_3$) δ 0.68-1.90 (m, 17H), 2.6 (t, J ≃ 8.0 Hz, 2H), 6.84-7.0 (m, 1H), 7.04-7.96 (m, 5H). IR (Nujol) 3390 (NH), 748 cm^{-1} (indole H-2). Analysis calcd. for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.97; H, 10.55; N, 5.85.

3.2.37 Preparation of 3-dodecoyl indole (28):

To a solution of lauric acid (10.48 g, 0.0524 mol) in dry benzene (10 ml), oxalyl chloride (19.9 g, 0.1574 mol) was carefully added. The mixture was refluxed (0.5 hr) and allowed to stir at room temperature under a nitrogen atmosphere until used as outlined below.

A flask containing magnesium turnings (1.046 g, 0.0436 mol) was flame dried under a nitrogen atmosphere, cooled and charged with sodium dried diethyl ether (50 ml). Bromoethane (6.332 g, 0.0581 mol) was added dropwise and the mixture stirred and refluxed until all the magnesium had reacted. Sodium dried benzene (50 ml) was

then added and the mixture warmed under a stream of nitrogen to evaporate the ether and the excess bromoethane. A solution of indole (5.10 g, 0.0436 mol) in dry benzene (20 ml) was added slowly and the mixture refluxed (0.5 hr). Excess oxalyl chloride was evaporated from the dodecoyl chloride solution prepared previously and this solution was then added dropwise to a well-cooled and vigorously stirred indole-magnesium bromide mixture.

A dark red solid formed which was thoroughly mixed with hydrochloric acid (50 ml, 2N) and warm ethyl acetate (170 ml). The ethyl acetate solution was washed with water (50 ml), saturated aqueous sodium bicarbonate (2 x 50 ml), water (50 ml) and brine (35 ml). The solution was dried over magnesium sulphate and the solvent removed giving a tan coloured solid material which was recrystallised from ethanol to give 3-dodecoyl indole (28) as white crystals (3.44 g, 27% yield, m.p. 114-116°C).

^{1}H NMR ($CDCl_3$) δ 0.80-1.68 (m, 21H), 2.76 (t, J ≃ 6.5 Hz, 2H, CH_2-CO), 7.10-7.44 (m, 3H), 7.72-7.84 (m, 1H), 8.20-8.40 (m, 1H), 8.8-9.0 (m, 1H). IR (Nujol), 3120 (NH), 1610 (C=O), 748 cm^{-1} (indole H-2). Analysis calcd. for $C_{20}H_{29}NO$. C, 80.22; H, 9.76; N, 4.67. Found: C, 79.99; H, 9.66; N, 4.61.

3.2.38 Preparation of 3-doedcyl indole (29):

The 3-dodecyl indole (29) was prepared according to method 3.2.26, using the following amounts of material. 3-Dodecoyl indole (28)

(3 g, 0.011 mol), lithium aluminium hydride (2.07 g) and dry diethyl ether (280 ml). The product (29) was obtained as white crystals after recrystallisation from pet. ether (60-80°C) (1.61 g, 51% yield, m.p. 51-52°C). ^{1}H NMR ($CDCl_3$) δ, 0.70-1.90 (m, 23H), 2.6 (t, J ≈ 7.0 Hz, 2H), 6.8-6.9 (m, 1H), 6.94-7.34 (m, 3H), 7.44-7.59 (m, 1H), 7.6-7.92 (m, 1H). IR (Nujol) 3330 (NH) 748 cm^{-1} (indole H-2). Analysis calculated for $C_{20}H_{31}N$: C, 84.15; H, 10.95; N, 4.91. Found: C, 84.36; H, 10.87; N, 4.83.

3.2.39 Preparation of 3-octadecoyl indole (30):

To a solution of octadecanoic acid (25.56 g, 0.09 mol) in dry benzene (40 ml), oxalyl chloride (34.29 g, 0.27 mol) was carefully added. The mixture was refluxed (0.5 hr) and allowed to stir at room temperature, under a nitrogen atmosphere, until used as below.

A flask containing magnesium turnings (1.92 g, 0.08 mol) was flame dried under a nitrogen atmosphere, cooled and charged with sodium dried diethyl ether (70 ml). Bromoethane (10.9 g, 0.1 mol) was added dropwise and the mixture stirred and refluxed until all the magnesium had reacted. Sodium dried benzene (75 ml) was then added and the mixture warmed under a stream of nitrogen to evaporate the diethyl ether and excess bromoethane. A solution of indole (9.36 g, 0.08 mol) in dry benzene (60 ml) was added slowly and the mixture refluxed (0.5 hr). Excess oxalyl chloride was evaporated from the octadecoyl chloride solution prepared previously and this solution was then added dropwise to the well-cooled and vigorously stirred indole-magnesium bromide mixture.

A dark red solid formed which was thoroughly mixed with hydrochloric acid (75 ml, 2N) and warm ethyl acetate (250 ml). The ethyl acetate solution was washed with water (75 ml), saturated aqueous sodium bicarbonate (2 x 75 ml), water (75 ml) and brine (50 ml). A solid material precipitated out which was filtered and recrystallised with a hot filtration from acetone. 3-Octadecoyl indole (30) was obtained as white crystals (5.08 g, 16% yield, m.p. 112-113°C). ^{1}H NMR ($CDCl_3$) δ, 0.80-1.96 (m, 33H), 2.8 (t, J ≃ 6.5 Hz, 2H, $-COCH_2$), 7.20-7.50 (m, 3H), 7.8-7.96 (m, 1H), 8.3-8.8 (m, 2H). IR- (Nujol) 3160 (NH), 1625 (C=O), 748 cm^{-1} (indole H-2). Analysis calcd. for $C_{26}H_{41}NO$: C, 81.40; H, 10.77; N, 3.65. Found: C, 81.18; H, 10.66; N, 3.54.

3.2.40 Preparation of 3-octadecyl indole (31):

3-Octadecyl indole (31) was prepared according to the method described in Section 3.2.36. The materials were used as follows: 3-Octadecoyl indole (30) (4.22 g, 0.011 mol), lithium aluminium hydride (2.0 g) and dry diethyl ether (250 ml). The product (31) was recrystallised from pet-ether (60-80°C) and obtained as white crystals. (2.87 g, 71% yield, m.p. 61-62°C). ^{1}H NMR data ($CDCl_3$) δ, 0.80-1.90 (m, 35H), 2.7 (t, J ≃ 7.0 Hz, 2H), 7.00-7.12 (m, 1H), 7.14-7.52 (m, 3H), 7.6-7.80 (m, 1H), 7.84-8.00 (m, 1H). IR - (Nujol), 3400 (NH), 740 cm^{-1} (indole H-2). Analysis calcd. for $C_{26}H_{43}N$: C, 84.49; H, 11.73; N, 3.79. Found: C, 84.62, H, 11.92; N, 3.93.

3.2.41 Preparation of 3-acetyl indole (32):

N-N-dimethyl acetamide (18 ml) was cooled to 5°C and phosphorous-oxy chloride (7.0 ml, 0.072 mol) was added at such a rate as to keep the temperature below 20°C. After the addition was complete a solution of indole (6.55 g, 0.056 mol) and N,N-dimethyl acetamide (9.0 ml) was added, keeping the temperature below 40°C. The mixture was heated (87°C) for two hrs and allowed to cool. The red mass was dissolved in water and extracted with diethyl ether. The water layer was separated and made basic with aqueous sodium hydroxide and filtered. The solid was washed well with water, refluxed in ethanol containing charcoal and then filtered. On cooling the solution gave the product which was recrystallised from ethanol (3 times) (4.07 g, 46% yield, m.p. 191-195°C, Lit. m.p. 191-193°C)[173]. ^{1}H NMR ($CDCl_3$) δ, 2.55 (s, 3H, CO-CH_3), 7.10-7.40 (m, 3H), 7.7-7.8 (m, 1H), 8.2-8.6 (m, 2H). IR (Nujol), 3110 (NH), 1600 (C=O), 748 cm^{-1} (indole H-2).

3.2.42 Preparation of N,N-dimethyl hexamide (33):

To a solution of hexanoic acid (21.0 g, 0.18 mol) in dry benzene (25 ml) oxalyl chloride (60.0 g, 0.47 mol) was carefully added. The mixture was refluxed (0.5 hr) and allowed to stir at room temperature under a nitrogen atmosphere until used as outlined below. Sodium dried diethyl ether (200 ml) was cooled using an ice/salt bath for 0.5 hr under a nitrogen atmosphere. Dimethyl amine (approx. 10 ml) was bubbled through the cold diethyl ether. The excess oxalyl chloride was removed from the above prepared hexanoyl chloride

and then added to the cooled diethyl ether/dimethyl amine solution, very carefully over a period of one hr, and this solution was then left to stir for 3-4 hrs. The solid formed was removed by filtration and the diethyl ether solution was washed with saturated aqueous sodium bicarbonate (40 ml) and water (2 x 50 ml). After drying over magnesium sulphate and evaporation to dryness a dark brown oil was obtained which was then distilled to give N,N-dimethyl hexamide (33) as a pale yellow oil (20.24 g, 79% yield, b.p. 115-140°C/approx. 16.0 mm). ^{1}H NMR ($CDCl_3$) δ, 0.68-1.88 (m, 9H), 2.6 (t, J ≃ 6.5 Hz, 2H, CO-CH_2), 2.72-3.2 (2s, 6H, -N-Me_2).

3.2.43 Preparation of 3-hexanoyl indole (34):

N,N-dimethyl hexamide (33) (14.3 g, 0.1 mol) was cooled to 5°C and, under a nitrogen atmosphere, phosphorus oxy-chloride (1.6 ml) was added at such a rate as to keep the temperature below 20°C. After the addition was complete a solution of indole (1.63 g, 0.014 mol) and N,N-dimethyl hexamide (33) (3.72 g, 0.026 mol) was added slowly, keeping the temperature below 40°C. The mixture was heated to 87-90°C for two hrs and then allowed to cool. The red mass was dissolved in water (200 ml) and extracted with diethyl ether (3 x 50 ml). The water solution was made basic with aqueous sodium hydroxide and filtered. The solid (residue) was washed well with water and recrystallised from ethanol. 3-Hexanoyl indole (34) was obtained as a white crystalline product. (10.14 g, 75% yield, m.p. 147-149°C, Lit. m.p. 153-154.5°C)[82] ^{1}H NMR ($CDCl_3$) δ, 0.8-1.1 (m, 3H), 1.1-1.24 (m, 6H), 2.8 (t, J ≃ 7.0 Hz, 2H, CH_2-CO), 7.28-7.6 (m, 3H), 7.88-8.0 (m, 1H), 8.4-8.6 (m, 1H), 8.76-9.00 (m, 1H). IR (Nujol) 3130 (NH), 1630 (C=O), 748 cm^{-1} (indole H-2).

3.2.44 Preparation of 3-hexyl indole (34b):

The 3-hexyl indole (34b) was prepared according to the method described in 3.2.36., using 3-hexanoyl indole (34)(10.14 g, 0.047 mol), lithium aluminium hydride (8.93 g) and dry diethyl ether (425 ml).

Distillation of the blue-violet liquid gave 3-hexyl indole (34b) as a pale yellow oil (8.40 g, 89% yield, b.p. $120^{o}/1$ mm., Lit. b.p. $120^{o}/1$ mm [82]). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.9 (m, 11H), 2.7 (t, J $\simeq$ 7.5 Hz, 2H), 7.0-7.10 (m, 1H), 7.16-7.56 (m, 3H), 7.68-8.0 (m, 2H), IR (Nujol), 3400 (NH), 748 cm^{-1} (indole H-2).

3.2.45 Preparation of N,N-dimethyl nonamide (35):

To a solution of nonoic acid (20.54 g, 0.13 mol) in dry benzene (25 ml), oxalyl chloride (33.0 g, 0.26 mol) was carefully added over a period of one hr. The mixture was refluxed (0.5 hr) and then allowed to stir at room temperature under a nitrogen atmosphere until used as outlined below.

Under a nitrogen atmosphere, sodium dried diethyl ether (500 ml) was cooled using an ice/salt bath for 0.5 hr. Dimethylamine (approx. 10 ml) was then bubbled through the cold diethyl ether. The excess oxalyl chloride was removed from the above prepared nonyl chloride which was added, over one hr, to the cooled diethyl ether/dimethylamine solution. This solution was then left to stir for 3-4 hrs. The solid formed was removed by filtration and the organic layer

washed with saturated aqueous sodium bicarbonate (40 ml) and water (2 x 50 ml). After drying over magnesium sulphate and evaporating to dryness, a pale yellow liquid, N,N-dimethyl nonamide (35) (20.81 g, 87% yield) was obtained. ^{1}H NMR ($CDCl_3$) δ, 0.72-1.84 (m, 15H), 2.2 (t, J ≃ 7.0 Hz, 2H, CO-CH_2-), 2.84-3.10 (2s, 6H, N-Me_2). Analysis calcd. for $C_{11}H_{23}NO$: C, 71.29; H, 12.51; N, 7.55. Found: C, 71.24; H, 12.66; N, 7.35. MS; m/e (%, dev. mmu), M^+, $C_{11}H_{23}NO$, 185.1723 (2, -5.7), $C_9H_{18}NO$, 156.1332 (1.0, -5.6), C_3H_6NO, 72.0375 (29, -7.4).

3.2.46 Preparation of 3-nonoyl indole (26a):

N,N-dimethyl nonamide (35) (10.0 g, 0.05 mol) was cooled to 5°C and, under a nitrogen atmosphere, phosphorous oxychloride (8.24 ml, 0.09 mol) was added at such a rate as to keep the temperature below 20°C. After the addition was complete, a solution of indole (7.02 g, 0.06 mol) and N,N-dimethyl nonamide (35) (10.0 g, 0.05 mol) was added slowly, keeping the temperature below 40°C. The reaction mixture was heated (90°C, 2 hr) and then allowed to cool. The dark red material was dissolved in water (300 ml) and extracted with diethyl ether (3 x 50 ml). The water solution and the ether insoluble solid was made basic with aqueous sodium hydroxide and filtered. The residue was washed with water and recrystallised from ethanol to give 3-nonoyl indole (26a) as a white crystalline solid (10.83 g, 70% yield, m.p. 137 -139°C). ^{1}H NMR ($CDCl_3$) δ, 0.80-2.0 (m, 15H), 2.8 (t, J ≃ 6.5 Hz, 2H, CO-CH_2), 7.32-7.6 (m, 3H), 7.9-8.04 (m, 1H), 8.4-8.6 (m, 1H), 8.7-9.0 (m, 1H). IR (Nujol), 3130 (NH), 1610 (C=O), 748 cm^{-1} (indole H-2).

Anal. calcd. for $C_{17}H_{23}NO$: C, 79.38; H, 8.95; N, 5.45; Found: C, 79.18; H, 8.93; N, 5.73.

3.2.47 Preparation of 3-nonyl indole (27a):

The 3-nonyl indole (27a) was prepared by reduction of 3-nonoyl indole (26a) (10.02 g, 0.03 mol) using the method outlined in 3.2.36. Lithium aluminium hydride (5.93 g) was used as a reducing agent and dry diethyl ether (650 ml) was used as a solvent. The pale yellow solid was recrystallised from pet. ether (60-80°C) to give 27a as colourless crystals. (8.14 g, 85% yield, m.p. 65.5°-67°C). ^{1}H NMR ($CDCl_3$), δ 0.8-1.90 (m, 17H), 2.64 (t, J ≃ 7 Hz, 2H), 6.92-7.00 (m, 1H), 7.08-7.50 (m, 3H), 7.60-8.0 (m, 2H). IR (Nujol), 3390 (NH), 748 cm^{-1} (indole H-2). Anal. calcd. for $C_{17}H_2N^-$, C, 83.89; H, 10.35; N, 5.75. Found: C, 83.97; H, 10.55; N, 5.85.

3.2.48 Preparation of N,N-dimethyl dodecamide (36):

To a solution of lauric acid (dodecanoic acid, 26.0 g, 0.13 mol) in dry benzene (50 ml), oxalyl chloride (33.02 g, 0.26 mol) was carefully added over a period of one hour. The mixture was refluxed (0.5 hr) and allowed to stir at room temperature, under a nitrogen atmosphere, until used as outlined below.

Under a nitrogen atmosphere, sodium dried diethyl ether (500 ml) was cooled using an ice-salt bath for 0.5 hr. Dimethyl amine (approx. 10 ml) was then bubbled through the cold diethyl ether. The excess

oxalyl chloride and benzene were removed from the above prepared dodecoyl chloride which was added, over one hr, to the cooled diethyl ether/dimethyl amine solution. This solution was then left to stir for 3-4 hrs. The solid formed was removed by filtration and the organic layer washed with saturated aqueous sodium bicarbonate (50 ml) and water (2 x 50 ml). After drying over magnesium sulphate and evaporating to dryness a pale yellow liquid, N,N-dimethyl dodecamide (36) (26.85 g, 91% yield) was obtained. ^{1}H NMR ($CDCl_3$), δ, 0.7-1.8 (m, 21H), 2.2 (t, J ≃ 7.0 Hz, 2H, CO-CH_2), 2.9-3.2 (m, 6H, NMe_2). Anal. calcd. for $C_{14}H_{29}NO$: C, 73.95; H, 12.85; N, 6.16. Found: C, 74.19; H, 13.00; N, 6.27. MS; m/e (%, dev. mmu), M^+, $C_{14}H_{29}NO$, 227.2135 (1.0, -6.4), $C_{13}H_{26}NO$, 212.1961 (0.16, -5.4), $C_6H_{12}NO$, 114.0850 (4, -6.9), $C_5H_{10}NO$, 100.0648 (21, -11.4), C_3H_6NO, 72.0351 (21, -9.8).

3.2.49 Preparation of 3-dodecoyl indole (28a):

N,N-dimethyl dodecamide (36) (11.35 g, 0.05 mol) was cooled to 5°C and, under a nitrogen atmosphere, phosphorous oxychloride (13.77 g, 0.09 mol) was added at such a rate as to keep the temperature below 20°C. After the addition was complete, a solution of indole (7.02 g, 0.06 mol) and N,N-dimethyl dodecamide (36) (11.0 g, 0.05 mol) was added slowly, keeping the temperature below 40°C. The reaction mixture was heated (90°C, 3 hr) and then allowed to cool. The dark brown material was added to water (500 ml), but most of the solid was insoluble. After filtration and washing with diethyl ether (2 x 100 ml), the solid material was treated with aqueous sodium hydroxide (200 ml, 1N), filtered and washed with water (3 x 100 ml). The

crude product was refluxed in ethanol (0.5 hr) and allowed to cool, giving 3-dodecoyl indole (28a) as colourless crystals. (13.85 g, 77% yield, m.p. 122-124°C). ^{1}H NMR ($CDCl_3$) δ, 0.8-2.0 (m, 21H), 2.8 (t, J ≃ 6.5 Hz, 2H, CH_2-CO), 7.4-7.7 (m, 3H), 8.0-8.1 (m, 1H), 8.44-9.0 (m, 2H). IR (Nujol), 3130 (NH), 1610 (C=O), 745 cm^{-1} (indole H-2). Anal. calcd. for $C_{20}H_{29}NO$: C, 80.22; H, 9.76; N, 4.67. Found: C, 79.99; H, 9.66; N, 4.61. MS; m/e, (%, dev. mmu), M^+, $C_{20}H_{29}NO$, 299.2261 (7, +1.2), $C_{11}H_{10}NO$, 172.0842 (12, + 7.9), $C_{10}H_9NO$, 159.0696 (100, +1.2), C_9H_6NO, 144.0465 (83, + 1.6), C_8H_6N, 116.0504 (8, + 0.3).

3.2.50 Preparation of 3-dodecyl indole (29a):

The 3-dodecyl indole (29a) was prepared by reducing 3-dodecoyl indole (28a) (11.96 g, 0.05 mol) using lithium aluminium hydride (6.08 g) in the presence of dry diethyl ether (600 ml), according to the method used for section 3.2.36. 3-Dodecyl indole (29a) was obtained as colourless crystals after recrystallisation (3 times) from petroleum ether (60-80°C), (8.12 g, 71% yield, m.p. 51-52°C). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.94 (m, 23H), 2.7 (t, J ≃ 7.0 Hz, 2H), 7.0-7.08 (m, 1H), 7.20-7.56 (m, 3H), 7.6-8.10 (m, 2H). IR (Nujol), 3380 (NH), 738 cm^{-1} (indole H-2). Anal. calcd. for $C_{20}H_{31}N$: C, 84.15; H, 10.95; N, 4.91. Found: C, 84.36; H, 10.87; N, 4.83.

3.2.51 Preparation of N,N-dimethyl octadecamide (37):

To a solution of stearic acid (octadecanoic acid, 28.4 g, 0.1 mol) in dry benzene (50 ml), oxalyl chloride (25.4 g, 0.20 mol) was carefully added over a period of one hr. The mixture was refluxed

(0.5 hr) and allowed to stir at room temperature, under a nitrogen atmosphere, until used as outlined below.

Under a nitrogen atmosphere, sodium dried diethyl ether (500 ml) was cooled using an ice-salt bath for 0.5 hr. Dimethylamine (approx. 10 ml) was then bubbled through the cooled diethyl ether. The excess oxalyl chloride was removed from the above prepared octadecoyl chloride and was then added, over one hr, to the cooled ether/dimethylamine solution. This solution was then left to stir for 3-4 hrs. The solid formed was removed by filtration and the organic layer washed with saturated aqueous sodium bicarbonate (50 ml) and water (2 x 50 ml). After drying over magnesium sulphate and evaporating to dryness a pale yellow oil was obtained, which solidified on standing at room temperature. This was N,N-dimethyl octadecamide (37) (26.29 g, 85% yield, m.p. 39-41°C). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.8 (m, 33H), 2.2 (t, J ≃ 6.5 Hz, 2H, CH_2-CO), 2.96-3.20 (2s, 6H, NMe_2). MS; m/e (% dev. mmu), M^+, $C_{20}H_{41}NO$, 311.3161 (0.57,-2.7), $C_5H_{10}NO$, 100.0702 (20, -12.3), C_3H_6NO, 72.0390 (14, -6.0), C_4H_9NO, 87.0536 (100, -14.8).

3.2.52 Preparation of 3-octadecoyl indole (30a):

N,N-dimethyl octadecamide (37) (15.55 g, 0.05 mol) was cooled to 5°c and, under a nitrogen atmosphere, phosphorous oxychloride (13.77 g, 0.09 mol) was added at such a rate as to keep the temperature below 20°C. After the addition was complete, indole (7.02 g, 0.06 mol) and N,N-dimethyl octadecamide (37) (9.27 g, 0.03 mol) were added slowly, keeping the temperature below 40°C. The reaction mixture was

heated (90°C, 2 hrs) and allowed to cool. The residue was added to water (500 ml). After filtration and washing with diethyl ether (2 x 100 ml) the solid material was treated with aqueous sodium hydroxide (200 ml, 1N), filtered and washed with water (3 x 100 ml). The crude product was refluxed in ethanol (0.5 hr) and allowed to crystallise. 3-Octadecoyl indole (30a) was obtained as a brown solid after recrystallisation from ethanol (11.96 g, 52% yield, m.p. 112-113°C). ^{1}H NMR ($CDCl_3$) δ, 0.72-2.0 (m, 33H), 2.78 (t, J ≃ 6.5 Hz, 2H, CO-CH_2), 7.30-7.60 (m, 3H), 7.80-8.00 (m, 1H), 8.40-8.60 (m, 1H), 8.80-9.00 (m, 1H). IR (Nujol) 3140 (NH), 1610 (C=O), 740 cm^{-1} (indole H-2). Anal. calcd. for $C_{26}H_{41}NO$: C, 81.40; H, 10.77; N, 3.65. Found C, 81.18; H, 10.66; N, 3.54. MS; m/e (% dev. mmu), M^+, $C_{26}H_{41}NO$; 383.3120 (3, -6.8), $C_{11}H_{10}NO$, 172.0629 (11, -13.3), $C_{11}H_{13}N$, 159.1162 (100, + 11.5), C_9H_6NO, 114.0387 (60, -6.2), C_8H_6N, 116.0391 (7, -10.9).

3.2.53 Preparation of 3-octadecyl indole (31a):

The product (31a) was prepared by method 3.2.36, using 3-octadecoyl indole (9.0 g, 0.023 mol), lithium aluminium hydride (3.49 g) and dry diethyl ether (475 ml). 3-Octadecyl indole (31a) was obtained as colourless crystals after recrystallisation from petroleum ether (60-80°C) with decolourising charcoal (7.0 g, 82% yield, m.p. 61-62°C). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.9 (m, 35H), 2.70 (t, J ≃ 7.0 Hz, 2H), 7.0-7.12 (m, 1H), 7.14-7.52 (m, 3H), 7.6-7.8 (m, 1H), 7.84-8.0 (m, 1H). IR (Nujol), 3400 (NH), 740 cm^{-1} (indole H-2). Anal. calcd. for: $C_{26}H_{43}N$: C, 84.49; H, 11.73; N, 3.79. Found: C, 84.62; H, 11.92; N, 3.93.

3.2.54 Preparation of N,N-dimethyl(2-chlorophenyl)acetamide (38): To a solution of o-chlorophenyl acetic acid (2.04 g, 0.012 mol) in dry benzene (10 ml), oxalyl chloride (3.05 g, 0.024 mol) was carefully added. The mixture was refluxed (0.5 hr) and allowed to stir at room temperature under a nitrogen atmosphere until used as below.

Under a nitrogen atmosphere, sodium dried diethyl ether (150 ml) was cooled using an ice-salt bath for 0.5 hr. Dimethylamine (approx. 5 ml) was then bubbled through the cooled diethyl ether. The excess oxalyl chloride was removed from the above prepared o-chlorophenylacetyl chloride which was added, over one hr, to the cooled diethyl ether-dimethylamine solution. This solution was then left to stir for 2 hrs. The solid formed was removed by filtration and the organic layer was washed with saturated aqueous sodium bicarbonate (25 ml) and water (2 x 25 ml). After drying over magnesium sulphate and evaporating to dryness, a white solid N,N-dimethyl-(2-chlorophenyl)acetamide (38) (1.69 g, 71% yield) was obtained. ^{1}H NMR ($CDCl_3$) δ, 3.00-3.20 (2d, 6H, NMe_2), 3.80 (s, 2H, CH_2-PhCl), 7.20-7.60 (m, 4H, aromatic protons).

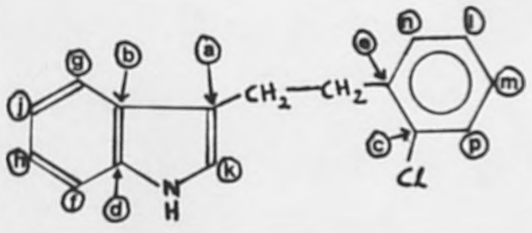
3.2.55 Preparation of 3-(2-chlorophenacetyl) indole (39): N,N-dimethyl(2-chlorophenyl)acetamide (38) (1.123 g, 0.0057 mol) was cooled (5°C) and, under a nitrogen atmosphere, phosphorous oxychloride (1.224 g, 0.008 mol) was added at such a rate as to keep the temperature below 20°C. After the addition was complete, indole (0.67 g, 0.0057 mol) and N,N-dimethyl(2-chlorophenyl)acetamide (38)

(0.57 g, 0.0029 mol) was added slowly, keeping the temperature below 40°C. The reaction mixture was heated (90°-100°C, 2 hrs) and allowed to cool. The solid formed was dissolved in water (100 ml) and washed with diethyl ether (2 x 25 ml). The water layer was made basic with aqueous sodium hydroxide and filtered. The solid was washed with water and recrystallised from ethanol to give 3-(2-chlorophenacetyl) indole (39) as a colourless crystalline product (0.58 g, 37% yield, m.p. 204.5°-205.5°C). IR (Nujol) 3190 (NH), 1630 (C=O), 748 cm^{-1} (indole H-2). Analysis calcd. for $C_{16}H_{12}OCl$: C, 71.25; H, 4.48; N, 5.19. Found: C, 71.10; H, 4.46; N, 5.16.

3.2.56 Preparation of 3-([2-(2-chloro)phenyl]-ethyl)indole (40):

The product (40) was prepared according to the method described in section 3.2.36, using 3-(2-chlorophenacetyl)-indole (39) (0.4 g, 0.0015 mol) and lithium aluminium hydride (0.27 g) in dry diethyl ether (125 ml) 3-([2-(2-chloro)phenyl]-ethyl)indole (40) was obtained as a white solid (0.3 g, 78% yield, m.p. 82°C, b.p. 110°C/approx. 0.001 mm Hg). ^1H NMR ($CDCl_3$) δ, 3.10-3.38 (m, 4H), 7.04-7.16 (m, 1H), 7.20-7.60 (m, 7H), 7.80-8.20 (m, 2H). MS; m/e (% dev. mmu), M^+, $C_{16}H_{14}N^{35}Cl$, 255.0802 (16, 1.3), $C_{16}H_{14}N^{37}Cl$, 257.0801 (5.37, + 1.5), $C_{16}H_{14}N$, 220.1134 (2, + 0.8), $C_{16}H_{13}N$, 219.1069 (3, + 2.1), C_9H_7N, 129.0589 (2, + 1.0). Anal. calcd. for $C_{16}H_{14}NCl$: C, 75.14; H, 5.52; N, 5.48. Found: C, 75.37; H, 5.48; N, 5.42.

^{13}C ($CDCl_3$) ppm.



111.33 (f), 119.18 / 119.50 [g/h], 122.23 / 121.62 [J/k], 127.60 / 126.95 [ℓ/m],

129.72 / 130.81 [n/p], 116.21 (a), 128.62 (b), 134.28 (c), 140.09 / 136.63 [d/e]

3.2.57 Preparation of pyridinium dichromate (41):

Pyridine (60.45 ml) was gradually added to a cooled solution of chromium trioxide (75.0 g, 0.75 mol) in water (75 ml) at a temperature of < 30°C. The solution was diluted with acetone (300 ml) and cooled to -20°C. After three hrs, orange crystals were collected, which were washed with acetone and dried at room temperature. Pyridinium dichromate (41) was recrystallised from aqueous acetone (57.0 g, 20% yield, m.p. 140-142°C, Lit. m.p. 144-146°C).[235]

3.2.58 Preparation of citronellic acid (3,7-dimethyl octenoic acid) (42):

Dry dimethyl formamide (75 ml) was placed in a dry three-necked round bottom flask under a nitrogen atmosphere. Citronellol (6.55 g, 0.042 mol) and pyridinium dichromate (41) (56.38 g, 3.5 eq. molar) were added and the reaction mixture was stirred (15 hrs), keeping the temperature below 20°C.

Water (1 litre) was added to the reaction mixture and the solution extracted with diethyl ether (2 x 250 ml). The ether layers were combined, back-washed with water, and dried over magnesium sulphate. The solvent was removed under reduced pressure and the crude product distilled to give citronellic acid (42) as a colourless oil (6.0 g, 84% yield, b.p. 80-90°C/approx. 0.1 mm, Lit. b.p. 96-97°C/0.2 mm Hg).[236] ^{1}H NMR ($CDCl_3$) δ, 0.98 (d, 3H, -CH-Me), 1.20-1.56 (m, 3H), 1.56 (2S, 6H, $CH{=}CMe_2$), 1.80-2.5 (m, 4H, CH_2-CO and $-CH_2{=}C$), 4.96 (t, 1H), 9.68-10.06 (m, 1H, -OH). IR (neat), 1300 cm^{-1} (C—O) stretch).

3.2.59 Preparation of 3,7-dimethyl octenamide (43) via 3,7-dimethyl octenyl chloride:

To a solution of 3,7-dimethyl octenoic acid (42) (6.5 g, 0.04 mol) in dry benzene (50 ml), oxalyl chloride (5.5 ml, 0.06 mole) was carefully added. The mixture was refluxed (10 hrs) and then stirred at room temperature under a nitrogen atmosphere until used as below.

Diethyl ether (Na-dried, 200 ml) was cooled using an ice-salt bath for 30 minutes under a nitrogen atmosphere. Dimethylamine (approx. 10 ml) was then bubbled through the cold diethyl ether. The excess oxalyl chloride and benzene was removed from the above prepared acid chloride which was added, over one hr, to the cooled diethyl ether-dimethylamine solution. The solution was then left to stir overnight at room temperature. The solid formed was removed by filtration and the organic layer washed with saturated aqueous sodium bicarbonate (50 ml) and water (2 x 50 ml). After drying over

magnesium sulphate and evaporating to dryness, a white solid 3,7-dimethyloctenamide (43) (6.56 g, 87% yield, b.p. 95-120°C/approx. 1 mm Hg) was obtained. ^{1}H NMR ($CDCl_3$) δ, 0.88 (d, 3H, Me-CH), 1.08-1.44 (m, 3H, CH, CH_2), 1.52 (2s, 6H, $(CH_3)_2C{=}CH$), 1.80-2.36 (m, 4H, CH_2-CO, CH_2-CH=C-), 2.84 (2s, 6H, $(CH_3)_2N$-), 4.80 (t, 1H). MS; m/e (%, dev mmu); M^+, $C_{12}H_{23}NO$, 197.1678 (13, -10.2), $C_6H_{12}NO$, 114.0910 (28, -0.9), $C_5H_{10}NO$, 100.0706 (18, -5.6), C_4H_9NO, 87.0653 (100, -3.1), C_3H_6NO, 72.0445 (57, -0.5).

3.2.60 Preparation of 3-(1-keto-3,7-dimethyl octene)indole (44):

3,7-Dimethyl octenamide (43) (3.2 g, 0.015 mole) was cooled to 5°C and, under a nitrogen atmosphere, phosphorous oxychloride was added at such a rate as to keep the temperature below 20°C. After the addition was complete indole (2.9 g, 0.025 mole) and 3,7-dimethyl-octenamide (43) (3.2 g, 0.015 mole) were added slowly keeping the temperature below 40°C. The reaction mixture was heated (90°C, 2 hrs) and then left to stir overnight at room temperature. The resultant viscous oil was then diluted with water (250 ml). The water layer and immissible gum were washed with ether, treated with aqueous sodium hydroxide (100 ml, 1N), filtered and washed with water (2 x 100 ml). The crude product was then refluxed with ethanol (15 min) and allowed to cool, to give a dark red coloured viscous oil which was chromatographed on silica gel (Merck), using ethyl acetate-petroleum ether (60-80°C) as eluents, to give pure 3-(1-keto-3,7-dimethyl octene)indole (44) as a deep red oil (1.7 g, 19% yield, b.p. 180°C/approx. 1.0 mm Hg).

^{1}H NMR ($CDCl_3$) δ, 0.96 (d, 3H, CH-CH_3), 1.20-1.60 (m, 3H), 1.60 (2s, 6H, CH=C(CH_3)$_2$), 1.88-2.2 (m, 2H, -CH_2-$\underline{CH}_2$-CH=C), 2.6-2.94 (m, 2H, CH_2-CO-), 5.04 (t, 1H, -CH_2-$\underline{CH}$=C-Me_2), 7.20-7.80 (m, 3H), 8.0-8.2 (m, 1H, indole H-2), 8.5-8.70 (m, 1H, indole H-4), 9.4-9.8 (br. m, 1H, NH). Anal. calcd. for $C_{18}H_{23}NO$: C, 80.25; H, 8.60; N, 5.20. Found: C, 79.91; H, 8.60; N, 5.08. MS; m/e (%, dev mmu) M^+, $C_{18}H_{23}NO$, 269.1798 (3, +1.8), $C_{10}H_9NO$, 159.0718 (22, +3.4), C_9H_7NO, 145.0601 (4, +7.4), C_9H_6NO, 144.0510 (40, +6.0), C_8H_6N, 116.0592 (14, +9.2).

3.2.61 Preparation of 3-(3,7-dimethyl octene)indole (45):

To a suspension of 3-(1-keto-3,7-dimethyl octene)indole (44) (1.5 g, 0.056 mole) in sodium dried diethyl ether (50 ml), a suspension of lithium aluminium hydride (0.85 g, 0.023 mole) in dry diethyl ether (50 ml) was added dropwise. The solution was refluxed under a nitrogen atmosphere (15 hrs), cooled and treated with water (10 ml), sodium hydroxide solution (15%, 10 ml) and additional water until all unreacted lithium aluminium hydride was destroyed. The ether layer was separated and the alumina formed washed with ether (2 x 50 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a red powder. Distillation of this material gave a yellow oil which was chromatographed on silica gel (Merck), using diethyl ether-ethyl acetate as eluents, to give pure 3-(3,7-dimethyl octene)indole (45) (0.7 g, 49% yield, b.p. 120-130°C/0.1 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.96 (d, 3H, Me-CH-), 1.06-1.44 (m, 5H, -CH_2-CH-CH_2-), 1.60 (2s, 6H,

$-CH=C(Me)_2$), 1.80-2.08 (m, 2H, $-CH_2-CH=C\langle$), 2.72 (t, 2H), 4.80 (t, 1H, $-CH_2-CH=C\langle$), 6.60-6.76 (m, 1H, indole H-2), 6.80-7.20 (m, 3H), 7.28-7.50 (m, 1H, indole H-4), 7.52-7.80 (m, 1H, indole NH). Anal. calcd. for $C_{18}H_{25}N$: C, 84.71; H, 9.80; N, 5.49. Found: C, 84.88; H, 9.93; N, 5.39.

3.2.62 Preparation of 6-(3-citronellyl-1-indolyl)hexyl bromide (46):

Crushed pellets of potassium hydroxide (2.0 g, 0.037 mole) were added to dimethyl sulphoxide (25 ml) and stirred for 30 minutes. 3-(3,7-Dimethyl octene)indole (45) (0.7 g, 0.003 mole) was then added and the reaction mixture stirred for a further 1 hr, under a nitrogen atmosphere. In a separate reaction vessel, 1,6-dibromohexane (1.3 g, 0.005 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,6-dibromohexane solution, over a period of one hr, and the reaction mixture left stirring for 3 hrs.

Water (100 ml) was then added and the solution extracted with diethyl ether (4 x 50 ml). Each of the ether extracts was back washed with water (4 x 30 ml). The ether layers were combined, dried over magnesium sulphate and filtered. Evaporation to dryness of the ether solution gave a yellow oil (0.27 g, 20% yield, b.p. 170°C/approx. 0.1 mm Hg). ^1H NMR ($CDCl_3$) δ, 0.80-1.04 (d, 3H, CH_3-CH-), 1.16-1.60 (m, 13H), 1.6-1.8 (2d, 6H, $-CH=C(CH_3)_2-$), 1.8-2.20 (m, 2H, $-CH_2-CH=C\langle$), 2.70-3.0 (m, 2H), 3.3 (t, 2H, $Br-CH_2-$), 4.04 (t, 2H, $N-CH_2-$), 4.94 (t, 1H, $-CH=C\langle$), 6.90-7.04 (m, 1H, indole H-2), 7.10-7.50 (m, 3H), 7.64-7.80 (m, 1H, indole H-4).

3.2.63 Preparation of 6-(3-citronellyl-1-indolyl)hexyl trimethyl ammonium bromide (47):

Under a nitrogen atmosphere, 6-(3-citronellyl-1-indolyl)hexyl bromide (46) (0.27 g, 0.0006 mole) was dissolved in absolute ethanol (50 ml) and 50% anhydrous trimethyl amine/ethanol solution (7.0 ml). The stirred solution was refluxed (12 hrs), cooled and the solvent evaporated. Addition of diethyl ether (dry, 25 ml) yielded a gummy solid upon scratching and cooling. The product was collected and freeze dried to yield white fluffy crystals (0.05 g, 17% yield, hygroscopic). ^{1}H NMR ($CDCl_3$) δ, 0.80 (d, 3H, CH-CH_3), 1.10-1.60 (m, 13H), 1.60-1.80 (2s, 6H, -CH=CMe_2), 1.80-2.20 (m, 2H, -CH_2-CH=C), 2.80 (m, 2H), 3.40 (s, 9H, -NMe_3), 3.42 (t, 2H, Br-CH_2-), 5.0 (m, 1H, -CH=C), 7.00-7.10 (m, 1H, indole H-2), 7.20-7.60 (m, 2H), 7.80-7.94 (m, 1H, indole H-4).

3.2.64 Preparation of N-methyl indole (1b) using potassium hydroxide and DMSO:

Crushed pellets of potassium hydroxide (5.6 g, 0.1 mol) were added to dimethyl sulphoxide (50 ml) and stirred for 15 minutes. Indole (2.9 g, 0.025 mol) was then added and the reaction mixture stirred for a further half hr, under a nitrogen atmosphere. Methyl iodide (3.70 g, 0.026 mol) in dimethyl sulphoxide (50 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring overnight.

Water (125-150 ml) was then added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each

of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give N-methyl indole (1b) as a pale yellow oil (2.56 g, 69% yield, b.p. 110°C/2.15 mm, Lit. b.p. 133°C/26 mm).[165] ^{1}H NMR ($CDCl_3$) δ, 3.72 (s, 3H, -N-Me), 6.50-6.60 (m, 1H, indole H-2), 7.0-7.42 (m, 4H), 7.60-7.80 (m, 1H, indole H-4).

3.2.65 Preparation of N-propyl indole (48) using potassium hydroxide and DMSO:

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (2.24 g, 0.04 mol) were added to dimethyl sulphoxide (40 ml) and stirred for half an hr. Indole (1.17 g, 0.01 mol) was then added and the reaction mixture stirred for a further 1 hr. n-Bromopropane (1.35 g, 0.011 mol) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of half an hr and the reaction mixture left stirring overnight.

Water (100 ml) was then added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give an orange coloured liquid which on distillation gave N-propyl indole (48) as a pale yellow oil (1.0 g, 63% yield, b.p. 120°C/0.05 mm.Hg.
^{1}H NMR ($CDCl_3$) δ, 0.80 (t, 3H, CH_2-CH_3), 1.70 (q, J ≃ 7.0 Hz, 2H, CH_3-CH_2-), 3.90 (t, J ≃ 7.0 Hz, 2H, -N-CH_2-$\underline{CH_2}$), 6.30-6.40 (m, 1H, indole H-2), 6.88-7.28 (m, 4H), 7.40-7.60 (m, 1H, indole H-4).

3.2.66 Preparation of N-dodecyl indole (3b) using potassium hydroxide and DMSO:

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (5.6 g, 0.1 mole) were added to dimethyl sulphoxide (50 ml) and stirred for half an hr. Indole (2.9 g, 0.025 mole) was then added and the reaction mixture stirred for a further 1 hr. Bromododecane (11.04 g, 0.05 mole) in dimethyl sulphoxide (60 ml) was then added dropwise over a period of half an hr and the reaction mixture left stirring for 7 hrs.

Water (125-150 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. On removal of the solvent and after distillation, N-dodecyl indole (3b) was obtained as a pale yellow oil (4.86 g, 74% yield, b.p. 140-150°C/0.35 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.0 (t, 3H, CH_2-Me), 1.1-2.00 (m, 20 H), 4.0 (t, J ≃ 7 Hz, 2H, -N-CH_2-), 6.20 (d, J ≃ 4Hz, 1H, indole H-2), 7.00-7.40 (m, 4H), 7.54-7.70 (m, 1H, indole H-4).

3.2.67 Preparation of 1-(10-bromodecyl)indole (49) using potassium hydroxide and DMSO:

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (5.6 g, 0.1 mole) were added to dimethyl sulphoxide (50 ml) and stirred for half an hr. Indole (2.92 g, 0.025 mole) was then added and the reaction mixture stirred for a further 1 hr. 1,10-Dibromo-

decane (11.25 g, 0.0375 mole) in dimethyl sulphoxide (50 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring overnight.

Water (100 ml) was then added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a brown coloured liquid which on distillation gave 1-(10-bromodecyl)indole (49) as a pale yellow oil (3.76 g, 45% yield, b.p. 150-160°C/0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 1.04-2.0 (m, 16H), 3.30 (t, J ≃ 7.0 Hz, 2H, Br-CH_2-), 4.02 (t, J ≃ 7.0 Hz, 2H, -N-CH_2-), 6.24-6.40 (m, 1H, indole H-2), 7.08-7.44 (m, 4H), 7.60-7.72 (m, 1H, indole H-4). Anal. calcd. for $C_{18}H_{26}NBr$: C, 64.28; H, 7.79; N, 4.16. Found: C, 64.08; H, 7.93; N, 4.14. The undistilled dark brown gum was found to be 1,10-bis(indolyl)decane (50) (1.79, 18% yield). ^{1}H NMR ($CDCl_3$) δ, 1.04-2.0 (m, 16H), 4.0 (t, 4H, N-$(CH_2)_2$), 6.44-6.60 (m, 2H, indole H-2), 7.00-7.50 (m, 8H), 7.60-7.80 (m, 2H, indole H-4).

3.2.68 Preparation of 1-(11-hydroxy undecyl)indole (51):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (11.2 g, 0.2 mole) were added to dimethyl sulphoxide (50 ml) and stirred for half an hr. Indole (5.85 g, 0.05 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanol (12.80 g, 0.051 mole) in dimethyl sulphoxide (50 ml) was then added

dropwise over a period of one hr, and the reaction mixture left stirring overnight (12 hrs).

Water (150 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 150 ml, 1 x 75 ml). Each of the ether extracts was back washed with water (3 x 75 ml, 1 x 50 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow liquid which on distillation gave 1-(11-hydroxyundecyl)indole (51) as a pale yellow oil (9.0 g, 63% yield, b.p. 165-170°C/0.1 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 1.2-2.1 (m, 18H), 3.64 (t, J ≃ 6.5 Hz, 2H, Br-CH_2-), 4.12 (t, J ≃ 8.0 Hz, 2H, CH_2-N-), 6.60-6.76 (m, 1H, indole H-2), 7.26-7.64 (m, 4H), 7.80-8.00 (m, 1H, indole H-4). Anal. calcd. for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found: C, 79.47; H, 9.99; N, 4.78.

3.2.69 Preparation of 10-(3-methyl,1-indolyl)-decyltrimethyl ammonium bromide (52):

Under a nitrogen atmosphere, 1-(10-bromodecyl)3-methyl indole (4) (0.5 g, 0.0014 mole) was dissolved in absolute ethanol (30 ml) and 50% anhydrous trimethyl amine/ethanol solution (5 ml). The stirred solution was refluxed (15 hrs), cooled and the solvent evaporated. Addition of diethyl ether (dry, 25 ml) yielded a gummy solid upon scratching and cooling. Ether was removed by filtration and the product was recrystallised from benzene (dry). Benzene was decanted off and the product dried and then dissolved in water (25 ml). Any water insoluble material was removed by filtration. The filtrate

was freeze dried to yield white fluffy crystals (0.36 g, 63% yield, hydroscopic). ^{1}H NMR (D_2O) δ, 0.9-1.80 (m, 16H), 2.2 (s, 3H, indole-Me), 2.9-3.2 (m, 11H, NMe_3 & $-CH_2-Br$), 3.7-4.00 (m, 2H, $-CH_2-N-$), 3.6-3.8 (m, 1H, indole H-2), 7.00-7.34 (m, 3H), 7.4-7.6 (m, 1H, indole H-4). Anal. calcd. for $C_{22}H_{37}N_2Br.H_2O$; C, 61.81; H, 9.19; N, 6.55. Found: C, 61.87; H, 9.11; N, 6.30.

3.2.70 Preparation of 1-(11-hydroxy undecyl)-3-methyl indole (7a): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (2.24, 0.04 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Methyl indole (2.62 g, 0.02 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanol (5.02 g, 0.02 mole) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (10 hrs).

Water (150 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 100 ml, 1 x 50 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow liquid which on distillation gave 1-(11-hydroxy undecyl)3-methyl indole (7a) as a pale yellow oil. The product was further purified by preparative TLC using silica gel (Merck) and Pet. ether (60-80°C), ethyl acetate (4.2 g, 67% yield, b.p. 170°C/0.1 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 1.16-2.00 (m, 18H), 2.36 (s, 3H, $-CH_3$), 3.54 (t, J ≃ 6.0 Hz, 2H, CH_2-OH),

3.96 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.80-6.98 (m, 1H, indole H-2), 7.0-7.40 (m, 3H), 7.50-7.70 (m, 1H, indole H-4). Anal. calcd. for $C_{20}H_{31}ON$; C, 79.68; H, 10.36; N, 4.65. Found: C, 79.43; H, 10.30; N, 4.50.

3.2.71 Preparation of 11-(3-methyl-1-indolyl)undecanoic acid (53): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (3.36 g, 0.06 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Methyl indole (2.0 g, 0.015 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanoic acid (4.77 g, 0.018 mole) in dimethyl sulphoxide (25 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring (12 hrs).

Water (200 ml) was added to the reaction mixture, and then treated with hydrochloric acid (5M) to pH 6.5. The solution was extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a brown liquid which on distillation gave 11-(3-methyl-1-indolyl)undecanoic acid (53) as a pale yellow oil (3.26 g, 69% yield, b.p. 157-160°C/approx. 0.01 mm Hg). ^1H NMR ($CDCl_3$) δ, 1.10-2.0 (m, 16H), 2.26-2.50 (t, 2H, $-CH_2-CO_2H$), 2.32 (s, 3H, indole-CH_3), 3.96 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 3.8 (s, 1H, indole H-2), 7.0-7.4 (m, 3H), 7.48-7.64 (m, 1H, indole H-4). Anal. calcd. for $C_{20}H_{29}NO_2$: C, 76.15; H, 9.27; N, 4.44. Found: C, 76.26; H, 9.45; N, 4.36.

3.2.72 Preparation of sodium dodecanoate (54):

Lauric acid (dodecanoic acid, 2.0 g, 0.01 mole, 95% pure) was dissolved in industrial methylated spirit (20 ml) and sodium bicarbonate (0.84 g, 0.01 mole) in water (20 ml) was added. The mixture was refluxed for half an hr. The solvents were removed leaving a semi solid material which was dissolved in absolute ethanol and then filtered. The solvent was evaporated to dryness and the remaining material was recrystallised from isopropanol to give sodium dodecanoate (54) as a white crystalline solid (1.95 g, 88% yield).

3.2.73 Preparation of sodium 11-(3-methyl-1-indolyl)undecanoate (55):

11-(3-Methyl-1-indolyl)undecanoic acid (0.97 g, 0.0031 mole) was dissolved in ethanol (20 ml) and sodium bicarbonate (0.26 g, 0.0031 mole) in water (20 ml) was added. The mixture was refluxed for half an hr. The solvents were removed, the residue washed with sodium dried diethyl ether and then dissolved in absolute ethanol (20 ml). Any insoluble material was removed by filtration and the solvent was evaporated to dryness to give 11-(3-methyl-1-indolyl) sodium undecanoate (55) as a pale yellow solid (0.83 g, 79% yield).

3.2.74 Preparation of 1-(6-bromohexyl)-3-hexyl indole (56):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.12 g, 0.02 mole) were added to dimethyl sulphoxide (20 ml) and stirred for half an hr. 3-Hexyl indole (34b) (1.0 g, 0.005 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel 1,6-dibromohexane (1.83 g, 0.0075 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,6-dibromohexane solution, over a period of one hr, and the reaction mixture left stirring (20 hrs).

Water (125 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil (1.32 g), which on distillation (three times) gave 1-(6-bromohexyl)-3-hexyl indole (56)[82] (0.4 g, 22% yield, b.p. 110-131°C/approx. 0.01 mm Hg) and 1-6 bis(3-hexyl-indolyl)-hexane (57) (0.31 g, 13% yield, b.p. 210-250°C/approx. 0.01 mm Hg) as a by-product. ^{1}H NMR for 1-(6-bromohexyl)-3-hexyl indole (56) ($CDCl_3$) δ, 0.76 (br. t, 3H, CH_3-CH_2), 1.08-2.0 (m, 16H), 2.6 (t, J ≃ 7.5 Hz, 2H), 3.26 (t, J ≃ 6.5 Hz, CH_2-Br), 3.96 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.76 (br.s, 1H, indole H-2), 6.96-7.40 (m, 3H), 7.50-7.70 (m, 1H, indole H-4). MS; m/e (%, dev. mmu), M^+, $C_{20}H_{30}N^{81}Br$, 365.1491 (24, -5.1), $C_{20}H_{30}N^{79}Br$, 363.1481 (26, -8.1), $C_{15}H_{19}N^{79}Br$, 292.0526 (100, -17.6), $C_{15}H_{19}N^{81}Br$, 294.0562 (98, -11.9), C_9H_7N, 129.0403 (18, -17.6).

^{1}H NMR for 1,6-bis(3-hexyl-indolyl)-hexane (57) ($CDCl_3$) δ, 0.76 (br. t, 6H, 2 x CH_3-CH_2), 1.16-2.0 (m, 24H), 2.64 (t, J ≃ 7.5 Hz, 4H), 3.92 (t, J ≃ 7.0 Hz, 4H, 2 x CH_2-N-), 6.72 (br. s, 2H, 2 x indole H-2), 7.0-7.36 (m, 6H), 7.50-7.70 (m, 2H, 2 x indole H-4).

MS; m/e (%, dev mmu), M^+, $C_{34}H_{48}N_2$, 484.3800 (4, -1.7), $C_{15}H_{20}N$, 214.1552 (4, -4.3), $C_{12}H_{13}N$, 171.1059 (6, +1.1), $C_{10}H_{10}N$, 144.0799 (5, -1.4), C_9H_8N, 130.0655 (12, -0.2).

3.2.75 Preparation of 6-(3-hexyl-1-indolyl)hexyl trimethyl ammonium bromide (58):

Under a nitrogen atmosphere, 6-(3-hexyl-1-indolyl)hexyl bromide (56) (0.4 g, 0.0011 mole) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine/ethanol solution (10 ml). The stirred solution was refluxed (16 hrs), cooled and the solvent evaporated. Addition of diethyl ether (dry, 30 ml) yielded a gummy solid upon scratching and cooling. The emulsion was centrifuged and the precipitated solid recrystallised from benzene. The benzene was then removed after further centrifugation. The solid material was dissolved in distilled water and filtered. Freeze drying of the filtrate gave 6-(3-hexyl-1-indolyl)hexyl trimethyl ammonium bromide (58) as white fluffy crystals (0.26 g, 56% yield, hygroscopic).[82] ^{1}H NMR ($CDCl_3$) δ, 0.80-1.10 (br. t, 3H, CH_3-CH_2), 1.24-1.90 (m, 16H), 2.72 (t, J ≃ 8.0 Hz, 2H), 3.4-3.8 (m, 11H, -CH_2-Br, NMe_3), 4.1 (t, J ≃ 8.0 Hz, 2H, -CH_2-N-), 7.04 (br. s, 1H, indole H-2), 7.3-7.62 (m, 3H), 7.8-8.0 (m, 1H, indole H-4). Anal. calcd. for $C_{23}H_{39}N_2Br$. ½ H_2O: C, 63.87; H, 9.32; N, 6.48. Found: C, 63.86; H, 9.35; N, 6.26.

3.2.76 Preparation of 1-(10-bromodecyl)-3-hexyl indole (59):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.12 g, 0.02 mole) were added to dimethyl sulphoxide (20 ml) and

stirred for half an hr. 3-Hexyl indole (34b) (1.0 g, 0.005 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel 1,10-dibromodecane (3.0 g, 0.01 mole) in dimethyl sulphoxide (20 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,10-dibromodecane solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which on distillation (2 times) gave 1-(10-bromodecyl)-3-hexyl indole (59) (1.0 g, 47% yield, b.p. 140-150°C/approx. 0.001 mm Hg), and a mixture of 1,10-bis(3-hexyl-1-indolyl)decane (60) and a minor amount of 1-(10-bromodecyl)-3-hexyl indole (59) (≃ 0.36 g, 17% yield) as an undistilled dark brown gum. ^{1}H NMR for 1-(10-bromodecyl)3-hexyl indole (59), ($CDCl_3$) δ, 0.8 (br. t,3H, CH_3-CH_2-), 1.16-2.0 (m, 24H), 2.64 (t, J ≃ 7.5 Hz, 2H), 3.30 (t, J ≃ 6.5 Hz, 2H, -CH_2-Br), 3.96 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.8 (br. s,1H, indole H-2), 7.0-7.40 (m, 3H), 7.50-7.70 (m, 1H, indole H-4). ^{1}H NMR for 1,10-bis(3-hexyl-indolyl)decane (60), ($CDCl_3$) δ, 0.70 (br. t,6H, 2 x CH_3-CH_2-), 1.10-2.0 (m, 32H), 2.6 (t, J ≃ 7.5 Hz, 4H, 2 x $\underline{CH_2}$-CH_2-), 3.9 (t, J ≃ 7.0 Hz, 4H, 2 x CH_2-N-), 6.8 (br. s, 2H, 2 x indole H-2), 7.0-7.4 (m, 6H), 7.5-7.7 (m, 2H, 2 x indole H-4).

MS for 1-(10-bromodecyl)-3-hexyl indole (59), m/e (%, dev. mmu), $C_{24}H_{38}N.^{81}Br$, 421.1965 (11, -20.3), $C_{24}H_{38}N^{79}Br$, 419.2127 (8, -6.1), $C_{19}H_{27}N^{81}Br$, 350.1128 (27, -18.0), $C_{19}H_{26}N$, 268.1962 (11, -10.3), $C_{10}H_9N$, 143.0739 (27, +0.4), C_9H_8N, 130.0623 (76, -3.3).

3.2.77 Preparation of 10-(3-hexyl-1-indolyl)decyl trimethyl ammonium bromide (61):

Under a nitrogen atmosphere, 10-(3-hexyl-1-indolyl)decyl bromide (59) (0.5 g, 0.012 mole) was dissolved in absolute ethanol (30 ml) and 50% anhydrous trimethyl amine/ethanol solution (10 ml). The stirred solution was refluxed (16 hrs), cooled and the solvent evaporated. Addition of diethyl ether (dry, 30 ml) yielded a gummy solid upon scratching and cooling. Ether was removed by filtration and the product was recrystallised from dry benzene. The product was dissolved in water (30 ml). The water solution was filtered and the filtrate freeze dried to give 10-(3-hexyl-1-indolyl)decyl trimethyl ammonium bromide (61) as white fluffy crystals (hygroscopic). ^{1}H NMR (D_2O) δ, 0.54-2.0 (m, 27H), 2.4 (br. t, 2H), 2.8-3.28 (m, 11H, CH_2-Br & NMe_3), 3.6-3.92 (br. t, 2H, CH_2-N-), 6.40-6.76 (m, 1H, indole H-2), 6.80-7.36 (m, 3H), 7.38-7.60 (m, 1H, indole H-4). Anal. calcd. for $C_{27}H_{47}N_2Br.H_2O$: C, 65.17; H, 9.92; N, 5.62. Found: C, 65.04; H, 10.02; N, 5.70.

3.2.78 Preparation of 11-(3-hexyl-1-indolyl)undecanol (62):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.12 g, 0.02 mole) were added to dimethyl sulphoxide (20 ml) and stirred for half an hr. 3-Hexyl indole (34b) (1.0 g, 0.005 mole)

was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanol (1.76 g, 0.007 mole) in dimethyl sulphoxide (20 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which was distilled and chromatographed (prep. TLC), on silica gel (Merck) using petroleum ether (60-80°C)-ethyl acetate as eluents, to give 11-(3-hexyl-1-indolyl)-undecanol (62) as a pale yellow oil (1.12 g, 60% yield, b.p. 130-150°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.76-1.02 (br.t, 3H, CH_3-CH_2), 1.12-2.0 (m, 26H), 2.66 (t, J ≃ 7.5 Hz, 2H), 3.58 (t, J ≃ 6.5 Hz, 2H, CH_2-OH), 4.00 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.84 (br. s, 1H, indole H-2), 7.0-7.44 (m, 3H), 7.58-7.80 (m, 1H, indole H-4). Anal. calcd. for $C_{25}H_{41}NO$: C, 80.80; H, 11.12; N, 3.76. Found: C, 80.80; H, 10.19; N, 3.73.

3.2.79 Preparation of sodium 11-(3-hexyl-1-indolyl)undecyl sulphate (63):

11-(3-Hexyl-1-indolyl)undecyl alcohol (62) (1.12 g, 0.003 mole) was treated with trimethyl ammonium sulphur trioxide complex (0.7 g, 0.0045 mole) in 1,2-dichloroethane (50 ml) and heated under reflux (24 hrs). The excess of trimethyl ammonium sulphur trioxide was removed by filtration and 1,2-dichloroethane was evaporated to dryness.

The residue was dissolved in water (25 ml) and an excess of a sodium hydroxide solution (50 ml, 1M) added to it. The solution was then treated with hydrochloric acid (0.1 M) to pH 8.5 to 9.0. Water was removed and the residue added to absolute ethanol (50 ml) and filtered. The ethanol was then evaporated to dryness to give sodium 11-(3-hexyl-1-indolyl)-undecyl sulphate (63) as a deep orange coloured solid[117] (0.20 g, 14% yield). A minor amount of unreacted starting material (62) was also found to be present (IR) ^{1}H NMR ($CDCl_3$) δ, 0.75-1.00 (br.t, 3H, CH_3-CH_2-), 1.00-1.200 (m, 26H), 2.60 (t, J ≃ 8.0 Hz, 2H), 3.00-3.60 (br.m, 2H, $-CH_2-o-\bar{S}O_3\overset{+}{N}a$), 3.75-4.25 (br.t, 2H, $-CH_2-N-$), 6.75 (s, 1H, indole H-2), 7.00-7.40 (m, 3H), 7.50-7.70 (m, 1H, indole H-4). IR (neat) 740 (indole H-2), 1070 (SO_4), 1240 cm^{-1} (S=O). MS; m/e (% dev. mmu), $C_{24}H_{35}NO_4S$, 433.2115 (6, -17.1), $C_{10}H_{10}N$, 144.0652 (73, -16.1), C_9H_8N, 130.050 (100, -15.3).

3.2.80 Preparation of 11-(3-hexyl-1-indolyl)undecanoic acid (64): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.12 g, 0.02 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Hexyl indole (34b) (1.0 g, 0.005 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanoic acid (1.59 g, 0.006 mole) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture, followed by hydrochloric acid (5M) to pH 6.5 and the solution extracted with

diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which on distillation gave 11-(3-hexyl-1-indolyl)undecanoic acid (64) (1.26 g, 65% yield, b.p. 185-190°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.1 (br. t, 3H, CH_3-CH_2), 1.2-2.0 (m, 24H), 2.28 (t, J ≃ 7.5 Hz, 2H, CH_2-CO_2H), 2.68 (t, J ≃ 7.0 Hz, 2H), 4.0 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.88 (br. s, 1H, indole H-2), 7.08-7.50 (m, 3H), 7.60-7.80 (m, 1H, indole H-4). Anal. calcd. for $C_{25}H_{39}NO_2$: C, 77.88; H, 10.19; N, 3.63. Found: C, 77.90; H, 10.28; N, 3.55.

3.2.81 Preparation of sodium 11-(3-hexyl-1-indolyl)undecanoate (65): 11-(3-Hexyl-1-indolyl)undecanoic acid (64) (0.5 g, 0.0013 mole) was dissolved in diethyl ether (20 ml), and sodium bicarbonate (0.1092 g, 0.0013 mole) in water (20 ml) was added. The reaction mixture was refluxed with stirring for half an hr. The solvents were removed, the residue washed with sodium dried diethyl ether and then dissolved in absolute ethanol (20 ml). Any immiscible material was removed by filtration and the solvent was evaporated to dryness to give sodium 11-(3-hexyl-1-indolyl)undecanoate (65) as a dark brown solid (0.2 g, 38% yield). ^{1}H NMR ($CDCl_3$) δ, 0.6-1.8 (m, 27H), 1.9-2.4 (m, 2H), 2.5-2.8 (m, 2H), 3.6-3.94 (m, 2H), 6.5-6.7 (m, 1H, indole H-2), 6.8-7.2 (m, 3H), 7.4-7.6 (m, 1H, indole H-4). Unidentified impurity was present (NMR).

3.2.82 Preparation of 6-(3-nonyl-1-indolyl)hexyl bromide (66):

Under a nitrogen atmosphere crushed pellets of potassium hydroxide (0.93 g, 0.016 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Nonyl indole (27a) (1.0 g, 0.0041 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel 1,6-dibromohexane (1.95 g, 0.008 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,6-dibromohexane solution, over a period of one hr, and the reaction mixture left stirring (4 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which on distillation (2 times) gave 6-(3-nonyl-1-indolyl)hexyl bromide (66) (1.10 g, 66% yield, b.p. 160-170°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.04 (br. t, 3H, CH_3-CH_2-), 1.20-2.0 (m, 22H), 2.70 (t, J ≃ 7.5 Hz, 2H), 3.34 (t, J ≃ 6.5 Hz, 2H, CH_2-Br), 4.08 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.90 (br. s, 1H, indole H-2), 7.16-7.54 (m, 3H), 7.64-7.8 (m, 1H, indole H-4). MS; m/e (%, dev mmu), M^+, $C_{23}H_{36}N^{81}Br$, 407.2051 (24, +4.0), $C_{23}H_{36}N^{79}Br$, 405.1997 (24, -3.4), $C_{15}H_{19}N^{81}Br$, 294.0485 (95, -19.2), $C_{15}H_{19}N^{79}Br$, 292.0487 (100, -16.4), C_9H_7N, 129.0547 (12, -3.2).

The undistilled dark brown solid was found to be 1-6-bis(3-nonyl-indolyl)hexane (67) (minor amount). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.04 (br.t, 6H, 2 x CH_3-CH_2), 1.08-2.0 (m, 36H), 2.64 (t, J ≃ 7.5 Hz, 4H), 3.96 (t, J ≃ 7.0 Hz, 4H, 2 x CH_2-N-), 6.80 (br.s, 2H, 2 x indole H-2), 7.04-7.32 (m, 6H), 7.54-7.70 (m, 2H, 2 x indole H-4). MS; m/e, (%), M^+, $C_{40}H_{60}N_2$, 568.4706 (37, -5.1 mmu), 156.0531 (43), 143.0457 (47), 129.0357 (42).

3.2.83 Preparation of 6-(3-nonyl-1-indolyl)hexyl trimethyl ammonium bromide (68):

Under a nitrogen atmosphere, 6-(3-nonyl-1-indolyl)hexyl bromide (66) (0.5 g, 0.0012 mole) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The stirred solution was refluxed (16 hrs), cooled and the solvent evaporated. Addition of sodium dried diethyl ether (30 ml) yielded a gummy solid upon scratching and cooling. Ether was decanted off after centrifuging. The product was recrystallised from dry benzene and the solvent was decanted off after centrifuging the product. The solid material was dissolved in distilled water (40 ml) and filtered. The filtrate was freeze dried to give 6-(3-nonyl-1-indolyl)hexyl-trimethyl ammonium bromide (68) (0.2 g, 35% yield, hygroscopic). ^{1}H NMR ($CDCl_3$) δ, 0.68-0.98 (br.t, 3H, CH_3-CH_2-), 1.04-2.0 (m, 22H), 2.56 (t, J ≃ 7.5 Hz, 2H), 3.20-3.52 (m, 11H, $Me_3\overset{+}{N}$ & CH_2-Nr), 3.9 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.7 (br. s, 1H, indole H-2), 6.88-7.24 (m, 3H), 7.36-7.60 (m, 1H, indole H-4). Anal. calcd. for $C_{26}H_{45}N_2Br.\frac{1}{2}H_2O$: C, 65.82; H, 9.70; N, 5.90. Found: C, 65.74; H, 9.78; N, 6.01.

3.2.84 Preparation of 10-(3-nonyl-1-indolyl)decyl bromide (11a):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.8 g, 0.032 mole) were added to dimethyl sulphoxide (40 ml) and stirred for half an hr. 3-Nonyl indole (27a) (2.0 g, 0.0082 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel, 1,10-dibromo decane (4.92 g, 0.0164 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,10-dibromodecane solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which on distillation gave 10-(3-nonyl-1-indolyl)decyl bromide (11a) as a pale yellow oil (2.63 g, 69% yield, b.p. 150-170°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.02 (br.t, 3H, CH_3-CH_2-), 1.10-2.00 (m, 30H), 2.66 (t, J ≃ 7.5 Hz, 2H), 3.32 (t, J ≃ 6.5 Hz, 2H, -CH_2-Br), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.88 (br. s, 1H, indole H-2), 7.0-7.44 (m, 3H), 7.6-7.74 (m, 1H, indole H-4). MS; m/e (% dev. mmu), M^+, $C_{27}H_{44}N^{81}Br$, 463.2755 (5, + 11.7), $C_{27}H_{44}N^{79}Br$, 461.2799 (8, +14.2), $C_{19}H_{27}N^{81}Br$, 350.1187 (19, -12.0), $C_{19}H_{27}N^{79}Br$, 348.1326 (38, -0.1), C_9H_7N, 129.0617 (14, +3.8).

3.2.85 Preparation of 10-(3-nonyl-1-indolyl)decyl trimethyl ammonium bromide (70):

Under a nitrogen atmosphere, 10(3-nonyl-1-indolyl)decyl bromide (69) (0.5 g, 0.0011 mole) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The solution was refluxed (15 hrs), cooled and the solvent evaporated. Addition of sodium dried diethyl ether (30 ml) yielded a gummy solid upon scratching and cooling. The solid was centrifuged and the precipitates recrystallised from dry benzene. The solvent was decanted off after centrifugation. The solid obtained was dissolved in distilled water (30-40 ml) and filtered. The filtrate was freeze dried to give 10(3-nonyl-1-indolyl)decyl-trimethyl ammonium bromide (70) (0.4 g, 74% yield, hygroscopic). ^{1}H NMR ($CDCl_3$) δ, 0.72-1.0 (br. t, 3H, CH_3-CH_2-), 1.08-2.0 (m, 30H), 2.6 (t, J ≃ 7.5 Hz, 2H), 3.2-3.6 (m, 11H, NMe_3 & CH_2-Br), 3.92 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.7 (br, s, 1H, indole H-2), 6.88-7.28 (m, 3H), 7.4-7.6 (m, 1H, indole H-4). Anal. calcd. for $C_{30}H_{53}N_2Br.H_2O$: C, 66.77; H, 10.27; N, 5.19. Found: C, 66.85; H, 10.33; N, 5.23.

3.2.86 Preparation of 3-(3-nonyl-1-indolyl)propyl alcohol (71):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (2.68 g, 0.048 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Nonyl-indole (27a) (2.29 g, 0.0094 mole) was then added and the reaction mixture stirred for a further 1 hr. 3-Bromopropyl alcohol (1.31 g, 0.0094 mole) in dimethyl sulphoxide (25 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which was distilled and then chromatographed (prep. TLC) on silica gel (Merck) using petroleum ether (60-80°C) and ethyl acetate as eluents. 3-(3-Nonyl-1-indolyl)propanol (71) was obtained as a pale yellow oil (1.5 g, 53% yield, b.p. 120-130°C/approx. 0.1 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.80-1.0 (br.t, 3H, CH_3-CH_2-), 1.12-1.80 (m, 14H), 1.84-2.2 (m, 2H, -CH_2-$\underline{CH_2}$-CH_2-OH), 2.6 (t, J ≃ 7.5 Hz, 2H), 3.40 (br.t, 2H, -CH_2-OH), 4.04 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.7 (br. s, 1H, indole H-2), 6.84-7.36 (m, 3H), 7.40-7.60 (m, 1H, indole H-4). MS; m/e (%, dev. mmu), M^+, $C_{20}H_{31}NO$, 301.2406 (16, 0.0), $C_{12}H_{14}NO$, 188.1226 (100, +15.1), $C_{10}H_{10}N$, 144.0826 (30, +1.3), C_9H_8N, 130.0723 (17, +6.6).

3.2.87 Preparation of 11-(3-nonyl-1-indolyl)undecanol (72):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.65 g, 0.012 mole) were added to dimethyl sulphoxide (20 ml) and stirred for half an hr. 3-Nonyl indole (27a) (0.7 g, 0.0029 mole) was then added and the reaction mixture stirred for a further .1 hr. 11-Bromoundecanol (0.87 g, 0.0035 mole) in dimethyl sulphoxide (20 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which was distilled and chromatographed (Prep. TLC) on silica gel (Merck) using petroleum ether (60-80°C)/ethyl acetate as eluents, to obtain 11-(3-nonyl-1-indolyl)undecanol (72) as a white solid (0.73 g, 61% yield, b.p. 140-150°C/approx. 0.001 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.80-1.04 (br.t, 3H, CH_3-CH_2-), 1.08-2.0 (m, 32H), 2.64 (t, J ≃ 7.5 Hz, 2H), 3.56 (t, J ≃ 6.5 Hz, 2H, -CH_2-OH), 3.96 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.8 (br. s, 1H, indole H-2), 7.0-7.40 (m, 3H), 7.50-7.70 (m, 1H, indole H-4). Anal. calcd. for $C_{28}H_{47}NO$: C, 81.29; H, 11.45; N, 3.39. Found: C, 81.10; H, 11.41; N, 3.28.

3.2.88 Attempted preparation of sodium 11-(3-nonyl-1-indolyl) undecyl sulphate (73):

11-(3-Nonyl-1-indolyl)undecanol (72) (0.7 g, 0.0017 mole) was treated with trimethyl ammonium sulphur trioxide complex (0.34 g, 0.0024 mole) in 1,2-dichloroethane (50 ml) and heated under reflux (24 hrs), under a nitrogen atmosphere. Excess trimethyl ammonium sulphur trioxide was removed by filtration and 1,2-dichloroethane was evaporated to dryness. The residue was dissolved in water (50 ml) and then passed through a sodium ion exchange column (zeo Karb 225 SRC 14 Resin). The aqueous solution was then washed with diethyl ether (2 x 25 ml), and the water was evaporated to give a brown solid. ^{1}H NMR and IR analysis of this solid showed that the product formation had only

occurred to a very small extent. The major constituent was trimethyl ammonium 11-(3-nonyl-1-indolyl)undecyl sulphate.

3.2.89 Preparation of 11-(3-nonyl-1-indolyl)undecanoic acid (74): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.92 g, 0.016 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Nonyl indole (27a) (1.0 g, 0.0041 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanoic acid (1.3 g, 0.0049 mole) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture, and then treated with hydrochloric acid (0.5 M) to pH 6.5. The solution was then extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness and the excess of 11-bromo-undecanoic acid was removed by distillation. The undistilled brown oil solidified on standing at room temperature to give 11-(3-nonyl-1-indolyl)undecanoic acid (74) (1.61 g, 92% yield, b.p. 155-160°C/ approx. 0.001 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.08 (br.t, 3H, CH_3-CH_2-), 1.2-2.02 (m, 30H), 2.24 (t, J ≃ 6.5 Hz, 2H, -CH_2-CO_2H), 2.64 (t, J ≃ 7.5 Hz, 2H), 4.0 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.9 (br. s, 1H, indole H-2), 7.04-7.44 (m, 3H), 7.60-7.80 (m, 1H, indole H-4). Anal. calcd. for $C_{28}H_{45}NO_2$: C, 78.64; H, 10.60; N, 3.28. Found:

C, 78.52; H, 10.67; N, 3.22. MS; m/e (%, dev. mmu) M^+, $C_{28}H_{45}NO_2$, 427.3555 (45, -4.0), $C_{20}H_{28}NO_2$, 314.2304 (100, +18.5), $C_{10}H_{10}N$, 144.0755 (40, -3.8), C_9H_8N, 130.0648 (56, -0.9).

3.2.90 Preparation of sodium 11-(3-nonyl-1-indolyl)undecanoate (75): 11-(3-Nonyl-1-indolyl)undecanoic acid (74) (0.46 g, 0.0011 mole) was dissolved in ethyl alcohol (25 ml) and sodium bicarbonate (0.0924 g, 0.0011 mole in water (20 ml)) was added. The reaction mixture was refluxed with stirring for half an hr. The solvents were removed, the residue washed with sodium dried diethyl ether and then dissolved in absolute ethanol. Any immiscible material was removed by filtration and the solvent evaporated to dryness to give sodium 11-(3-nonyl-1-indolyl)undecanoate (75) as a dark brown gum (0.2 g, 41% yield). ^{1}H NMR ($CDCl_3$) δ, 0.70-1.90 (m, 35H), 1.94-2.2 (m, 2H), 2.4-2.8 (m, 2H), 3.5-3.7 (m, 2H), 6.4-6.74 (m, 1H, indole H-2), 6.76-7.20 (m, 3H), 7.3-7.6 (m, 1H, indole H-4).

3.2.91 Preparation of 6-(3-dodecyl-1-indolyl)hexyl bromide (76): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.8 g, 0.014 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Dodecyl indole (29a) (1.0 g, 0.0035 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel, 1,6-dibromohexane (1.7 g, 0.007 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,6-dibromohexane

solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which on distillation gave 6-(3-dodecyl-1-indolyl)hexyl bromide (76) (0.64 g, 40% yield, b.p. 160-180°C/approx. 0.05 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.0 (br.t, 3H, CH_3-CH_2-), 1.1-2.0 (m, 28H), 2.64 (t, J ≃ 8.0 Hz, 2H), 3.28(t, J ≃ 6.5 Hz, 2H, -CH_2-Br), 4.0 (t, J ≃ 7.0 Hz, 2H, CH_2--N-), 6.84 (br. s, 1H, indole H-2), 7.0-7.40 (m, 3H), 7.56-7.72 (m, 1H, indole H-4).

3.2.92 Preparation of 6-(3-dodecyl-1-indolyl)hexyl trimethyl ammonium bromide (69):

Under a nitrogen atmosphere, 6-(3-dodecyl-1-indolyl)hexyl bromide (76) (0.54 g, 0.0012 mole) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The stirred solution was refluxed (12 hrs), cooled and the solvent evaporated. Addition of sodium dried diethyl ether (30 ml) yielded a gummy solid upon scratching and cooling. The ether was decanted off after centrifuging. The product was recrystallised from benzene and the solvent was again decanted off after centrifuging the solid. The solid material was dissolved in distilled water (50 ml) and filtered. The filtrate was freeze dried to give

6-(3-dodecyl-1-indolyl)hexyl trimethyl ammonium bromide (69) as a white fluffy crystalline solid (0.3 g, 50% yield, hygroscopic). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.0 (br.t, 3H, CH_3-CH_2-), 1.1-2.0 (m, 28H), 2.54 (t, J ≃ 8.0 Hz, 2H), 3.2-3.50 (m, 11H, NMe_3, & -CH_2-Br), 3.92 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.7 (br. s, 1H, indole H-2), 6.9-7.3 (m, 3H), 7.4-7.6 (m, 1H, indole H-4). Anal. calcd. for $C_{29}H_{51}N_2Br$.$\frac{3}{4}H_2O$. C, 66.83; H, 10.15; N, 5.37. Found: C, 66.93; H, 10.24; N, 5.26.

3.2.93 Preparation of 10-(3-dodecyl-1-indolyl)decyl bromide (77): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.784 g, 0.014 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Dodecyl indole (29a) (0.0035 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel 1,10-dibromodecane (2.1 g, 0.007 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,10-dibromodecane solution over a period of one hr and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 mls). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined, dried over magnesium sulphate and the solvent evaporated to dryness to give a dark brown oil. An attempt was made to purify this material by distillation but was not successful.

From the residue, 10-(3-dodecyl-1-indolyl)-decyl bromide (77) was obtained along with a minor amount of unidentified impurities (NMR) (1.71 g, 97% yield). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.0 (br.t, J ≃ 5.0 Hz, 3H, CH_3-CH_2-), 1.08-2.0 (m, 36H), 2.68 (t, J ≃ 7.5 Hz, 2H) 3.32 (t, J ≃ 7.0 Hz, 2H, CH_2-Br), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.86 (br.s, 1H, indole H-2), 7.0-7.42 (m, 3H), 7.6-7.76 (m, 1H, indole H-4). MS; m/e (% dev. mmu); M^+, $C_{30}H_{50}N^{81}Br$, 505.3114 (53, +0.6), $C_{30}H_{50}N^{79}Br$, 503.3139 (53, +1.2), $C_{19}H_{27}N^{81}Br$, 350.0988 (100, -31.9), $C_{19}H_{27}N^{79}Br$, 348.0991 (99, -33.6), C_9H_7N, 129.0389 (12, -18.9).

3.2.94 Preparation of 10-(3-dodecyl-1-indolyl)decyl trimethyl ammonium bromide (78):

Under a nitrogen atmosphere, 10-(3-dodecyl-1-indolyl)decyl bromide (77) (0.5 g, 0.00099 mole) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The stirred solution was refluxed (15 hrs), cooled and the solvent evaporated. Addition of sodium dried diethyl ether (30 ml) yielded a gummy solid upon scratching and cooling. The ether was decanted off after using a centrifuge. An attempt was made to recrystallise the product from dry benzene but was not successful. The solid material was dissolved in water (50 ml), filtered off and the filtrate freeze dried to give 10-(3-dodecyl-1-indolyl)decyl trimethyl ammonium bromide (78) as white fluffy crystals (0.2 g, 36% yield, hygroscopic). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.04 (br.t, J ≃ 5.0 Hz, 3H, CH_3-CH_2), 1.08-2.0 (m, 36H), 2.52 (t, J ≃ 7.0 Hz, 2H), 3.2-3.8 (m, 11H, N-Me_3 & -CH_2-Br), 3.9 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.68 (br.s, 1H, indole H-2), 7.0-7.38 (m, 3H), 7.4-7.64 (m, 1H, indole H-4).

Analysis of this material by mass spectroscopy indicated that the obtained material was a mixture of 10-(3-dodecyl-1-indolyl)decyl trimethyl ammonium bromide (78), 10(3-dodecyl-1-indolyl)-decyl bromide (77) (minor amount < 5%) and 1,10-dibromodecane (minor amount < 5%). MS m/e, M^+, 468, 313, 298, 130.

3.2.95 Preparation of 11-(3-dodecyl-1-indolyl)undecanol (79):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.8 g, 0.014 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Dodecyl indole (29a) (1.0 g, 0.0035 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanol (0.97 g, 0.00385 mole) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which was distilled and then chromatographed (prep. TLC) on silica gel (Merck) using petroleum ether (60-80°C)-ethyl acetate as eluents. 11-(3-Docyl-1-indolyl)undecanol (79) solidified on standing at room temperature (0.87 g, 54% yield, b.p. 180°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.04 (br.t, 3H, CH_3-CH_2-), 1.08-2.0 (m, 38H), 2.70 (t, J ≃ 7.5 Hz, 2H), 3.64 (t, J ≃ 6.5 Hz, 2H, CH_2-OH), 4.04 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.96 (br.s, 1H, indole H-2), 7.04-7.44

(m, 3H), 7.6-7.8 (m, 1H, indole H-4). Anal. calcd. for $C_{31}H_{53}NO$: C, 81.70; H, 11.72; N, 3.07. Found: C, 81.51; H, 11.90; N, 3.01.

3.2.96 Preparation of sodium 11-(3-dodecyl-1-indolyl)undecyl sulphate (80):

Under a nitrogen atmosphere, 11-(3-dodecyl-1-indolyl)undecanol (79) (0.87 g, 0.0019 mole) was treated with trimethyl ammonium sulphur trioxide complex (0.3 g, 0.0022 mole) in 1,2-dichloroethane (50 ml) and heated under reflux (24 hrs). Excess of trimethyl ammonium sulphur trioxide was removed by filtration and 1,2-dichloroethane was evaporated to dryness. The residue was dissolved in water (50 ml) and an excess of sodium hydroxide solution (50 ml, 1M) added. The solution was then treated with hydrochloric acid (0.1 M) to pH 8.5 to 9.0. Water was removed and the residue was dissolved in absolute ethanol (50 ml) filtered, and the solvent evaporated to dryness to give a deep orange coloured solid.

Analysis of this material by ^1H NMR spectroscopy indicated that the material was contaminated with unidentified impurities. MS; m/e (%, dev. mmu), $C_{30}H_{50}NO_2$; 456.3957 (7, +11.5), $C_{31}H_{51}NO$, 453.3775 (19, -19.6), $C_{20}H_{30}NO$, 300.2168 (68, -15.9), $C_{20}H_{28}NO$, 298.2212 (86, +4.1), C_9H_8N, 130.0637 (87, +1.5).

3.2.97 Preparation of 10-(3-dodecyl-1-indolyl)undecanoic acid (81):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.8 g, 0.014 mole) were added to dimethyl sulphoxide (25 ml) and

stirred for half an hr. 3-Dodecyl indole (29a) (1.0g, 0.0035 mole) was then added and the reaction mixture stirred for a further hr. 11-Bromoundecanoic acid (1.02 g, 0.0038 mole) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and then treated with hydrochloric acid (0.5 M) to pH 6.5. The solution was then extracted with diethyl ether (3 x 150 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 100 ml, 1 x 50 ml). The ether layers were combined, dried over magnesium sulphate and the solvent evaporated to dryness to give a yellow oil which on distillation gave 11-(3-dodecyl-1-indolyl)undecanoic acid (81), (1.57 g, 95% yield, b.p. 195-205°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.0 (br.t, 3H, CH_3-CH_2), 1.08-2.0 (m, 36H), 2.2 (t, J ≃ 8.0 Hz, 2H, -CH_2-CO_2H), 2.64 (t, J ≃ 7.5 Hz, 2H), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 2.84 (br.s, 1H, indole H-2), 7.0-7.40 (m, 3H), 7.6-7.8 (m, 1H, indole H-4). Anal. calcd. for $C_{31}H_{51}NO_2$: C, 79.26; H, 10.94; N, 2.98. Found: C, 79.03; H, 10.91; N, 3.14.

3.2.98 Preparation of sodium-11-(3-dodecyl-1-indolyl)undecanoate (82):

11-(3-Dodecyl-1-indolyl)undecanoic acid (81) (0.469 g, 0.001 mole) was dissolved in ethanol (20 ml), and sodium bicarbonate (0.084 g, 0.001 mole) in water (20 ml) was added. The reaction mixture was refluxed with stirring (0.5 hr). The solvents were removed, the

residue washed with sodium dried diethyl ether and then dissolved in absolute ethanol. Any insoluble material was removed by filtration and the solvent evaporated to dryness to give sodium 11-(3-dodecyl-1-indolyl)undecanoate (82) as a dark brown gum (0.16 g, 33% yield). ^{1}H NMR ($CDCl_3$) δ, 0.7-1.8 (m, 39H), 2.4-2.9 (m, 4H), 3.52-3.9 (m, 2H, $-CH_2-N-$), 6.4-6.6 (m, 1H, indole H-2), 6.8-7.10 (m, 3H), 7.3-7.5 (m, 1H, indole H-4).

3.2.99 Preparation of 6-(3-octadecyl-1-indolyl)hexyl bromide (83): Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.61 g, 0.011 mole) were added to dimethyl sulphoxide (20 ml) and stirred for half an hr. 3-Octadecyl indole (31a) (1.0 g, 0.0027 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel 1,6-dibromohexane (1.31 g, 0.0054 mole) in dimethyl sulphoxide (20 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,6-dibromohexane solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a yellow oil which solidified on standing at room temperature. Any unreacted 1,6-dibromohexane was removed by

washing the solid material with absolute ethanol (0.64 g, 45% yield, m.p. 35-45°C). ^{1}H NMR ($CDCl_3$) δ, 0.80-1.04 (br.t, 3H, CH_3-CH_2-), 1.08-2.04 (m, 40H), 2.68 (t, J ≃ 7.0 Hz, 2H), 3.3 (t, J ≃ 7.0 Hz, 2H, -CH_2-Br), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.84 (br.s, 1H, indole H-2), 7.0-7.44 (m, 3H), 7.6-7.80 (m, 1H, indole H-4). MS; m/e (%, dev. mmu), M^+, $C_{32}H_{54}N\,^{81}Br$, 533.3549 (26, +12.9), $C_{32}H_{54}N\,^{79}Br$, 531.3632 (16, +19.2), $C_{15}H_{19}N\,^{81}Br$, 294.1071 (90, +21.3), $C_{15}H_{19}N\,^{79}Br$, 292.0969 (96, +26.8), C_9H_7N, 129.0753 (16, +17.4).

3.2.100 Preparation of 6-(3-octadecyl-1-indolyl)hexyl trimethyl ammonium bromide (84):

Under a nitrogen atmosphere, 6-(3-octadecyl-1-indolyl)hexyl bromide (83) (0.5 g, 0.0093 mole) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The stirred solution was refluxed (36 hrs), cooled and the solvent evaporated. Addition of sodium dried diethyl ether (30 ml) yielded a gummy solid upon scratching and cooling. The ether was decanted off after centrifuging the solid residue. Addition of dry benzene gave an emulsion upon cooling. The solid material was again centrifuged and the benzene decanted off. The product was dissolved in distilled water (25 ml), filtered and the filtrate freeze dried to give 6-(3-octadecyl-1-indolyl)-hexyl trimethyl ammonium bromide (84) as a white fluffy crystalline solid (0.3 g, 56% yield, hygroscopic). ^{1}H NMR ($CDCl_3$) δ, 0.84-1.02 (br.t, J ≃ 5.0 Hz, 3H, CH_3-CH_2-), 1.24-2.0 (m, 40H), 2.68 (t, J ≃ 7.5 Hz, 2H), 3.24-3.60 (m, 11 H, NMe_3 & -CH_2-N-), 6.8 (br.s, 1H, indole H-2), 7.0-7.40 (m, 3H), 7.5-7.70 (m, 1H, indole H-4). Anal. calcd. for $C_{35}H_{63}N_2Br$ .1½ H_2O: C, 67.93; H, 4.73; N, 10.75; Found: C, 67.92; H, 4.51; N, 10.82.

3.2.101 Preparation of 10-(3-octadecyl-1-indolyl)decyl bromide (85):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.6 g, 0.011 mole) were added to dimethyl sulphoxide (20 ml) and stirred for half an hr. 3-Octadecyl indole (31a) (1.0 g, 0.0027 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel, 1,10-dibromodecane (1.21 g, 0.004 mole) in dimethyl sulphoxide (20 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,10-dibromodecane solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined, dried over magnesium sulphate and the solvent evaporated to dryness to give a yellow oil. The unreacted 1,10-dibromodecane was removed by distillation. The residue was washed with absolute ethanol to give 10-(3-octadecyl-1-indolyl)decyl bromide (85) as a brown gummy solid (0.74 g, 46% yield, m.p. 26°C). ^{1}H NMR ($CDCl_3$) δ, 0.7-1.0 (br.t, 3H, CH_3-CH_2-), 1.4-2.0 (m, 48H), 2.50 (t, J ≃ 7.5 Hz, 2H), 3.16 (t, J ≃ 6.5 Hz, 2H, -CH_2-Br), 3.8 (t, J ≃ 7.0 Hz, 2H, CH_2-N-), 6.5 (br.s, 1H, indole H-2), 6.70-7.04 (m, 3H), 7.2-7.4 (m, 1H, indole H-4). MS; m/e (%, dev. mmu), $C_{36}H_{62}N\,^{81}Br$, 589.3818 (6, -22.2), $C_{36}H_{62}N\,^{79}Br$, 587.3860 (4, -20.6),

$C_{19}H_{27}N\,^{81}Br$, 350.1383 (11, +7.5), $C_{19}H_{27}N\,^{79}Br$, 348.1622 (12, +29.5), $C_{19}H_{26}N$, 268.2118 (23, +5.3), C_9H_8N, 130.0689 (61, +3.2).

3.2.102 Preparation of 10-(3-octadecyl-1-indolyl)decyl trimethyl ammonium bromide (86):

Under a nitrogen atmosphere, 10-(3-octadecyl-1-indolyl)decyl bromide (85) (0.5 g, 0.00085 mole) was dissolved in absolute ethanol (15 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The stirred solution was refluxed (48 hrs), cooled and the solvent evaporated. Addition of sodium dried diethyl ether (30 ml) yielded a gummy solid upon scratching and cooling. The ether was decanted off after centrifuging the solid. This was then dissolved in dry benzene (20 ml) and an emulsion was obtained upon cooling and scratching. The benzene was decanted off after further centrifuging the solid which was then dissolved in distilled water (30 ml), filtered and the filtrate was freeze dried to give 10-(3-octadecyl-1-indoyl)decyl trimethyl ammonium bromide (86) as a white solid (0.2 g, 36% yield, hygroscopic). ^1H NMR ($CDCl_3$) δ, 0.8-1.08 (br.t, 3H, CH_3-CH_2-), 1.1-2.2 (m, 48H), 2.6 (t, J ≃ 8.0 Hz, 2H), 3.30-3.94 (m, 11H, NMe_3 and -CH_2-Br), 3.96 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.8 (br.s, 1H, indole H-2), 7.0-7.44 (m, 3H), 7.5-7.7 (m, 1H, indole H-4). Microanalysis showed the product to be impure.

3.2.103 Preparation of 11-(3-octadecyl-1-indolyl)undecanol (87):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.54 g, 0.0096 mole) were added to dimethyl sulphoxide (20 ml)

and stirred for half an hr. 3-Octadecyl indole (31a) (0.9 g, 0.0024 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanol (0.73 g, 0.0029 mole) in dimethyl sulphoxide (20 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and the solution extracted with diethyl ether (3 x 50 ml, 1 x 25 ml). Each of the ether extracts was back washed with water (3 x 50 ml, 1 x 25 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a tan powder. The unreacted 11-bromoundecanol was removed by distillation. The crude product was crystallised from petroleum ether (60-80°C) and chromatographed (prep. TLC), using silica gel (Merck) and petroleum ether (60-80°C)-ethyl acetate as eluents, to give 11-(3-octadecyl-1-indolyl)undecanol (87) (0.5 g, 38% yield, m.p. 50.5-51.5°C). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.04 (br.t, 3H, CH_3-CH_2-), 1.08-2.0 (m, 50H), 2.64 (t, J ≃ 7.5 Hz, 2H), 3.58 (t, J ≃ 6.5 Hz, 2H, CH_2-OH), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.84 (br.s, 1H, indole H-2), 7.0-7.42 (m, 3H), 7.56-7.76 (m, 1H, indole H-4). Anal. calcd. for $C_{37}H_{65}NO$: C, 82.30; H, 12.14; N, 2.60. Found: C, 82.21; H, 12.25; N, 2.65.

3.2.104 Preparation of 11-(3-octadecyl-1-indoyl)undecanoic acid (88):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (0.6 g, 0.01 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 3-Octadecyl indole (31a) (1.0 g, 0.0027 mole)

was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanoic acid (0.768 g, 0.0029 mole) in dimethyl sulphoxide (25 ml) was then added dropwise over a period of one hr and the reaction mixture left stirring (48 hrs).

Water (150 ml) was added to the reaction mixture and then treated with hydrochloric acid (0.5 M) to pH 6.5. The solution was then extracted with dichloromethane (3 x 100 ml, 1 x 50 ml). The dichloromethane extracts were back washed with water (3 x 100 ml, 1 x 50 ml), combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a semi-solid material which on distillation gave 11(3-octadecyl-1-indolyl)undecanoic acid (88) (1.0 g, 67% yield, b.p. 210-220°C/approx. 0.01 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.74-1.0 (br.t, 3H, CH_3-CH_2-), 1.08-2.0 (m, 48H), 2.2 (t, J ≃ 6.5 Hz, 2H, -CH_2-CO_2H), 2.6 (t, J ≃ 7.0 Hz, 2H), 3.88 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.70 (br.s, 1H, indole H-2), 6.84-7.20 (m, 3H), 7.38-7.56 (m, 1H, indole H-4). Anal. calcd. for $C_{37}H_{63}NO_2$: C, 80.23; H, 11.46; N, 2.53. Found: C, 80.64; H, 11.85; N, 2.61.

3.2.105 Preparation of sodium 11-(3-octadecyl-1-indolyl) undecanoate (89):

11-(3-Octadecyl-1-indolyl)undecanoic acid (88) (0.5 g, 0.00088 mole) was dissolved in ethanol (30 ml), and sodium bicarbonate (0.074 g, 0.00088 mole) in water (30 ml) added. The reaction mixture was refluxed with stirring (0.5 hr). The solvents were

removed, the residue washed with sodium dried diethyl ether and then dissolved in absolute ethanol. Any immiscible material was removed by filtration and the solvent was evaporated to dryness to give sodium 11-(3-octadecyl-1-indolyl)undecanoate (89) as an orange yellow gum (0.36 g, 71% yield).

3.2.106 Attempted preparation of 3-methyl indole (90) using indole, methyl iodide and DMF:

Indole (1.17 g, 0.01 mole) and methyl iodide (1.5 g, 0.0106 mole) in dimethyl formamide (30 ml) were heated together under reflux (80-90^{o}C) for 72 hrs. Diethyl ether (50 ml) was then added to the reaction mixture and extracted with water (4 x 30 ml). The ether layer was dried over magnesium sulphate and evaporated to dryness to give a dark red viscous material (1.4 g). After analysis of this material by ^{1}H NMR spectroscopy and on consideration of the respective integrals it was apparent that the material isolated was a mixture of 3-methyl indole (90) (41%), indole, and a minute amount of N-methyl indole. ^{1}H NMR ($CDCl_3$) δ, 2.24 (s, 3H, indole Me-3), 6.76 (br.s, 1H, indole H-2), 6.92-7.38 (m, 3H), 7.4-8.0 (m, 2H, indole H-4 & NH).

3.2.107 Preparation of 1-iodododecane (91) from 1-bromododecane:

1-Bromododecane (4.98 g, 0.02 mole) and sodium iodide (6.0 g, 0.04 mole) were added to dry acetone (50 ml) and the whole reaction mixture was shaken for 5 days. The solid was filtered off and the solvent removed from the filtrate. The residue was dissolved in sodium dried diethyl ether (30 ml) and filtered. The filtrate was

washed with an aqueous solution of sodium thiosulphate (20 ml) and then dried over magnesium sulphate. The solvent was evaporated to dryness to give 1-iodododecane (91) (3.0 g, 51% yield). ^{13}C ($CDCl_3$) ppm, 6.94 (C-1), 14.09 (C-12), 22.7 (C-11), 28.6 (C-9*), 29.6 (C-4*/C5* to C-8), 30.5 (c-3*), 31.9 (C-10), 33.6 (C-2). *Assignment may be reversed.

3.2.108 Attempted preparation of 3-dodecyl indole (29b) using iodododecane, indole and DMF:

Indole (0.4 g, 0.0035 mole), iodododecane (1.0 g, 0.0035 mole) and DMF (20 ml) were stirred at room temperature for 60 hrs. Diethyl-ether (40 ml) was added to the reaction mixture and extracted with water (3 x 30 ml, 1 x 20 ml). The ether layer was dried over magnesium sulphate and the solvent evaporated to dryness to give a viscous oil. Analysis of this material by ^{1}H NMR spectroscopy indicated that none of the desired product was present. The major constituents were shown to be indole and iodododecane.

3.2.109 Attempted synthesis of 3-dodecyl indole (29b) using indole, iodododecane and DMF:

Indole (0.4 g, 0.0035 mole), iodododecane (1.0 g, 0.0035 mole) and DMF (20 ml) were heated under reflux at 80-90^{o}C, with stirring, for 48 hrs. Diethyl ether (40 ml) was added to the reaction mixture and extracted with water (3 x 30 ml, 1 x 20 ml). The ether layer was dried over magnesium sulphate and the solvent evaporated to dryness to give a viscous oil (0.7 g). Analysis of this material by ^{1}H NMR spectroscopy and from consideration of the respective

integrals it was apparent that the isolated material contained none of the desired product, but was instead a mixture of N-dodecyl indole (3c) (49%), indole, iododododecane and very minor amounts of unidentified materials. ^{1}H NMR of N-dodecyl indole (3c) ($CDCl_3$) δ, 0.8-1.04 (br.t, 3H, CH_3-CH_2-), 1.08-1.90 (m, 20H), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 6.4-6.5 (m, 1H, indole H-2), 6.96-7.32 (m, 4H), 7.88-8.00 (m, 2H, indole H-4 & NH).

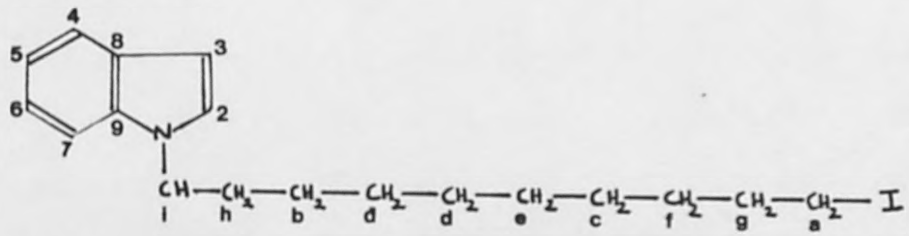
3.2.110 Attempted synthesis of 11-(3-acetyl-1-indolyl)undecanoic acid (92):[173,237]

Under a nitrogen atmosphere, anhydrous potassium carbonate (2.0 g, 0.0144 mole) was added to dry acetone (20 ml) and stirred for 15 mins. 3-Acetyl indole (32) (1.0 g, 0.0062 mole) was then added and the reaction mixture stirred for half an hr. 11-Bromoundecanoic acid (3.28 g, 0.0124 mole) in dry acetone (20 ml) was then added dropwise, over a period of 15 mins, and the reaction mixture heated under reflux (20 hrs). After filtration the solvent was evaporated to dryness to give a colourless solid. Analysis of this material by ^{1}H NMR spectroscopy indicated that none of the desired product was present. The major constituents were shown to be 3-acetyl indole and 11-bromoundecanoic acid.

3.2.111 Preparation of 10-(1-indolyl)decyl iodide (93):

10-(1-indolyl)decyl bromide (49) (1.0 g, 0.003 mole) and sodium iodide (0.9 g, 0.006 mole) were added to dry acetone (50 ml) and the reaction mixture was shaken for 3 days. The unreacted sodium iodide was filtered off and the solvent removed from the filtrate.

Sodium dried diethyl ether (30 ml) was added to the residue and filtered. The filtrate was washed with an aqueous sodium thiosulphate solution (20 ml), water (25 ml), dried over magnesium sulphate and the solvent evaporated to dryness to give 10-(1-indolyl)decyl iodide (93) as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ, 1.1-2.0 (m, 16H), 3.04 (t, J ≃ 7.0 Hz, 2H, $-CH_2-I$), 4.0 (t, J ≃ 7.0 Hz, 2H, $-CH_2-N-$), 6.44 (br.d, J ≃ 4.0 Hz, 1H, indole H-2), 7.0-7.48 (m, 4H), 7.6-7.8 (m, 1H, indole H-4). ^{13}C ($CDCl_3$) ppm.



7.16 (a), 26.9 (b), 28.4 (c), 29.2 (d*), 30.15 (e*), 30.4 (f*), 32.7 (g*), 33.4 (h*), 46.3 (i), 100.9 (C-3), 109.4 (C-7), 119.2 (C-6), 121.04 (C-4), 121.4 (C-5), 127.8 (C-2), 128.7 (C-8), 136.1 (C-9).

*Assignment may be altered.

MS; m/e (%, dev. mmu); M^+, $C_{18}H_{26}NI$, 383.1103 (15, -0.9), $C_{18}H_{26}N$, 256.1988 (5, -7.7), $C_{18}H_{25}N$, 255.1945 (5, -4.2), C_9H_8N, 130.0670 (100, +1.3).

3.2.112 Preparation of 10-(1-benzimidazolyl)decyl bromide (94):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (4.48 g, 0.04 mole) were added to dimethyl sulphoxide (50 ml) and

stirred for half an hr. Imidazole (2.36 g, 0.02 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel 1,10-dibromodecane (0.12 g, 0.04 mole) in dimethyl sulphoxide (50 ml) was stirred for 10 mins. The former mixture was then added dropwise to the 1,10-dibromodecane solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 100 ml, 1 x 50 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a viscous material. The unreacted 1,10-dibromodecane was removed by distillation, leaving 10-(1-benzimidazolyl)decyl bromide (94) as a dark brown gum (5.0 g, 74% yield). A minor amount of 1,10-bis(1-benzimidazolyl)decane (95) was found to be present as an additional contaminant (NMR).
^{1}H NMR ($CDCl_3$) , 1.1-2.4 (m, 16H), 3.34 (t, J ≃ 6.5 Hz, 2H, $-CH_2-Br$), 4.48 (t, J ≃ 7.0 Hz, 2H, $-CH_2-N-$), 7.40-8.20 (m, 5H).
MS; m/e (%, dev. mmu), M^+, $C_{17}H_{25}N_2{}^{81}Br$, 338.1282 (0.08, +10.1), $C_{17}H_{25}N_2{}^{79}Br$, 336.1260 (0.14, +5.9), $C_{11}H_{13}N_2$, 173.0943 (13, -13.6), $C_8H_7N_2$, 131.0676 (42, +6.7).

3.2.113 Preparation of 10-(1-benzimidazolyl)decyl trimethyl ammonium bromide (96):

Under a nitrogen atmosphere 10-(1-benzimidazolyl)decyl bromide (94) (3.0 g, 0.009 mole) was dissolved in absolute ethanol (40 ml) and 50% trimethyl amine-ethanol (10 ml). The stirred solution was refluxed (48 hrs), cooled and the solvent evaporated. The residue was washed with dry benzene (40 ml), dissolved in water (50 ml), filtered and the filtrate freeze dried to give a pale yellow solid (2.5 g, 70% yield, hygroscopic). The ^{1}H NMR indicated that the product was contaminated with minor amounts of an unknown material.

3.2.114 Preparation of 2-octyl benzimidazole (97):

A mixture of o-phenylene diamine (2.16 g, 0.02 mole) and nonoic acid (3.16 g, 0.02 mole) were heated under reflux for 45 mins. The mixture was then dissolved in hot ethanol and aqueous potassium hydroxide was added to pH 8.0. The solution was then extracted with diethyl ether (40 ml) and the ether extract washed with water (2 x 25 ml), dried over magnesium sulphate and evaporated to dryness to give a solid material. This was recrystallised from aqueous ethanol (3 times) to give 2-octyl benzimidazole (97) as a crystalline solid (1.4 g, 29% yield, m.p. 135°C, lit. m.p. 139.5-140.5°C.)[189]. ^{1}H NMR ($CDCl_3$), 0.68-1.08 (br.t, J ≃ 4.5 Hz, 3H, CH_3-CH_2-), 1.1-2.08 (m, 12H), 2.88 (t, J ≃ 7.0 Hz, 2H), 6.84-7.08 (m, 2H, benzimidazole H-5,6),7.18-7.48 (m, 2H, benzimidazole H-4, 7)[143].

3.2.115 Preparation of 10-(2-octyl-1-benzimidazolyl)decyl-bromide (98):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.12 g, 0.02 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 2-Octyl benzimidazole (97) (1.22 g, 0.0053 mole) was then added and the reaction mixture stirred for a further 1 hr.

In a separate reaction vessel, 1,10-dibromodecane (3.0 g, 0.01 mole) in dimethyl sulphoxide (25 ml) was stirred for 10 minutes. The former mixture was then added dropwise to the 1,10-dibromodecane solution, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was then added and the solution extracted with diethyl ether (3 x 100 ml, 1 x 50 ml). Each of the ether extracts was back washed with water (3 x 100 ml, 1 x 50 ml). The ether layers were combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a solid material. The unreacted 1,10-dibromodecane was removed by distillation from the solid. This solid was then washed with diethyl ether (1 x 20 ml) (1.2 g, 50% yield, m.p. 174-177^{o}C). After analysis of this material by ^{1}H NMR spectroscopy it was apparent that the material was contaminated with unidentified impurities.

3.2.116 Preparation of 10-(2-octyl-1-benzimidazolyl)decyl trimethyl ammonium bromide (99):

Under a nitrogen atmosphere 10-(2-octyl-1-benzimidazolyl)decyl bromide (98) (0.8 g, 0.0018 mole) was dissolved in absolute ethanol (30 ml) and 50% anhydrous trimethyl amine-ethanol solution (12 ml). The stirred solution was refluxed (36 hrs), cooled and the solvent evaporated to dryness. The residue was dissolved in water and filtered. The filtrate was freeze dried to give a crystalline material. After analysis of this material by ^{1}H NMR, ^{13}C NMR and mass spectroscopy it was apparent that the material obtained was a mixture of 10-(2-octyl-1-benzimidazolyl) decyl trimethyl ammonium bromide (99), 1,10-bis-(2-octyl-1-benzimidazolyl)decane (100) and 10-(2-octyl-1-benzimidazolyl)decyl bromide (98).

3.2.117 Preparation of 2-hexyl benzimidazole (101):

A mixture of o-phenylene diamine (2.16 g, 0.02 mole) and haptoic acid (2.6 g, 0.02 mole) were heated under reflux at the boiling point temperature (223°C, b.p. of the acid) for 45 minutes. The mixture was then dissolved in hot ethanol (50 ml) and aqueous potassium hydroxide was added to pH 8.0. The solution was then extracted with diethyl ether (40 ml) and the ether extract washed with water (2 x 25 ml), dried over magnesium sulphate and evaporated to dryness to give a solid material which was recrystallised from ethanol. 2-Hexyl benzimidazole (101) was obtained as a colourless crystalline solid (1.6 g, 39% yield, m.p. 130°C, lit. m.p. 138°C).[189] ^{1}H NMR ($CDCl_3$) δ, 0.70-1.00 (br.t, 3H, CH_3-CH_2), 1.08-2.00 (m, 8H), 2.8 (t, J ≃ 7.5 Hz, 2H), 7.04-7.28 (m, 2H), 7.3-7.6 (m, 2H).[143]

3.2.118 Preparation of 11-(2-hexyl-1-benzimidazolyl)undecanoic acid (102):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (3.36 g, 0.06 mole) were added to dimethyl sulphoxide (25 ml) and stirred for 0.5 hrs. 2-Hexyl benzimidazole (3.03 g, 0.015 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanoic acid (3.975 g, 0.015 mole) in dimethyl sulphoxide (30 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture, treated with hydrochloric acid (5M) to pH 6.5 and then extracted with dichloromethane (3 x 70 ml). The dichloromethane extracts were back washed with water (3 x 50 ml), combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a pale yellow oil which solidified on standing at room temperature (2.55 g, 44% yield, b.p. 210°C/0.1 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.8-1.0 (br.t, 3H, CH_3-CH_2-), 1.1-2.0 (m, 24H), 2.2 (t, J ≃ 7.0 Hz, 2H, -CH_2-CO_2-), 2.8 (t, J ≃ 8.0 Hz, 2H), 4.0 (t, J ≃ 7.0 Hz, 2H, -CH_2-N-), 7.2-7.4 (m, 3H), 7.7-7.9 (m, 1H), 8.4-8.6 (m, 1H, -OH). Anal. calcd. for $C_{24}H_{38}N_2O_2$: C, 74.56; H, 9.91; N, 7.25. Found: C, 74.30; H, 9.72; N, 7.24. MS: m/e (%, dev. mmu), M^+, $C_{24}H_{38}N_2O_2$, 386.3092 (4.59, +15.9), $C_{18}H_{25}N_2O_2$, 301.2083 (41, +16.7), $C_9H_{10}N_2$, 146.0860 (93, +1.6), $C_9H_9N_2$, 145.0833 (44, +6.7), $C_8H_8N_2$, 132.0764 (100, +7.6).

3.2.119 Attempted synthesis of 10-(2-hexyl-1-benzimidazolyl) decyl bromide (103):

Bromine (0.82 g, 0.0052 mole) was slowly added to a warm, stirred mixture of 10-(2-hexyl-1-benzimidazolyl)decanoic acid (2.0 g, 0.0052 mole) and yellow mercuric oxide (1.12 g, 0.0052 mole) in carbon tetrachloride (100 ml). The reaction mixture was refluxed (3 hrs), filtered and the filtrate washed with an aqueous sodium hydroxide solution (5%, 30 ml). The solvent was evaporated to dryness to give a viscous oil. Analysis of this material by ^{1}H NMR spectroscopy showed no evidence for the desired product.

3.2.120 Preparation of 11-(2-hexyl-1-benzimidazolyl)undecanol (104):

Under a nitrogen atmosphere, crushed pellets of potassium hydroxide (1.68 g, 0.03 mole) were added to dimethyl sulphoxide (25 ml) and stirred for half an hr. 2-Hexyl benzimidazole (101) (2.02 g, 0.01 mole) was then added and the reaction mixture stirred for a further 1 hr. 11-Bromoundecanol (2.51 g, 0.01 mole) in dimethyl sulphoxide (25 ml) was then added dropwise, over a period of one hr, and the reaction mixture left stirring (15 hrs).

Water (100 ml) was added to the reaction mixture and the solution extracted with dichloromethane (3 x 70 ml, 1 x 30 ml). The dichloromethane extracts were back washed with water (3 x 50 ml), combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give 11-(2-hexyl-1-benzimidazolyl)undecanol (104) as a dark brown oil (2.15 g, 57% yield, b.p. 210°C/approx. 0.1 mm Hg).

^{1}H NMR ($CDCl_3$) δ, 0.8-1.2 (br.t, 3H, $-CH_2-CH_3$), 1.24-2.2 (m, 26H), 2.88 (t, J ≃ 8.0 Hz, 2H), 3.64 (t, J ≃ 6.5 Hz, 2H, $-CH_2-OH$), 4.08 (t, J ≃ 7.0 Hz, 2H, $-CH_2-N-$), 7.1-7.4 (m, 3H), 7.6-7.8 (m, 1H).
MS: m/e (%, dev. mmu), M^+, $C_{24}H_{40}N_2O$, 372.3101 (1.23, -3.9), $C_{19}H_{29}N_2O$, 301.2296 (2, +1.6), $C_{11}H_{13}N_2$, 173.1091 (32, +1.3), $C_{10}H_{11}N_2$, 159.0893 (22, -2.9).

3.2.121 Preparation of 11-(2-hexyl-1-benzimidazolyl)undecyl bromide (105):

To a vigorously stirred solution (mechanical stirrer) of 11-(2-hexyl-1-benzimidazolyl)undecanol (104) (1.86 g, 0.005 mole), dry pyridine (5 ml) and triphenyl phosphine (1.57 g. 0.006 mole) in dry diethyl ether (150 ml) and bromine (0.96 g, 0.006 mole) was added dropwise over a period of 40 minutes. The reaction mixture was stirred for a further 3 hrs. Water (150 ml) was added and the ether layer was separated. The solid residue was then dissolved in further ether and water. Each of the ether extracts was back washed with water (3 x 75 ml), combined and dried over magnesium sulphate. The solvent was evaporated to dryness to give a dark brown oil. Flash column chromatography using silica gel (Merck) and diethyl ether as a solvent gave 11-(2-hexyl-1-benzimidazolyl) undecyl bromide (105) contaminated with a minor amount of triphenyl phosphine oxide (< 5%) (0.93 g, 43% yield, b.p. 215°C/approx. 0.1 mm Hg). ^{1}H NMR ($CDCl_3$) δ, 0.7-0.96 (br.t, 3H, $-CH_2-CH_3$), 1.08-2.2 (m, 26H), 3.10-3.50 (2t, 4H), 4.2 (t, J ≃ 7.5 Hz, 2H, $-CH_2-N-$), 7.30-7.54 (m, 3H), 7.70-8.0 (m, 1H). MS; m/e (%, dev. mmu), M^+,

$C_{24}H_{39}N_2^{81}Br$, 436.2238 (2, -3.9), $C_{24}H_{39}N_2^{79}Br$, 434.2164 (2, -13.3), $C_{20}H_{29}N_2$, 297.2195 (16, -13.6), $C_9H_9N_2$, 145.0643 (46, -12.2), $C_8H_8N_2$, 132.0590 (100, -9.7).

3.2.122 Preparation of 11-(2-hexyl-1-benzimidazolyl)undecyl trimethyl ammonium bromide (106):

Under a nitrogen atmosphere, 11-(2-hexyl-1-benzimidazolyl)undecyl bromide (105) (0.93 g) was dissolved in absolute ethanol (25 ml) and 50% anhydrous trimethyl amine-ethanol solution (10 ml). The stirred solution was refluxed (15 hrs), cooled and the solvent evaporated. The residue was washed with dry diethyl ether then dissolved in water, filtered and the filtrate freeze-dried to give 11-(2-hexyl-1-benzimidazolyl)undecyl trimethyl ammonium bromide (106), although microanalysis showed the product to be impure.

3.2.123 Preparation of n-hexyl mesylate (107):

Under a nitrogen atmosphere, n-hexanol (5.1 g, 0.05 mole) was dissolved in sodium dried ether (200 ml). Trimethyl amine (7.375 g) was then added and the reaction mixture was stirred at a temperature of 0 to 10°C. Methane sulphonyl chloride (6.498 g, 0.057 mole) dissolved in dry diethyl ether (50 ml) was added dropwise, over 45 minutes, to the stirred solution. The mixture was stirred at room temperature for 3 hrs. The solvent and residual volatile reactants were evaporated to dryness and petroleum ether (60-80°C) was added to the residue. The solution was quickly filtered to remove any amine hydrochloride produced and the mother liquor was evaporated down to a clear amber liquid product (7.23 g, 73% yield). The material was used without any further purification.

3.2.124 Preparation of n-hexyl triethylene glycolyl ether (108):

Under a nitrogen atmosphere trigol (75 g, 0.5 mole) was heated to 70-80°C with vigorous stirring (mechanical). Sodium (1.0 g, 0.043 mole) was added, over 15 minutes, raising the temperature to 100°C. The mixture was maintained at this temperature until all the sodium was dissolved. n-Hexyl mesylate (7.0 g, 0.036 mole) was added dropwise with stirring over half an hr. The mixture was stirred (5 hrs) at 100°C temperature.

Brine (200 ml) was added to the reaction mixture and extracted with n-butanol (2 x 200 ml). The n-butanol layers were combined, back washed with brine solution (4 x 200 ml), dried with sodium sulphate and evaporated to dryness to give a pale yellow oil (6.71 g, 79% yield).

The product was transformed into its trisilyl derivative by mixing it with trisilyl compound (formula P) for 15 minutes (40-50°C). This derivative was analysed by GLC using 1% OVI column (70-250°C, 10°C/min. increase). The product was found to be 95% pure, with trigol and dialkyl derivatives as impurities.

3.3 Avenues for further research:

Further research could be carried out on the following topics regarding this project.

3.3.1 Determination of the CMC of host surfactant by determining the fluorescence quantum yield of indoles as a function of the host surfactant concentration:

When the cationic indolic surfactants are incorporated into a micellar solution of CTAB, a marked increase in the fluorescence quantum yield is observed. This change in the fluorescence quantum yield of the indolic surfactants can be used to determine the CMC of host surfactants. Cationic indolic surfactants with varying lengths of hydrocarbon chains on the 1 and 3 positions could be used for this study and the most suitable fluorescent probe can be identified.

3.3.2 Photo-oxidation studies:

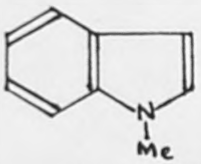
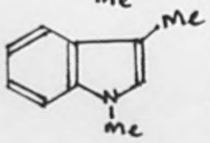
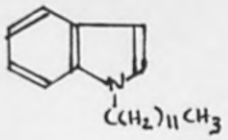
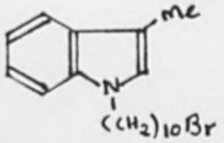
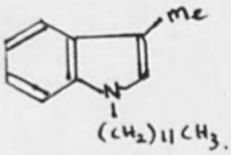
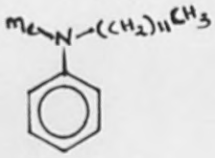
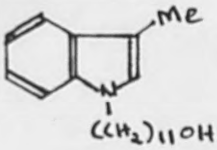
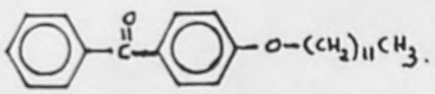
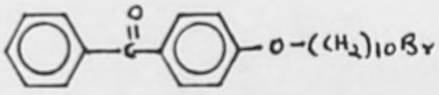
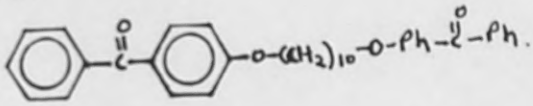
Using the cationic and anionic indolic surfactants in aqueous solution at concentrations above the CMC, a photo-oxidation study should be carried out using an anionic or a cationic dye as photo-sensitizers. Use of an anionic dye with a cationic indolic detergent should lead to some of the dye being attracted to the surface of the micelle and consequently favouring oxidation, whereas a cationic indole detergent with a cationic dye the reverse should be the case.

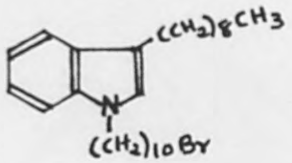
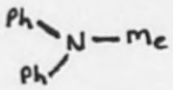
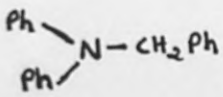
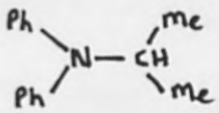
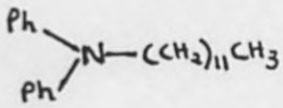
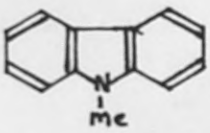
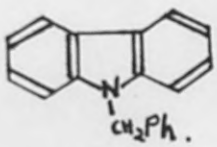
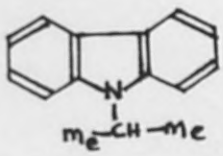
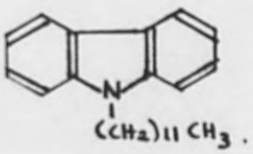
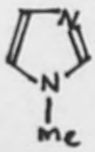
3.3.3 Formation of excited charge transfer complexes:

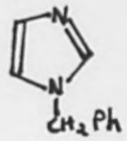
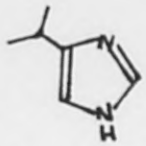
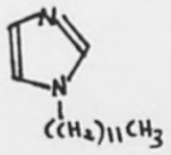
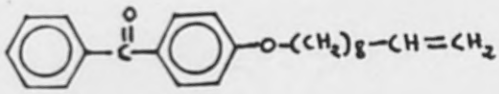
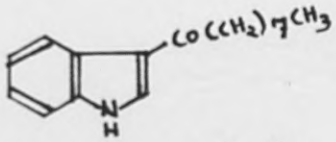
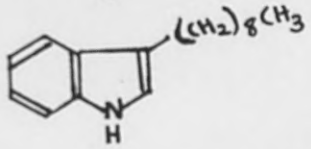
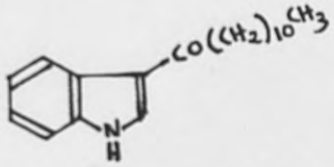
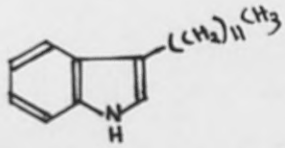
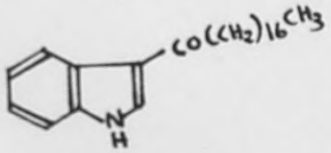
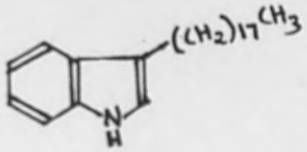
It has been shown previously that indoles form fluorescent complexes

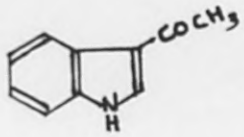
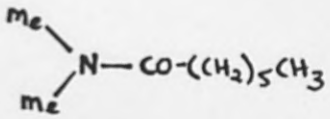
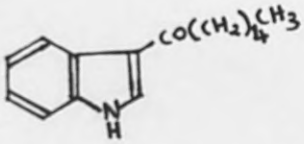
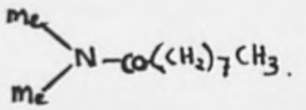
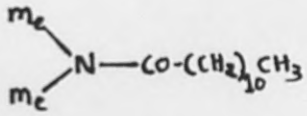
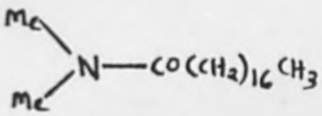
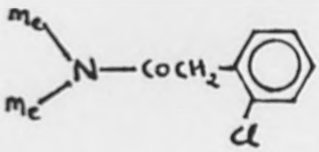
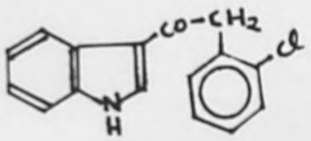
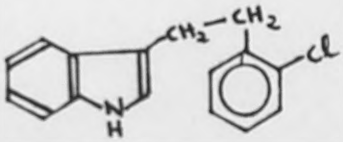
with aromatic hydrocarbons (e.g. 1-cyanonaphthalene).[238] When cationic and anionic indolic surfactant solutions are prepared in water, above the CMC concentration, they should dissolve hydrocarbons such as 1-cyanonaphthalene. Fluorescence studies on such systems should give some indication as to whether the indole nucleus is near the surface or in the interior of the micelle. Ultrasound could be utilised to dissolve the aromatic hydrocarbon into the indolic micellar solution.

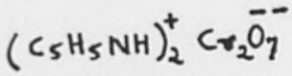
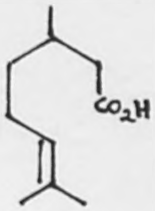
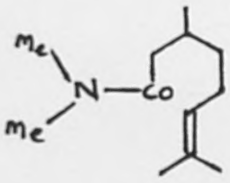
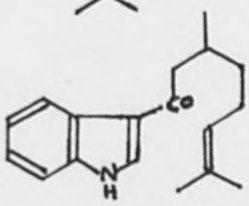
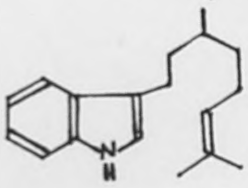
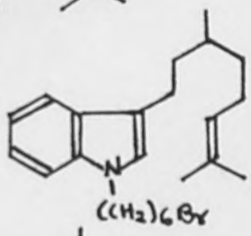
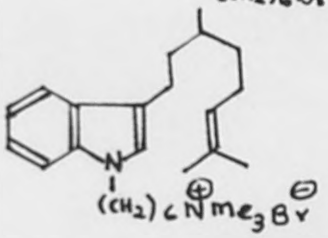
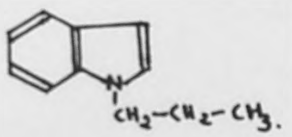
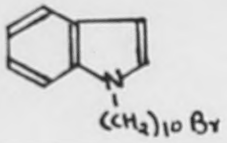
GLOSSARY OF ORGANIC COMPOUNDS AND THEIR STRUCTURES

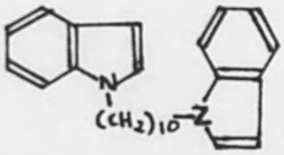
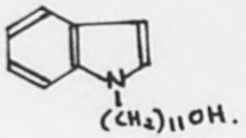
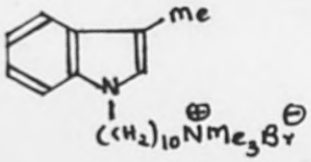
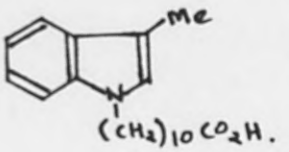
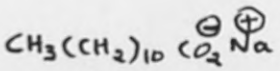
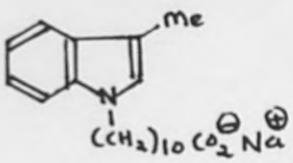
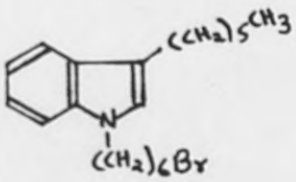
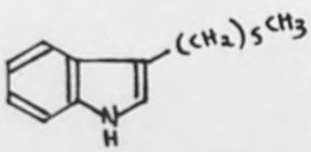
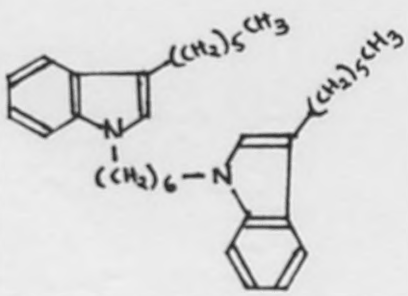
Number	Name of Compound	Structure
(1),(1a),(1b),	N-methyl indole	
(2),(2a)	1,3-dimethyl indole	
(3),(3a),(3b),(3c)	N-dodecylindole	
(4),(4a)	1-(10-bromodecyl)3-methyl indole	
(5)	1-dodecyl,3-methyl indole	
(6),(6a),(6b),(6c)	N-methyl,N-dodecyl aniline	
(7),(7a)	1-(11-hydroxy undecyl)-3-methyl indole	
(8),(8a),(8b)	3-(dodecyloxy)-benzophenone	
(9),(9a),(9b)	4-(10-bromodecyloxy) benzophenone	
(10),(10a),(10b)	1,10-bis-(4-benzophenonyl-oxy)-decane	

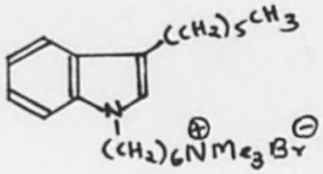
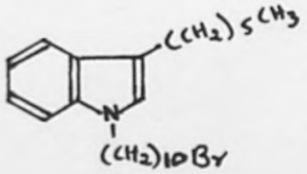
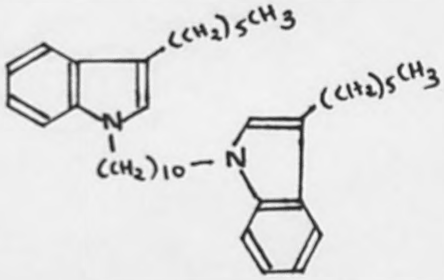
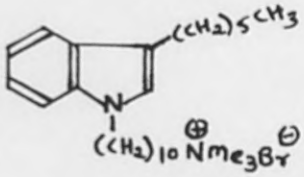
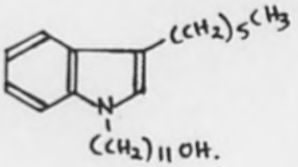
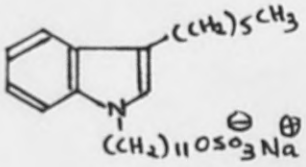
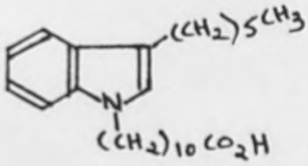
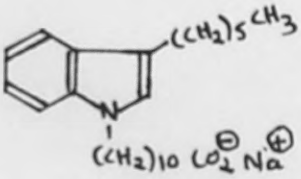
Number	Name of Compound	Structure
(11),(11a)	1-(10-bromodecyl)-3-nonyl indole	
(12)	N-methyl diphenyl amine	
(13)	N-benzyl diphenyl amine	
(14)	N-isopropyl diphenyl amine	
(15)	N-dodecyl diphenyl amine	
(16)	N-methyl carbazole	
(17)	N-benzyl carbazole	
(18)	N-isopropyl carbazole	
(19)	N-dodecyl carbazole	
(20)	N-methyl imidazole	

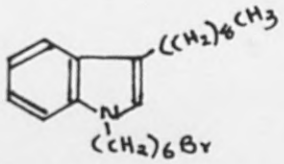
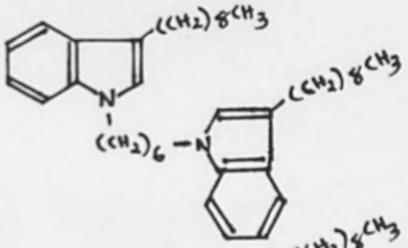
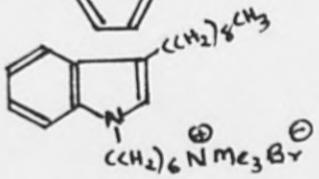
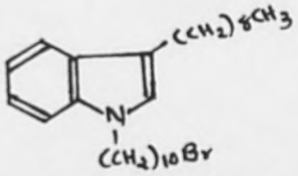
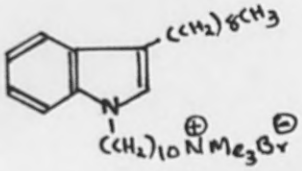
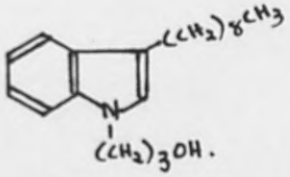
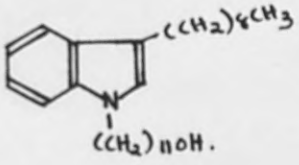
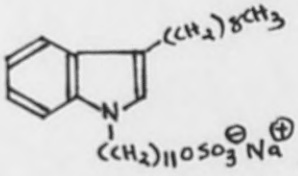
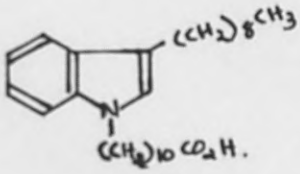
Number	Name of Compound	Structure
(21)	N-benzyl imidazole	
(22)	N-isopropyl imidazole	
(23)	4-isopropyl imidazole	
(24)	N-dodecyl imidazole	
(25)	4-(dec-9-enyloxy)-benzophenone	
(26),(26a)	3-nonoyl indole	
(27),(27a)	3-nonyl indole	
(28),(28a)	3-dodecoyl indole	
(29),(29a),(29b)	3-dodecyl indole	
(30),(30a)	3-octadecoyl indole	
(31),(31a)	3-octadecyl indole	

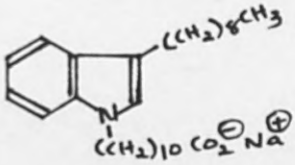
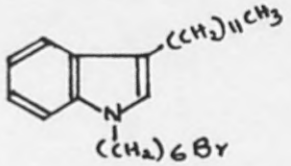
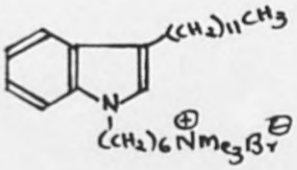
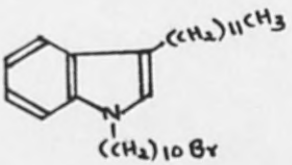
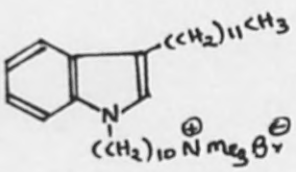
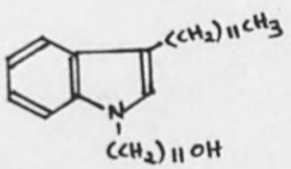
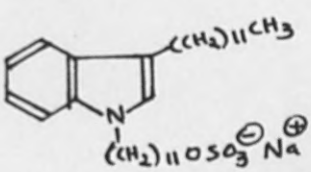
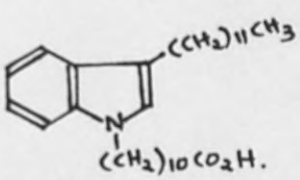
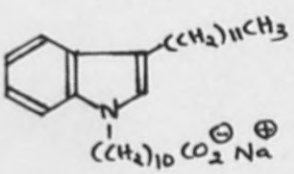
Number	Name of Compound	Structure
(32)	3-acetyl indole	
(33)	N,N-dimethyl hexamide	
(34)	3-hexanoyl indole	
(35)	N,N-dimethyl nonamide	
(36)	N,N-dimethyl dodecamide	
(37)	N,N-dimethyl octadecamide	
(38)	N,N-dimethyl-(2-chloro-phenyl)acetamide	
(39)	3-(2-chlorophenacetyl) indole	
(40)	3-{[2-(2-chloro)phenyl]-ethyl}indole	

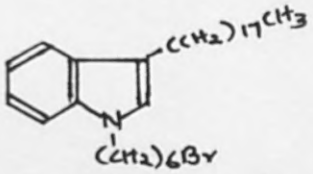
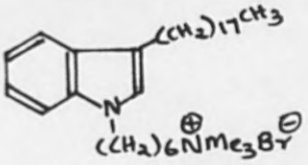
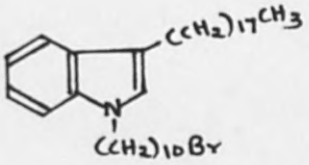
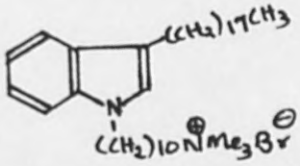
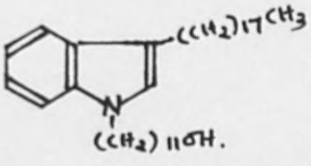
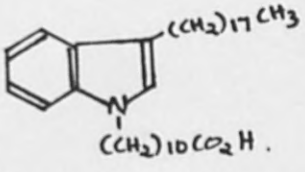
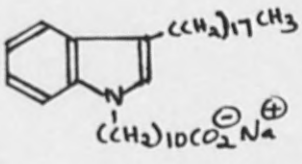
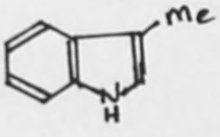
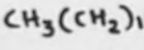
Number	Name of Compound	Structure
(41)	pyridinium dichromate (PDC)	
(42)	citronellic acid or 3,7-dimethyl octenoic acid	
(43)	3,7-dimethyl octenamide	
(44)	3-(1-keto-3,7-dimethyl octene)indole	
(45)	3-(3,7-dimethyl octene) indole	
(46)	6-(3-citronellyl-1-indolyl) hexyl bromide	
(47)	6-(3-citronellyl-1-indolyl) hexyl trimethyl ammonium bromide	
(48)	N-propyl indole	
(49)	1-(10-bromodecyl)indole or 10-(1-indolyl)decyl bromide	

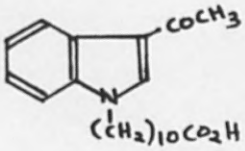
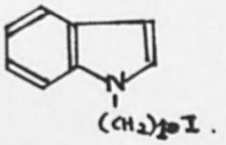
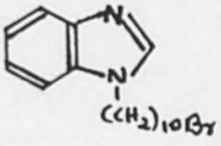
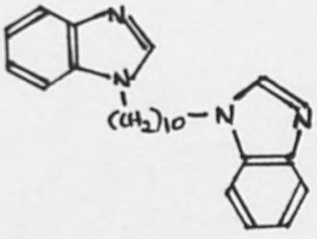
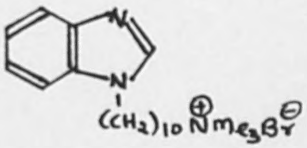
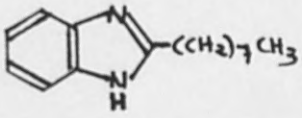
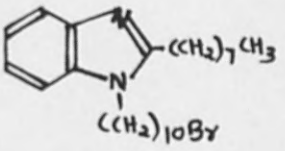
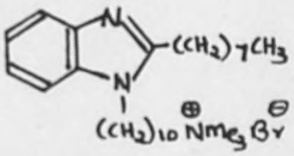
Number	Name of Compound	Structure
(50)	1,10-bis-(indolyl)decane	
(51)	1-(11-hydroxy undecyl) indole	
(52)	10-(3-methyl-1-indolyl)-decyl trimethyl ammonium bromide	
(53)	11-(3-methyl-1-indolyl) undecanoic acid	
(54)	sodium dodecanoate	
(55)	sodium 11-(3-methyl-1-indolyl)undecanoate	
(56)	1-(6-bromohexyl)-3-hexyl indole or 6-(3-hexyl-1-indolyl) hexyl bromide	
(34b)	3-hexyl indole	
(57)	1,6-bis-(3-hexyl-1-indolyl)hexane	

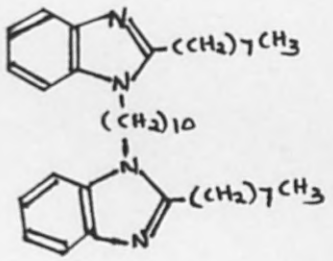
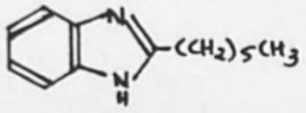
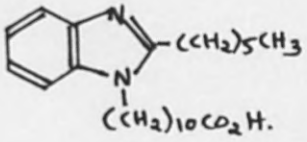
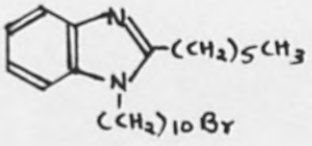
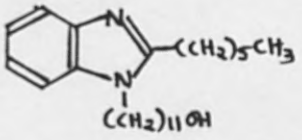
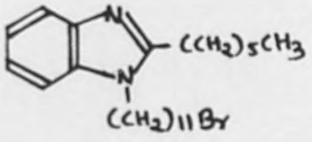
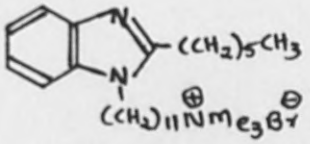
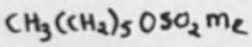
Number	Name of Compound	Structure
(58)	6-(3-hexyl-1-indolyl) hexyl trimethyl ammonium bromide	
(59)	1-(10-bromodecyl)-3-hexyl indole or 10-(3-hexyl-1-indolyl) decyl bromide	
(60)	1,10-bis(3-hexyl-1-indolyl)decane	
(61)	10-(3-hexyl-1-indolyl) decyl trimethyl ammonium bromide	
(62)	11-(3-hexyl-1-indolyl) undecanol	
(63)	sodium 11-(3-hexyl-1-indolyl)undecyl sulphate	
(64)	11-(3-hexyl-1-indolyl) undecanoic acid	
(65)	sodium 11-(3-hexyl-1-indolyl)undecanoate	

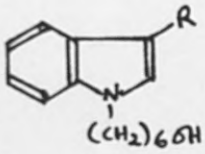
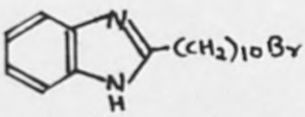
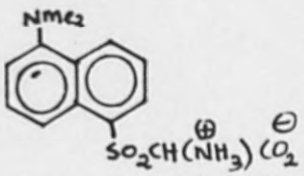
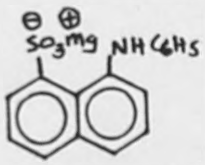
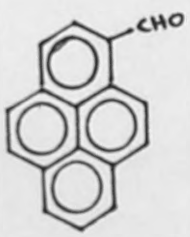
Number	Name of Compound	Structure
(66)	6-(3-nonyl-1-indolyl) hexyl bromide	
(67)	1,6-bis-(3-nonyl-1-indolyl)hexane	
(68)	6-(3-nonyl-1-indolyl) hexyl trimethyl ammonium bromide	
(11a)	10-(3-nonyl-1-indolyl) decyl bromide	
(70)	10-(3-nonyl-1-indolyl) decyl trimethyl ammonium bromide	
(71)	3-(3-nonyl-1-indolyl) propyl alcohol	
(72)	11-(3-nonyl-1-indolyl) undecanol	
(73)	sodium 11-(3-nonyl-1-indolyl)undecyl sulphate	
(74)	11-(3-nonyl-1-indolyl) undecanoic acid	

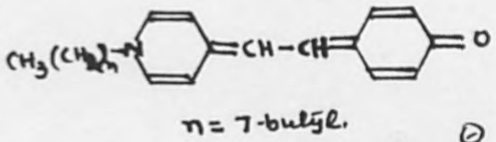
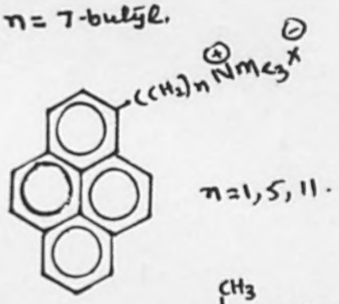
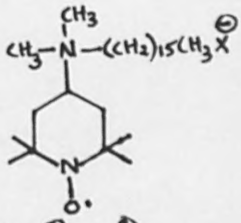
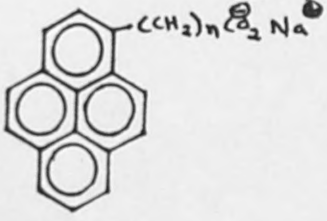
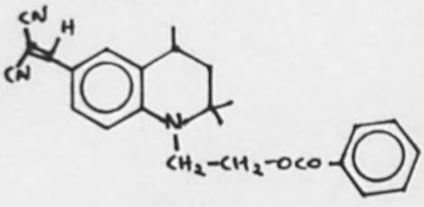
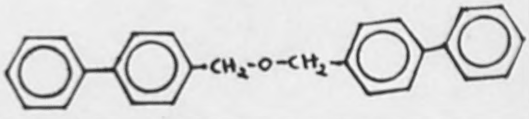
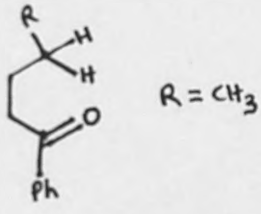
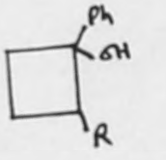
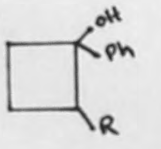
Number	Name of Compound	Structure
(75)	sodium 11-(3-nonyl-1-indolyl)undecanoate	
(76)	6-(3-dodecyl-1-indolyl) hexyl bromide	
(69)	6-(3-dodecyl-1-indolyl) hexyl trimethyl ammonium bromide	
(77)	10-(3-dodecyl-1-indolyl) decyl bromide	
(78)	10-(3-dodecyl-1-indolyl) decyl trimethyl ammonium bromide	
(79)	11-(3-dodecyl-1-indolyl) undecanol	
(80)	sodium 11-(3-dodecyl-1-indolyl)undecyl sulphate	
(81)	10-(3-dodecyl-1-indolyl) undecanoic acid	
(82)	sodium 11-(3-dodecyl-1-indolyl)undecanoate	

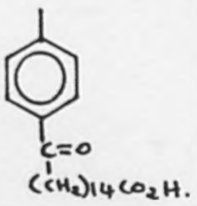
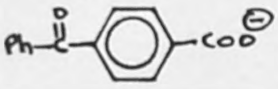
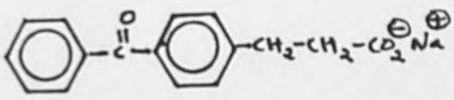
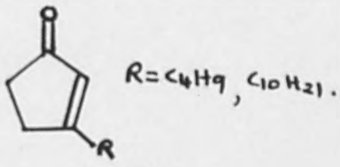
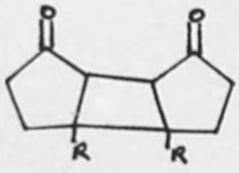
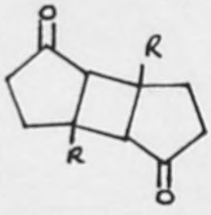
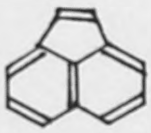
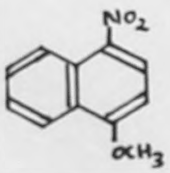
Number	Name of Compound	Structure
(83)	6-(3-octadecyl-1-indolyl)hexyl bromide	
(84)	6-(3-octadecyl-1-indolyl)hexyl trimethyl ammonium bromide	
(85)	10-(3-octadecyl-1-indolyl)decyl bromide	
(86)	10-(3-octadecyl-1-indolyl)decyl trimethyl ammonium bromide	
(87)	11-(3-octadecyl-1-indolyl)undecanol	
(88)	11-(3-octadecyl-1-indolyl)undecanoic acid	
(89)	sodium 11-(3-octadecyl--1-indolyl)undecanoate	
(90)	3-methyl indole	
(91)	1-iodododecane	

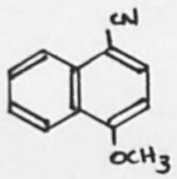
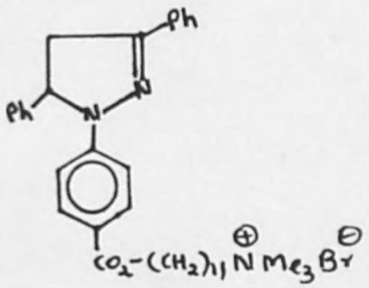
Number	Name of Compound	Structure
(92)	11-(3-acetyl-1-indolyl) undecanoic acid	
(93)	10-(1-indolyl)decyl iodide	
(94)	10-(1-benzimidazolyl) decyl bromide	
(95)	1,10-bis(1-benzimidazolyl)decane	
(96)	10-(1-benzimidazolyl) decyl trimethyl ammmonium bromide	
(97)	2-octyl benzimidazole	
(98)	10-(2-octyl-1-benzimidazolyl)decyl bromide	
(99)	10-(2-octyl-1-benzimidazolyl)decyl trimethyl ammonium bromide	

Number	Name of Compound	Structure
(100)	1,10-bis-(2-octyl-1-benzimidazolyl)decane	
(101)	2-hexyl benzimidazole	
(102)	11-(2-hexyl-1-benzimidazolyl) undecanoic acid	
(103)	10-(2-hexyl-1-benzimidazolyl)decyl bromide	
(104)	11-(2-hexyl-1-benzimidazolyl) undecanol	
(105)	11-(2-hexyl-1-benzimidazolyl)undecyl bromide	
(106)	11-(2-hexyl-1-benzimidazolyl)undecyl trimethyl ammonium bromide	
(107)	n-hexyl mesylate	

Number	Name of Compound	Structure
(108)	n-hexyl triethylene glycolyl ether	$CH_3(CH_2)_5O(CH_2-CH_2-O)_3H$.
(109)	1-bromo hexan-6-ol	$Br(CH_2)_6OH$.
(110)	6-(3-alkyl-1-indolyl) hexanol	 R = alkyl.
(111)	sodium 1-hexyl sulphate	$CH_3(CH_2)_5OSO_3^{\ominus}Na^{\oplus}$
(112)	2-(10-bromo)decyl benzimidazole	
(113)	1-cyanohexane bromide	$Br(CH_2)_6CN$
(114)	1,6-dicyanohexane	$CN(CH_2)_6CN$
(115)	1-dimethyl aminonaphthalene-5-sulphonyl glycine	
(116)	magnesium salt of 8-anilino-naphthalene-1-sulphonate	
(117)	pyrene-3-carboxaldehyde	

Number	Name of Compound	Structure
(118)	merocyanine dyes	
(119)	cationic pyrene derivative	
(120)	surfactant nitroxyl radical	
(121)	anionic pyrene derivative sodium-5-(1-pyrenyl) pentanoate	
(122)	2-[6-(2,2-dicyanovinyl)-1,2,3,4-tetrahydro-2,2,4-trimethylquinol-1-yl]ethyl benzoate	
(123)	4-biphenyl derivative	
(124)	phenyl heptyl ketone (octanophenone)	
(125)	cyclobutanol derivative	
(126)	cyclobutanol derivative	

Number	Name of Compound	Structure
(127)	ketone 16-oxo-16 (p-tolyl)hexadecanoic acid	
(128)	4-methyl acetophenone	
(129)	4-benzoyl benzoate anion	
(130)	benzophenone derivative 2(-4-benzoyl phenyl) propionate	
(131)	3-alkyl cyclopentanoate	
(132)	head to head 3-alkyl-cyclopentanoate dimer	
(133)	head to tail 3-alky cyclo-pentanoate dimer	
(134)	acenaphthalene	
(135)	4-methoxy-1-nitro naphthalene	

Number	Name of Compound	Structure
(136)	4-methoxy-1-naphthalene carbonitrile	
(137)	pyrazoline surfactant	

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