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Vapor-liquid equilibria and mixture densities for 2,2,4,4,6,8,8-heptamethylnonane + N_2 and n-hexadecane + N_2 binary mixtures to 535 K and 135 MPa

Supplemental Information

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This document contains data tables for BP/DP transitions and mixture densities for 2,2,4,4,6,8,8-heptamethylnonane (HMN) + N_2 and n-hexadecane (HXD) + N_2 binary mixtures.

Table S1. Isopleths with bubble (BP) and dew points (DP) obtained in this study for HMN + N_2 at varying compositions listed with the N_2 mole fraction, x_{N2}, the N_2 weight fraction, w_{N2}, the pressure, and the temperature. BP data are listed without an asterisk and DP data are marked with an asterisk.

x_{N2}	w_{N2}	p/MPa	T/K	x_{N2}	w_{N2}	p/MPa	T/K
0.149	0.021	11.6	297.8	0.671	0.201	114.6	356.2
		9.9	374.8			81.5	415.4
		8.4	467.2			63.5	473.4
		7.9	526.8	0.76	0.282	104.5	423.3
0.29	0.048	24.5	299.8			89.4	452.1
		19.4	380.6			77.6	478.4
		15.8	463.5	0.773	0.296	96.5	441.4
		12.2	575.6			81.4	470.2
0.392	0.074	42.5	305.7			67.5	503.7
		33.3	375.2			56.5	533.2
		25.7	469.1	0.874	0.463	101.3	492.6
		21.8	527.1			90.0	511.5
0.571	0.141	91.0	298.0			76.6	533.3
		67.7	352.1	0.894	0.511	95.8*	474.8
		52.5	416.8			83.3*	495.5
		43.4	474.8			74.4*	510.9
		38.7	519.4			64.0*	531.4

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K. The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 with a coverage factor, k = 2. *Dew point pressure

Table S2. Isopleths with BP data obtained in this study for HXD + N_2 at varying compositions listed with the N_2 mole fraction, x_{N2}, the N_2 weight fraction, w_{N2}, the pressure, and the temperature. Only BP data are observed for this system at the conditions shown here.

x_{N2}	w_{N2}	p/MPa	T/K	x_{N2}	w_{N2}	p/MPa	T/K
0.209	0.032	19.2	323.2	0.686	0.212	127.5	394.7
		15.4	387.0			95.3	438.5
		12.3	466.9			76.9	478.1
		10.9	525.4			59.7	529.4
0.29	0.048	27.3	325.3	0.816	0.354	127.0	469.0
		21.0	397.1			110.3	487.6
		17.6	468.4			96.4	508.8
		14.7	535.8			85.5	527.2
0.453	0.093	59.8	327.1	0.902	0.533	127.6	498.5
		41.9	396.2			110.2	517.3
		34.3	458.6			99.1	531.4
0.581	0.147	106.7	324.9				
		71.3	391.3				
		51.0	471.2				
		41.6	528.9				

[a] Standard uncertainties u are $u(p) = 0.07$ MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T) = 0.2$ K. The combined expanded uncertainties U_c are $U_c(x_{N2}) = 0.001$ with a coverage factor, $k = 2$.

Tables S3 and S4 list densities for HMN + N_2 mixtures and HXD + N_2 mixtures, respectfully. The first pressure-density data point at each fixed composition and temperature listed in these tables represents the limit of the single phase region, which is the two phase boundary for a given isopleth. These density data are obtained to pressures as high as ~135 MPa and temperatures as high as ~535 K.

Table S3. Liquid densities, ρ, obtained in this study for single-phase, HMN + N_2 mixtures at varying compositions listed with the N_2 mole fraction, x_{N2}, the N_2 weight fraction, w_{N2}, the pressure, and the temperature. Nearly all the isotherms are held at a constant temperature within 0.2 K, except for the 526.9 K isotherm, which is held within 0.3 K, and the 528.0 K isotherm, which is held within 0.5 K.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
x_{N2} = 0.149; w_{N2} = 0.021							
T/K = 297.8		T/K =374.8		T/K = 467.1		T/K = 526.6	
11.6	759	9.9	706	8.4	638	7.9	594
24.6	774	20.6	726	17.3	664	17.2	625
34.9	781	34.9	743	31.3	688	31.3	653
44.4	789	51.8	758	44.9	704	44.7	674
51.7	794	62.9	766	58.7	719	58.9	691
62.3	800	73.5	773	72.3	732	72.2	705
72.1	806	85.7	779	85.3	742	84.0	716
84.9	812	98.2	788	98.1	751	97.5	727
98.4	819						
x_{N2} = 0.392; w_{N2} = 0.074							
T/K = 305.7		T/K =375.2		T/K = 469.1		T/K = 526.9	
42.5	762	33.3	710	25.7	642	21.8	589
43.8	764	42.3	717	27.5	647	27.6	600
58.7	772	50.9	730	41.6	667	45.5	639
59.0	768	62.0	741	55.2	688	45.5	640
71.5	782	72.2	748	72.6	708	58.2	661
85.2	791	84.7	759	84.7	719	72.1	678
98.6	799	98.2	769	97.7	730	84.4	692

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 526.9 K ($u(T)$ = 0.2 K) and 528.0 K ($u(T)$ = 0.5 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho)$ = 0.008•ρ kg•m^{-3} with a coverage factor, k = 2.

Table S3. Continued: Densities, ρ, obtained in this study for single-phase, HMN + N_2 mixtures.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
			x_{N2} = 0.571;	w_{N2} = 0.141			
T/K K = 298.0		T/K = 416.7		T/K = 474.8		T/K = 519.2	
91.0	786	52.5	663	43.4	615	38.7	569
98.2	793	62.6	684	51.0	630	44.6	586
		71.5	700	62.4	654	55.1	609
T/K = 352.1		85.4	717	73.0	670	73.4	638
67.7	720	97.8	731	84.3	685	86.9	657
73.7	731			99.0	703	100.5	673
85.3	749						
98.6	763						
			x_{N2} = 0.671;	w_{N2} = 0.201			
T/K = 356.2		T/K = 415.4		T/K = 473.4		T/K = 527.0	
114.6	756	81.5	687	63.5	622	51.2	555
119.0	760	91.0	700	74.7	641	58.4	572
125.9	766	96.9	707	88.2	661	71.2	599
		104.7	715	100.9	679	84.3	622
		111.1	722	115.0	695	98.0	642
		117.2	728	125.3	706	111.4	659
		124.4	735			124.5	674

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 526.9 K ($u(T)$ = 0.2 K) and 528.0 K ($u(T)$ = 0.5 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho) = 0.008 \bullet \rho$ kg•m^{-3} with a coverage factor, k = 2.

Table S3. Continued: Densities, ρ, obtained in this study for single-phase, HMN + N_2 mixtures.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
x_{N2} = 0.760; w_{N2} = 0.282							
T/K = 423.3		T/K = 478.4		T/K = 502.1		T/K = 528.0	
104.5	696	77.6	610	68.1	575	59.5	535
110.0	704	83.8	623	74.4	588	73.8	570
116.7	713	90.0	635	82.0	605	82.1	588
128.2	727	94.1	643	87.1	614	100.3	621
T/K = 452.1		101.0	654	95.3	630	116.7	647
89.4	654	109.3	666	101.2	639	127.0	661
94.2	661	114.0	674	109.1	651		
101.4	673	122.7	684	114.2	659		
108.0	682	127.8	692	122.4	669		
114.4	691			127.8	677		
120.6	699						
127.8	708						
x_{N2} = 0.773; w_{N2} = 0.296							
T/K = 441.4		T/K = 470.2		T/K = 503.4		T/K = 533.2	
96.5	669	81.4	621	67.5	565	56.5	515
98.8	673	85.4	628	72.2	578	58.3	518
		91.3	640	78.3	592	72.2	557
		98.9	653	84.7	606	79.0	573
				91.6	619	85.2	587
				98.3	631	91.6	600
						98.6	613

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 526.9 K ($u(T)$ = 0.2 K) and 528.0 K ($u(T)$ = 0.5 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho) = 0.008\ \rho$ kg•m^{-3} with a coverage factor, k = 2.

Table S3. Continued: Densities, ρ, obtained in this study for single-phase, HMN + N_2 mixtures.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
			x_{N2} = 0.874; w_{N2} = 0.463				
T/K = 492.6		T/K = 511.5		T/K = 533.4			
101.3	559	90.0	520	76.6	470		
105.3	568	97.5	537	81.6	482		
112.3	581	103.9	551	88.1	498		
		110.8	564	94.5	513		
		119.7	580	100.6	525		
				108.1	541		
				113.9	551		
				121.5	564		
				128.0	574		

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 526.9 K ($u(T)$ = 0.2 K) and 528.0 K ($u(T)$ = 0.5 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho)$ = 0.008•ρ kg•m^{-3} with a coverage factor, k = 2.

Table S4. Liquid densities, ρ, obtained in this study for single-phase, HXD + N_2 mixtures at varying compositions listed with the N_2 mole fraction, x_{N2}, the N_2 weight fraction, w_{N2}, the pressure, and the temperature. Nearly all the isotherms are held at a constant temperature within 0.2 K, except for the 527.0 K isotherm, which is held within 0.8 K, and the 528.6 K isotherm, which is held within 0.3 K.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
x_{N2} = 0.209; w_{N2} = 0.032							
T/K = 323.1		T/K =387.0		T/K = 466.9		T/K = 527.0	
19.2	741	15.4	688	12.3	632	10.9	586
34.1	760	33.7	721	26.0	666	31.7	638
48.0	771	55.0	742	46.8	694	52.2	668
61.9	782	76.0	758	61.3	709	72.2	691
75.7	791	88.3	767	86.1	731	91.9	708
89.5	799	104.6	777	106.2	746	104.7	719
102.7	806	125.3	789	126.2	759	125.2	734
115.9	812						
124.3	816						
x_{N2} = 0.290; w_{N2} = 0.048							
T/K = 325.5		T/K =397.1		T/K = 468.4		T/K = 535.8	
27.3	733	21.0	678	17.6	628	14.7	567
40.5	750	30.4	696	31.0	656	27.2	604
48.2	758	51.2	722	44.6	676	42.4	630
62.6	770	63.7	733	58.7	692	55.9	648
77.2	781	84.2	750	71.5	704	71.4	666
88.9	789	103.8	764	84.9	717	86.8	680
102.3	797	124.2	777	97.6	727	98.5	691
114.9	805			111.6	737	111.5	700
				124.9	747	124.6	712

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 527.0 K ($u(T)$ = 0.8 K) and 528.6 K ($u(T)$ = 0.3 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho)$ = 0.008•ρ kg•m^{-3} with a coverage factor, k = 2.

Table S4. Continued: Densities, ρ, obtained in this study for single-phase, HXD + N_2 mixtures.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
x_{N2} = 0.452; w_{N2} = 0.093							
T/K = 327.1		T/K = 396.2		T/K = 458.4			
59.8	752	41.9	696	34.3	645		
72.2	764	58.5	716	44.9	663		
84.9	774	71.4	729	58.3	680		
98.3	784	84.4	741	73.3	698		
111.6	793	98.0	752	82.9	707		
124.9	801	111.1	762	97.4	721		
		124.1	771	111.8	733		
				124.3	743		
x_{N2} = 0.581; w_{N2} = 0.147							
T/K = 324.8		T/K =391.4		T/K = 471.1		T/K = 528.6	
106.7	790	71.3	703	51.0	630	41.6	574
114.4	798	77.7	713	62.5	652	52.4	597
121.4	803	84.3	723	75.7	671	61.7	614
127.6	809	92.4	736	89.0	688	68.3	625
		103.9	753	103.0	703	84.7	649
		115.7	763	114.7	715	95.9	663
		125.0	773	123.9	724	103.9	673
						113.3	683
						125.4	696
x_{N2} = 0.685; w_{N2} = 0.212							
T/K = 394.7		T/K = 438.5		T/K = 478.3		T/K = 529.5	
127.5	730	95.3	676	76.9	630	59.7	566
130.8	732	100.9	682	84.3	640	64.6	576
		107.5	690	97.1	657	78.0	600
		113.9	696	110.2	672	90.7	620
		120.8	703	120.2	682	104.6	638
		128.2	709	128.7	690	116.9	653
						129.9	667

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 527.0 K ($u(T)$ = 0.8 K) and 528.6 K ($u(T)$ = 0.3 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho)$ = 0.008•ρ kg•m^{-3} with a coverage factor, k = 2.

Table S4. Continued: Densities, ρ, obtained in this study for single-phase, HXD + N_2 mixtures.

p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
$x_{N2} = 0.816$; $w_{N2} = 0.354$							
T/K = 468.8		T/K = 487.6		T/K = 508.6		T/K = 527.1	
127.0	668	110.3	635	96.4	599	85.5	566
131.6	673	114.6	641	104.1	612	91.8	579
133.8	677	121.4	651	111.6	623	97.5	589
		127.5	658	117.9	633	105.8	603
		133.1	665	124.8	642	111.2	612
				130.7	650	117.7	622
						125.7	633
						131.7	641
$x_{N2} = 0.902$; $w_{N2} = 0.533$							
T/K = 498.5		T/K = 517.3		T/K = 531.3			
127.6	582	110.2	544	99.1	515		
131.4	592	116.3	554	104.7	524		
		123.9	568	110.6	536		
		131.3	581	117.6	549		
				124.1	561		
				131.0	572		

[a] Standard uncertainties u are $u(p)$ = 0.07 MPa at $p \leq 68.9$ MPa and 0.41 MPa at $p > 68.9$ MPa and $u(T)$ = 0.2 K with the exclusion of the 527.0 K ($u(T)$ = 0.8 K) and 528.6 K ($u(T)$ = 0.3 K). The combined expanded uncertainties U_c are $U_c(x_{N2})$ = 0.001 and $U_c(\rho) = 0.008 \bullet \rho$ kg•m^{-3} with a coverage factor, k = 2.

Equation S1 is Antoine's equation used to interpolate BP/DP data sets and table S5 lists values for parameters *A*, *B*, and *C* needed in equation S1.

$$ln\left(\frac{p}{MPa}\right) = A - \frac{B}{T+C} \tag{S1}$$

Table S5. Constants for Antoine's equation used to interpolate BP/DP isopleth data for HMN or HXD + N_2 mixtures at each N_2 mole fraction, x_{N2}, and weight fraction, w_{N2}. Refer to tables S1 and S2 for the applicable temperature range of application for Antoine's equation for each isopleth. The average, absolute percent deviation, Δ_{AAD}, and maximum deviation, Δ_{max} are also listed.

x_{N2}	w_{N2}	A	B	C	Δ_{AAD}	Δ_{max}
			HMN + N_2			
0.149	0.021	$8.5460 \bullet 10^{-1}$	$-1.1442 \bullet 10^{3}$	$4.2014 \bullet 10^{2}$	0.5	1.0
0.290	0.048	$-7.8546 \bullet 10^{-1}$	$-5.1832 \bullet 10^{3}$	1.0000E+03	0.2	0.4
0.392	0.074	$-2.5289 \bullet 10^{-1}$	$-4.4703 \bullet 10^{3}$	$8.1203 \bullet 10^{2}$	0.7	1.0
0.571	0.141	2.2256	$-8.4731 \bullet 10^{2}$	$7.2849 \bullet 10^{1}$	0.3	0.5
0.671	0.201	1.5823	$-1.5868 \bullet 10^{3}$	$1.4632 \bullet 10^{2}$	0.5	0.8
0.760	0.282	-10.625	$-4.2002 \bullet 10^{4}$	$2.3264 \bullet 10^{3}$	0.2	0.4
0.773	0.296	-21.732	$-1.1682 \bullet 10^{5}$	$4.0000 \bullet 10^{3}$	0.3	0.5
0.874	0.463	$-5.4273 \bullet 10^{5}$	$-4.2700 \bullet 10^{13}$	$7.8675 \bullet 10^{7}$	0.5	0.8
0.894	0.511	$-3.5627 \bullet 10^{5}$	$-1.7732 \bullet 10^{13}$	$4.9769 \bullet 10^{7}$	0.3	0.4
			HXD + N_2			
0.209	0.032	1.0993	$-8.4884 \bullet 10^{2}$	$1.3410 \bullet 10^{2}$	0.3	0.5
0.290	0.048	$7.8138 \bullet 10^{-1}$	$-1.6725 \bullet 10^{3}$	$3.3788 \bullet 10^{2}$	0.8	1.3
0.453	0.093	2.6123	$-3.2292 \bullet 10^{2}$	$-1.0872 \bullet 10^{2}$	0.0	0.0
0.581	0.147	1.9800	$-1.0272 \bullet 10^{3}$	$5.7106 \bullet 10^{1}$	0.4	0.7
0.685	0.212	1.2685	$-1.8005 \bullet 10^{3}$	$1.0838 \bullet 10^{2}$	0.3	0.4
0.816	0.354	1.2548	$-1.6971 \bullet 10^{3}$	3.9246	0.3	0.4
0.902	0.533	-3.9896	$-9.8479 \bullet 10^{3}$	$6.1571 \bullet 10^{2}$	0.0	0.0

Single phase, mixture density data are correlated with the Tait equation, equations S2. This application of the Tait equation uses a reference density, $\rho_0(T)$, calculated at p_0 equal to the BP/DP pressure at each T-x_{N2} value calculated with Antoine's equation. Values for parameters C, a_0, a_1, a_2, b_0, b_1, and b_2 are found in tables S5 and S6.

$$\frac{\rho-\rho_0(T)}{\rho} = C\log_{10}\left(\frac{P+B(T)}{P_0+B(T)}\right) \qquad \text{(S2)}$$

$$\rho_0(T)/kg \bullet m^{-3} = \sum_{i=0}^{2} a_i T^i \qquad \text{(S3)}$$

$$B(\mathrm{T})/MPa = \sum_{i=0}^{2} b_i T^i \qquad \text{(S4)}$$

Table S6a. Tait parameters for mixture density calculations for HMN + N_2 mixtures for each isopleth listed with the Δ_{AAD}, Δ_{max}, and the temperature-pressure ranges fit to the equation. Tait parameters for pure HMN are taken from Rowane et al.[1]

x_{N2}:	0	0.145	0.392	0.571	0.671	0.760	0.773	0.874
w_{N2}:	0	0.021	0.074	0.141	0.201	0.282	0.296	0.463
C:	0.2166	0.2077	0.2969	0.2387	0.3274	0.4573	0.6048	0.6324
a_2:	-1.9816•10^{-4}	-3.1470•10^{-4}	-5.3393•10^{-4}	4.8878•10^{-4}	-3.5305•10^{-4}	5.2342•10^{-4}	1.8416•10^{-4}	8.0139•10^{-5}
a_1:	-5.0985•10^{-1}	-4.7398•10^{-1}	-3.1585•10^{-1}	-1.3768	-8.6079•10^{-1}	-2.0549	-1.8164	-2.2699
a_0:	9.4778•10^{2}	9.3101•10^{2}	9.0605•10^{2}	1.1526•10^{3}	1.1072•10^{3}	1.4757•10^{3}	1.4330•10^{3}	1.6593•10^{3}
b_2:	6.6635•10^{-4}	7.5075•10^{-4}	7.8070•10^{-4}	8.3186•10^{-4}	8.6845•10^{-4}	4.1145•10^{-3}	2.1803•10^{-3}	2.2882•10^{-3}
b_1:	-8.9215•10^{-1}	-8.6166•10^{-1}	-9.7974•10^{-1}	-7.7500•10^{-1}	-9.5265•10^{-1}	-4.2046	-2.3543	-2.3593
b_0:	3.1015•10^{2}	2.5144•10^{2}	3.0754•10^{2}	1.5804•10^{2}	2.3909•10^{2}	1.0564•10^{3}	6.3004•10^{2}	5.8430•10^{2}
Δ_{AAD}:	0.1	0.2	0.2	0.2	0.1	0.2	0.3	0.1
Δ_{MAX}:	0.4	0.5	0.9	1.1	0.2	0.5	0.4	0.6
T/K	298 - 522	298 - 527	306 - 527	298 - 519	356 - 527	423 - 529	441 - 533	493 - 533
p/MPa	4 - 174	BP* - 99	BP* - 100	BP* - 100	BP* - 127	BP* - 129	BP*- 101	DP* - 129

BP*, DP* -- The minimum pressure is equal to the BP/DP at a given temperature for each mixture.

Table S6b. Tait parameters for mixture density calculations for HXD + N_2 mixtures for each isopleth listed with the Δ_{AAD}, Δ_{max}, and the temperature-pressure ranges fit to the equation. Tait parameters for pure HXD are taken from Rowane et al.[1]

x_{N2}:	0	0.209	0.290	0.453	0.581	0.686	0.816	0.902
w_{N2}:	0	0.032	0.048	0.093	0.147	0.212	0.354	0.533
C:	0.21	0.2025	0.2513	0.2793	0.3183	0.3334	0.4023	1.1791
a_2:	$-2.2800{\bullet}10^{-4}$	$4.2827{\bullet}10^{-4}$	$-4.5110{\bullet}10^{-4}$	$-1.3120{\bullet}10^{-4}$	$1.2020{\bullet}10^{-3}$	$-5.6523{\bullet}10^{-5}$	$3.1774{\bullet}10^{-4}$	$-3.0804{\bullet}10^{-3}$
a_1:	$-5.3980{\bullet}10^{-1}$	-1.1085	$-3.8873{\bullet}10^{-1}$	$-7.0477{\bullet}10^{-1}$	-2.0846	-1.1628	-2.0540	1.1020
a_0:	$9.5090{\bullet}10^{2}$	$1.0562{\bullet}10^{3}$	$9.0966{\bullet}10^{2}$	$9.9523{\bullet}10^{2}$	$1.3402{\bullet}10^{3}$	$1.1979{\bullet}10^{3}$	$1.5610{\bullet}10^{3}$	$7.9898{\bullet}10^{2}$
b_2:	$9.8970{\bullet}10^{-4}$	$6.7512{\bullet}10^{-4}$	$4.1450{\bullet}10^{-4}$	$-8.1536{\bullet}10^{-5}$	$5.2864{\bullet}10^{-4}$	$1.1140{\bullet}10^{-3}$	$-3.4550{\bullet}10^{-3}$	$-6.9053{\bullet}10^{-3}$
b_1:	-1.191	$-7.4976{\bullet}10^{-1}$	$-5.4141{\bullet}10^{-1}$	$-1.2693{\bullet}10^{-1}$	$-5.2003{\bullet}10^{-1}$	-1.2490	3.5381	6.7162
b_0:	$3.7410{\bullet}10^{2}$	$2.0975{\bullet}10^{2}$	$1.7818{\bullet}10^{2}$	$8.5495{\bullet}10^{1}$	$1.1839{\bullet}10^{2}$	$3.2744{\bullet}10^{2}$	$-9.4192{\bullet}10^{2}$	$-1.5720{\bullet}10^{3}$
Δ_{AAD}:	0.2	0.2	0.2	0.1	0.2	0.0	0.0	0.1
Δ_{MAX}:	0.5	0.6	0.9	0.2	0.7	0.1	0.1	0.4
T_{range}/K	323 - 526	323 - 525	325 - 536	327 - 459	325 - 529	395 - 529	469 - 527	499 - 531
p_{range}/MPa	4 - 210	BP*- 130	BP* - 128	BP* - 128	BP* - 131	BP* - 135	BP* - 138	BP* - 135

BP* -- The minimum pressure is equal to the BP at a given temperature for each mixture.

Modeling Mixture Densities

Table S7 lists the results for mixture density calculations for both HXD + N_2 and HMN + N_2 mixtures using the PC-SAFT EoS with T-GC[2] and S-GC[3] pure component parameters and with $k_{ij} = 0$. Both sets of GC parameters give identical Δ_{AAD} values. However, the values of the Δ_{bias} indicate that mixture densities are over predicted using the T-GC method and under predicted using the S-GC method, by almost the same absolute percentages. Although not shown here, better mixture density predictions are found using GC parameters reported by Burgess, et al.[4], which is not unexpected since Burgess regressed GC parameters from HPHT density data sets, while Sauer and Tihic both regressed parameters from low pressure, vapor pressure and saturated liquid density data. Table 3 also shows that mixture density calculations for the HMN + N_2 system are predicted slightly better using the PC-SAFT EoS with T-GC pure component parameters and with $k_{ij} = 0$. With both sets of pure component parameters the bias is negative although the results using the T-GC method are again slightly better than the results using the S-GC method.

Table S7. Results for PC-SAFT predicted mixture densities with GC-calculated pure component parameters and with $k_{ij} = 0$ for HXD + N_2 mixtures (a) Tihic's GC method and (b) Sauer's GC method and for HMN + N_2 mixtures (c) Tihic's GC method and (d) Sauer's GC method.

(a) HXD + N_2 (T-GC Method)

x_{N2}	0.209	0.290	0.452	0.581	0.685	0.816	0.902	Overall
Δ_{AAD}	1.9	3.2	2.6	3.1	5.7	3.9	5.9	3.5
Δ_{bias}	-1.9	-3.2	-2.6	-3.1	-5.7	-3.9	-5.9	– 3.5
Δ_{stdev}	0.6	0.8	0.3	1.4	0.6	0.4	0.3	1.5
Δ_{max}	3.8	5.4	3.3	5.2	7.1	4.8	6.4	7.1
Data points	30	33	21	27	21	22	12	166

(b) HXD + N_2 (S-GC Method)

x_{N2}	0.209	0.290	0.452	0.581	0.685	0.816	0.902	Overall
Δ_{AAD}	5.7	4.4	4.4	3.6	0.6	0.9	2.8	3.5
Δ_{bias}	5.7	4.4	4.4	3.6	0.4	0.9	-2.8	3.0
Δ_{stdev}	0.4	0.6	0.2	1.2	0.3	0.4	0.3	1.9
Δ_{max}	6.4	5.0	4.8	5.6	1.1	1.5	3.3	6.4
Data points	30	33	21	27	21	22	12	166

(c) HMN + N_2 (T-GC Method)

x_{N2}	0.149	0.392	0.571	0.671	0.760	0.773	0.874	0.894	Overall
Δ_{AAD}	3.0	4.0	5.8	6.1	5.2	9.2	9.9	6.5	5.5
Δ_{bias}	-3.0	-4.0	-5.8	-6.1	-5.2	-9.2	-9.9	-6.5	-5.5
Δ_{stdev}	0.5	0.4	1.2	1.2	1.1	1.2	1.1	0.6	2.3
Δ_{max}	4.1	5.0	8.3	8.9	7.7	11.5	11.7	7.8	11.7
Data points	33	29	23	10	36	19	17	16	183

(d) HMN + N_2 (S-GC Method)

x_{N2}	0.149	0.392	0.571	0.671	0.760	0.773	0.874	0.894	Overall
Δ_{AAD}	7.4	8.2	9.7	9.7	8.3	9.2	9.0	6.4	8.3
Δ_{bias}	-7.4	-8.2	-9.7	-9.7	-8.3	-9.2	-9.0	-6.4	-8.3
Δ_{stdev}	0.6	0.5	1.4	1.4	1.2	1.2	1.41	0.8	1.6
Δ_{max}	9.7	9.7	12.7	12.8	11.0	11.6	11.8	7.3	12.8
Data points	33	29	23	10	36	19	17	16	183

Modeling VLE

Tables S8a to S8d are the results from a comparison of Antoine-calculated p-x_{N2} isotherms at 323, 373, 423, 473, and 523 K for HXD + N_2 mixtures with PC-SAFT-calculated values with pure component parameters calculated with the two GC methods when k_{ij} = 0. The PC-SAFT-calculated isotherms severely under predict the experimental isotherms using either GC method when k_{ij} = 0. However, the results listed in tables S9a to S9d demonstrate that the agreement between predicted and observed phase behavior for both mixtures improves considerably with both GC methods when k_{ij} is set to a nonzero, positive value, reflecting the much higher sensitivity of phase behavior calculations to values of $\boldsymbol{\varepsilon/k}$, the energetic parameter.

Table S8. Results for PC-SAFT predictions of BP/DP pressures with GC-calculated pure component parameters and with k_{ij} = 0 for HXD + N_2 mixtures (a) Tihic's GC method and (b) Sauer's GC method and for HMN + N_2 mixtures (c) Tihic's GC method and (d) Sauer's GC method.

(a) HXD + N_2 (S-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	62	54	50	47	48	51
Δ_{bias}	62	54	50	47	48	51
Δ_{stdev}	4	3	6	6	6	7
Δ_{Max}	67	58	59	57	59	67

(b) HXD + N_2 (T-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	58	48	44	40	38	45
Δ_{bias}	58	48	44	40	38	45
Δ_{stdev}	5	4	7	7	5	9
Δ_{Max}	64	53	55	51	46	64

(c) HMN + N_2 (S-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	56	50	43	36	39	41
Δ_{bias}	56	50	43	36	39	41
Δ_{stdev}	4	6	5	5	24	10

Δ_{Max}	62	59	49	46	100	62

(d) HMN + N_2 (T-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	57	52	45	41	37	44
Δ_{bias}	57	52	45	41	37	44
Δ_{stdev}	4	6	5	5	5	8
Δ_{Max}	62	61	51	50	46	62

Table S9. Results for PC-SAFT predictions of BP/DP pressures with GC-calculated pure component parameters using the best-fit k_{ij} for HXD + N_2 mixtures (a) Tihic's GC method and (b) Sauer's GC method and for HMN + N_2 mixtures (c) Tihic's GC method and (d) Sauer's GC method.

(a) HXD + N_2 (S-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	21	8	11	12	18	14
Δ_{bias}	-12	7	11	12	18	9
Δ_{stdev}	25	6	5	6	8	11
Δ_{Max}	57	17	18	20	26	57

(b) HXD + N_2 (T-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	11	4	6	6	10	7
Δ_{bias}	-5	3	6	5	10	5
Δ_{stdev}	10	5	5	4	5	6
Δ_{Max}	24	11	11	12	16	24

(c) HMN + N_2 (S-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	6	7	5	13	13	10
Δ_{bias}	6	7	4	-8	-8	-2
Δ_{stdev}	6	6	5	16	14	12
Δ_{Max}	13	14	14	51	46	51

(d) HMN + N_2 (T-GC Method)

T/K	323	373	423	473	530	Overall
Δ_{AAD}	7	8	6	13	12	10
Δ_{bias}	3	8	6	-4	2	2
Δ_{stdev}	6	6	7	15	10	10
Δ_{Max}	14	16	18	49	31	49

<u>References</u>

1. Rowane, A. J.; Mallepally, R. R.; Gupta, A.; Gavaises, M.; McHugh, M. A., High-Temperatures, High-Pressure Viscosities and Densities of *n*-Hexadecane, 2,2,4,4,6,8,8-Heptamethylnonane, and Squalane Measured Using a Universal Calibration for a Rolling-Ball Viscometer/Densimeter. *Industrial & Engineering Chemistry Research* **2019,** 58, 4303-4316.
2. Tihic, A.; Kontogeorgis, G. M.; von Solms, N.; Michelsen, M. L., A Predictive Group-Contribution Simplified PC-SAFT Equation of State: Application to Polymer Systems. *Ind Eng Chem Res* **2008,** 47, 5092-5101.
3. Sauer, E.; Stavrou, M.; Gross, J., Comparison between a homo- and a heterosegmented group contribution approach based on the perturbed-chain polar statistical associating fluid theory equation of state. *Ind Eng Chem Res* **2014,** 53, 14854-14864.
4. Burgess, W. A.; Tapriyal, D.; Gamwo, I. K.; Wu, Y.; McHugh, M. A.; Enick, R. M., New group-contribution parameters for the calculation of PC-SAFT parameters for use at pressures to 276 MPa and temperatures to 533 K. *Ind Eng Chem Res* **2014,** 53, 2520-2528.