

Figure 5. Pressure-equilibrium phase composition diagram for the CO_2 -*m*-xylene system.

mization of the percent error in the calculated total pressure. Values of k_{ij} obtained and estimation of the data by the Peng-Robinson equation of state are also presented in Figures 2-5. A fairly good representation of the data by the Peng-Robinson equation was achieved.

While this work was in progress, Ng et al. (5) published a study reporting data for the system CO_2 -*m*-xylene. Some of these data were in the same temperature and pressure range as those previously measured in this work. Although the iso-

therms do not match exactly, the compatibility of the two sets of data is good. The estimation of CO_2 -*m*-xylene data measured in this work using the k_{ij} values reported by Ng et al. was good except for the 323.15 K isotherm, for which estimated pressures were always larger than the experimental values. Data for the system CO_2 -*m*-xylene at higher temperatures are available in the literature (6).

Glossary

P	pressure
R	universal gas constant
T	temperature
v	molar volume
a, b	parameters in Peng-Robinson equation of state
k	binary interaction parameter
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

i, j components

Registry No. CO_2 , 124-38-9; 2-methyl-1-pentene, 763-29-1; 1-hexene, 592-41-6; 1-heptene, 592-76-7; *m*-xylene, 108-38-3.

Literature Cited

- (1) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59-64.
- (2) Kalra, H.; Kubota, H.; Robinson, D. B.; Ng, H.-J. *J. Chem. Eng. Data* **1978**, *23*, 317-21.
- (3) Smith, B. D.; Bowden, W. W. *Anal. Chem.* **1964**, *36*, 87-9.
- (4) Orbey, H. Ph.D. Thesis, McGill University, Montreal, Canada, 1983.
- (5) Ng, H.-J.; Huang, S. S.-S.; Robinson, D. B. *J. Chem. Eng. Data* **1982**, *27*, 119-22.
- (6) Sebastian, H. M.; Simnick, J. J.; Lin, H.-M.; Chao, K.-C. *J. Chem. Eng. Data* **1980**, *25*, 246-8.

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Three-Phase Liquid-Liquid-Vapor Equilibria in the Methane + *n*-Hexane + Nitrogen and Methane + *n*-Pentane + Nitrogen Systems

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The phase behavior of two ternary systems (methane + *n*-hexane + nitrogen, methane + *n*-pentane + nitrogen) in their three-phase liquid-liquid-vapor (L_1 - L_2 -V) regions is presented, with specific attention paid to the nature of the boundaries of the regions. Liquid-phase compositions and molar volumes are reported as functions of temperature and pressure, both within the three-phase regions and at the boundaries. The methane + *n*-hexane + nitrogen system has a L_1 - L_2 -V region bounded by a Q-point (S- L_1 - L_2 -V) locus, a K-point (L_1 - L_2 = V) locus, an LCST (L_1 = L_2 -V) locus, and the binary methane + *n*-hexane L_1 - L_2 -V locus. The methane + *n*-pentane + nitrogen system's L_1 - L_2 -V region is bounded by Q-point, K-point, and LCST loci.

Introduction

We have undertaken an extensive study of liquid-liquid-vapor (L_1 - L_2 -V) phenomena in well-defined ternary prototype systems of liquefied natural gas (LNG). Previously, we have studied six ternary systems (1-3) composed of methane (solvent) plus *n*-octane (solute) with the following second solvents as the third component: ethane, propane, *n*-butane, *n*-pentane, *n*-hexane, and carbon dioxide. We also studied the system (3) methane *n*-hexane with carbon dioxide as the second solvent. In classifying these systems, we made special note of the nature of the boundaries of the L_1 - L_2 -V thermodynamic phase space. These spaces could be bounded by loci of (1) K points (L_1 - L_2 = V), (2) LCST points (L_1 = L_2 -V), (3) Q points (S- L_1 - L_2 -V), and (4) the methane + *n*-hexane binary L_1 - L_2 -V behavior, when applicable. The LCST and K-point loci can intersect as a tricritical point (L_1 = L_2 = V). In some of these ternary systems it should be recognized that the solute (e.g., *n*-octane) is not immiscible with either the primary or the secondary

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Table I. Raw Data for the *n*-Hexane-Rich Liquid Phase, L₁, of the System Methane + Nitrogen + *n*-Hexane

temp, K	press., atm	[<i>n</i> -hexane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)	temp, K	press., atm	[<i>n</i> -hexane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)
K (L ₁ -L ₂ = V)					L ₁ -L ₂ -V				
176.11	51.40	0.4020	0.0599	69.21	175.00	31.05	0.2224	0.0200	58.91
181.01	50.92	0.3106	0.2222	58.36	175.00	32.38	0.2499	0.0226	61.26
185.23	51.81	0.2988	0.0362	65.80	175.00	32.52	0.2526	0.0240	61.38
186.63	51.62	0.3211	0.0444	65.13	175.00	32.97	0.2570	0.0287	61.22
189.65	51.62	0.2972	0.0260	63.61	175.00	33.52	0.2636	0.0284	61.96
189.89	51.06	0.3091	0.0262	67.78	175.00	33.71	0.2658	0.0300	61.90
190.61	51.30	0.3040	0.0153	67.37	175.00	34.79	0.2809	0.0291	62.86
190.70	51.06	0.2983	0.0165	66.48	175.00	35.47	0.2907	0.0282	63.84
191.95	50.05	0.2858	0.0093	66.86	175.00	43.57	0.2930	0.0366	54.42
194.41	51.19	0.2589	0.0048	61.60	175.00	44.54	0.3736	0.0539	68.76
					175.00	50.85	0.4213	0.0591	71.98
Q (S-L ₁ -L ₂ -V)					L ₁ -L ₂ -V				
164.07	22.11	0.2005	0.0222	56.86					
164.20	23.16	0.2224	0.0256	58.47	180.00	33.78	0.2047	0.0125	59.14
164.23	23.51	0.2259	0.0275	58.59	180.00	35.75	0.2419	0.0183	61.57
164.46	24.39	0.2521	0.0305	59.74	180.00	37.76	0.2663	0.0227	63.02
164.51	24.67	0.2557	0.0329	59.90	180.00	37.93	0.2675	0.0260	62.79
164.52	25.34	0.2643	0.0299	60.75	180.00	38.81	0.2790	0.0290	63.51
164.65	25.95	0.2818	0.0319	61.96	180.00	38.82	0.2777	0.0277	63.33
165.13	27.94	0.3019	0.0379	63.01	180.00	39.83	0.2878	0.0289	63.83
166.11	34.18	0.2917	0.2368	53.51	180.00	41.19	0.3040	0.0278	65.30
166.76	38.15	0.3995	0.0175	70.35	180.00	43.05	0.3215	0.0359	66.34
167.64	45.68	0.4726	0.0635	78.07	180.00	48.90	0.3559	0.0444	67.42
					180.00	49.56	0.3038	0.0416	56.85
LCST (L ₁ = L ₂ -V)					L ₁ -L ₂ -V				
163.75	21.60	0.1001	0.0319	51.6					
165.12	23.40	0.2153	0.0246	58.0	185.00	38.47	0.2245	0.0070	61.34
165.76	22.76	0.0930	0.0318	51.4	185.00	41.75	0.2637	0.0225	63.38
167.19	22.34	0.1084	0.0354	53.2	185.00	43.44	0.2816	0.0265	64.81
168.86	25.41	0.1975	0.0207	57.4	185.00	43.68	0.2849	0.0219	65.20
170.64	25.95	0.1097	0.0278	54.0	185.00	44.39	0.2882	0.0255	64.78
173.05	27.45	0.1160	0.0248	54.0	185.00	44.80	0.2928	0.0252	65.12
177.27	31.06	0.1858	0.0143	57.7	185.00	45.08	0.2910	0.0254	64.40
182.02	33.37	0.1195	0.0072	55.9	185.00	47.45	0.3132	0.0257	66.22
					185.00	49.58	0.3373	0.0309	68.81
L ₁ -L ₂ -V ^a					L ₁ -L ₂ -V				
165.00	22.79	0.1955	0.0226	56.56					
165.00	22.99	0.2076	0.0234	57.17	190.00	44.80	0.2530	0.0071	63.87
165.00	23.84	0.2271	0.0290	58.24	190.00	44.94	0.2503	0.0045	62.99
165.00	24.19	0.2341	0.0312	58.35	190.00	45.41	0.2678	0.0176	66.10
165.00	24.80	0.2513	0.0314	59.63	190.00	47.26	0.2745	0.0192	64.90
165.00	25.08	0.2544	0.0339	59.77	190.00	49.50	0.2903	0.0369	65.26
165.00	25.68	0.2694	0.0301	61.06	190.00	50.10	0.2925	0.0230	65.26
165.00	26.36	0.2791	0.0320	61.51	190.00	50.42	0.2940	0.0316	64.77
L ₁ -L ₂ -V					L ₁ -L ₂ -V				
170.00	26.43	0.2049	0.0197	57.86					
170.00	27.69	0.2361	0.0241	59.78					
170.00	28.41	0.2488	0.0293	60.19					
170.00	28.48	0.2330	0.0290	59.35					
170.00	29.08	0.2582	0.0301	60.64					
170.00	30.37	0.2787	0.0284	62.34					
170.00	30.91	0.2827	0.0312	62.60					
170.00	32.43	0.3044	0.0639	63.57					
170.00	41.62	0.4162	0.0573	70.80					
170.00	48.54	0.4770	0.0484	77.76					

^a Compositions and volumes for the L₁ side of the 165 K isotherm were arrived at by estimating the L₂ values from cross-plots of K and LCST values.

solvent, but rather only exhibits immiscibility with mixtures of the solvents.

Interest has grown in the phase equilibria of LNG systems containing nitrogen. Nitrogen is sometimes used as a pressurizing gas in enhanced oil recovery processes, and processes for the separation of the LNG components from nitrogen-rich streams have been developed. The presence of nitrogen has been known to induce L₁-L₂-V behavior in LNG systems (4-7). This paper presents results for the L₁-L₂-V region of two nitrogen-containing systems: methane + *n*-hexane + nitrogen, and methane + *n*-pentane + nitrogen. Liquid-phase compositions and molar volumes are reported for the regions and their various boundaries. We are planning to study several other ternary systems in the future.

Experimental Section

This experimental study was performed on apparatus previously used by Kohn and co-workers. Earlier papers covered the details of the procedure (1, 2).

The phenomena reported were observed in glass cells marked and calibrated to permit direct visual inspection. Stoichiometric and volumetric measurements were made. These measurements permitted the computation of the composition and molar volume of each liquid phase. The temperature of the system was measured with a platinum resistance thermometer. This thermometer was calibrated to IPTS-1968 standards and is estimated to be accurate to ± 0.03 K. The system's pressure was measured with a Heise Bourdon tube

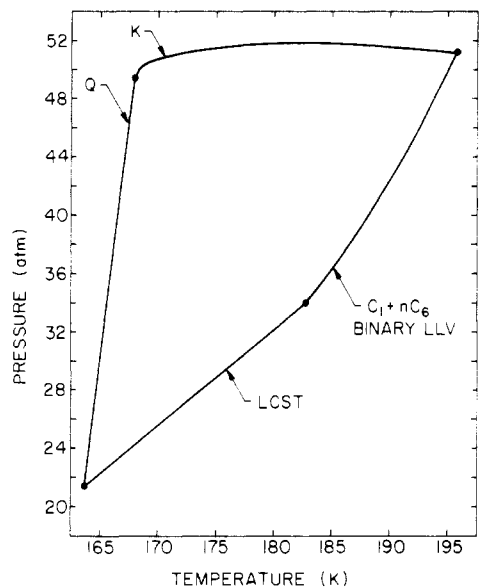


Figure 1. Immiscibility region of methane + *n*-hexane + nitrogen.

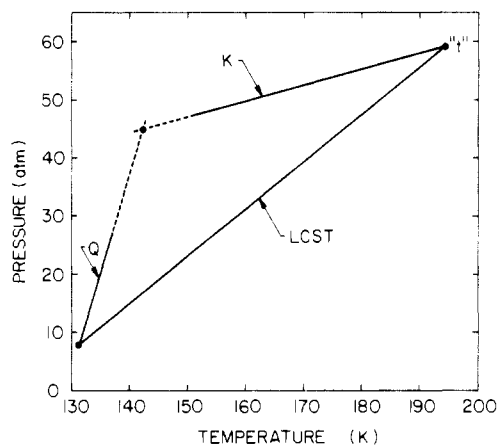


Figure 2. Immiscibility region of methane + *n*-pentane + nitrogen.

gauge, which was accurate to ± 0.07 atm. The cell markings allowed the volumes of the phases within the cell to be read to ± 0.02 cm³.

The gas phase was assumed to be a mixture of methane and nitrogen. The extremely low vapor-phase mole fraction for both *n*-hexane and *n*-pentane in the methane + *n*-hexane and methane + *n*-pentane binary systems justifies this assumption (8, 9). The mixture of methane and nitrogen was assumed to have the composition of the vapor phase of the methane + nitrogen binary system as reported by Hiza and co-workers (10). The vapor-space compressibility was estimated with the Soave-Redlich-Kwong equation of state, as modified by Graboski and Daubert (11, 12). We minimized any errors engendered by these assumptions by minimizing the vapor present in the cell.

The methane used in this study was Linde "Ultra Pure" grade with a stated purity of 99.97 mol %. The nitrogen used was Linde "High Purity" grade with a stated purity of 99.99 mol %. The *n*-hexane was a product of the Humphrey Chemical Co. with a stated purity of 99 mol %. The *n*-pentane was a product of the Phillips Chemical Co. and had a stated purity of 99 mol %. All of the materials were used without further purification.

Experimental Results

The immiscibility region of the methane + *n*-hexane + nitrogen system is illustrated in Figure 1. Figure 2 illustrates the immiscibility region of the methane + *n*-pentane + nitrogen

Table II. Raw Data for the *n*-Hexane-Lean Liquid Phase, L₂, of the System Methane + Nitrogen + *n*-Hexane

temp, K	press., atm	[<i>n</i> -hexane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)
K (L ₁ -L ₂ = V)				
168.48	50.25	0.0047	0.4119	102.77
169.90	50.80	0.0037	0.3748	93.50
176.96	51.46	0.0115	0.2490	80.36
179.67	51.73	0.0138	0.2203	84.63
181.95	51.80	0.0148	0.1973	88.61
183.61	51.81	0.0043	0.1784	96.05
184.25	49.62	0.0052	0.1707	125.15
185.04	51.73	0.0187	0.1617	97.32
186.90	51.75	0.0063	0.1270	90.80
189.01	51.61	0.0079	0.1005	95.36
190.19	51.61	0.0212	0.0420	86.32
191.10	51.54	0.0125	0.0732	96.12
Q (S-L ₁ -L ₂ -V)				
164.25	22.75	0.0804	0.0446	51.23
164.52	25.34	0.0528	0.0692	50.72
165.28	29.96	0.0305	0.1142	51.26
165.35	29.56	0.0281	0.1079	51.17
165.53	30.37	0.0319	0.1147	51.07
165.53	30.71	0.0298	0.1225	51.60
165.65	29.43	0.0368	0.1054	51.15
165.94	33.50	0.0193	0.1469	52.09
166.18	35.55	0.0204	0.1706	53.19
L ₁ -L ₂ -V				
170.00	31.80	0.0329	0.0867	51.63
170.00	32.00	0.0311	0.0923	52.45
170.00	34.05	0.0258	0.1099	52.89
170.00	34.86	0.0236	0.1188	53.16
170.00	38.26	0.0177	0.1495	54.26
170.00	39.43	0.0157	0.1750	55.55
170.00	40.04	0.0193	0.1805	56.06
L ₁ -L ₂ -V				
175.00	36.56	0.0278	0.0891	54.10
175.00	37.04	0.0264	0.0946	55.32
175.00	39.08	0.0195	0.1047	55.86
175.00	39.63	0.0193	0.1180	56.18
175.00	39.76	0.0193	0.1233	56.45
175.00	40.37	0.0177	0.1272	56.63
175.00	41.81	0.0155	0.1412	57.71
175.00	44.05	0.0124	0.1652	59.56
175.00	45.55	0.0078	0.1875	61.51
L ₁ -L ₂ -V				
180.00	37.17	0.0359	0.0459	54.70
180.00	37.24	0.0356	0.0489	55.81
180.00	45.48	0.0135	0.1218	61.42
180.00	45.68	0.0136	0.1272	59.64
180.00	45.76	0.0154	0.1187	60.21
180.00	45.89	0.0154	0.1287	62.36
180.00	48.82	0.0109	0.1686	68.96
180.00	49.29	0.0074	0.1674	70.22
180.00	51.05	0.0078	0.1963	75.08
L ₁ -L ₂ -V				
185.00	40.51	0.0352	0.0286	57.43
185.00	42.89	0.0392	0.0517	59.68
L ₁ -L ₂ -V				
190.00	44.47	0.0261	0.0176	63.51
190.00	45.83	0.0248	0.0352	63.98
190.00	49.57	0.0146	0.0610	68.86

system. Tables I and II present the liquid-phase compositions and the molar volumes for the methane + *n*-hexane + nitrogen systems. Tables III and IV present the liquid-phase compositions and molar volumes for the methane + *n*-pentane + nitrogen system. Tables I and III present the data for the solute-rich, L₁, phase. Tables II and IV present the data for the solute-lean, L₂, phase.

Data for the methane + *n*-hexane binary is reported by Lin et al. (9). The results for the binary system were later reported by this laboratory as well (3).

Table III. Raw Data for the *n*-Pentane-Rich Liquid Phase, L_1 , of the System Methane + Nitrogen + *n*-Pentane

temp, K	press., atm	[<i>n</i> -pentane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)	temp, K	press., atm	[<i>n</i> -pentane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)
K ($L_1-L_2 = V$)					L_1-L_2-V				
149.10	34.73	0.5679	0.0342	79.14	160.00	32.02	0.2201	0.0935	53.40
152.68	38.13	0.5368	0.0524	76.69	160.00	32.22	0.2318	0.0964	55.73
158.96	49.29	0.5220	0.1088	72.22	160.00	32.41	0.2321	0.0953	55.55
163.05	50.79	0.4407	0.0944	64.54	160.00	32.62	0.2409	0.0935	55.05
166.51	50.11	0.4198	0.0815	67.23	160.00	33.37	0.2614	0.0926	55.32
171.98	53.51	0.3553	0.0924	60.35	160.00	33.50	0.2662	0.0885	57.65
176.82	54.60	0.3134	0.0876	61.37	160.00	35.01	0.2950	0.1477	57.89
177.36	54.40	0.3422	0.0583	56.94	160.00	36.43	0.3234	0.0928	59.79
178.81	54.19	0.2760	0.0794	57.86	160.00	44.32	0.4931	0.0972	74.08
180.96	55.83	0.2664	0.0758	58.10	160.00	46.71	0.4631	0.0859	66.90
182.80	56.16	0.2589	0.0738	60.24					
190.61	58.42	0.1767	0.0646	58.58					
Q ($S-L_1-L_2-V$)					L_1-L_2-V				
133.79	16.22	0.3975	0.0875	60.61	165.00	36.23	0.2088	0.0928	54.99
134.32	18.88	0.4569	0.0838	63.76	165.00	36.44	0.2203	0.0932	54.56
134.95	19.96	0.5178	0.0876	70.88	165.00	37.05	0.2339	0.0979	56.61
					165.00	37.11	0.2532	0.0892	57.13
					165.00	37.72	0.2553	0.0908	57.63
					165.00	38.27	0.2644	0.0926	56.20
					165.00	39.08	0.2795	0.0879	59.11
153.08	25.55	0.1519	0.1238	51.11	165.00	40.44	0.3097	0.0962	59.65
162.19	33.51	0.1946	0.0965	53.15	165.00	41.60	0.3236	0.0938	60.76
169.78	39.29	0.1344	0.1123	53.84	165.00	44.46	0.3658	0.0843	62.22
172.88	41.94	0.1474	0.1043	54.78	165.00	48.34	0.4100	0.0904	65.06
174.09	43.04	0.1472	0.1005	54.36	165.00	48.34	0.4113	0.0826	64.91
177.06	45.49	0.1064	0.1118	54.76					
180.04	47.94	0.1049	0.1081	57.92					
180.04	48.01	0.1096	0.1022	54.76	170.00	41.07	0.2182	0.0900	55.69
181.71	49.30	0.0900	0.1064	57.89	170.00	41.75	0.2389	0.0839	56.71
183.11	50.59	0.0780	0.1043	57.09	170.00	42.22	0.2499	0.0922	58.56
184.09	51.21	0.1160	0.0989	59.03	170.00	42.28	0.2478	0.0911	57.67
187.13	53.52	0.1181	0.0896	58.91	170.00	43.23	0.2649	0.0875	57.34
189.09	56.31	0.1586	0.0705	57.73	170.00	43.64	0.2701	0.0866	57.92
					170.00	45.07	0.2929	0.0830	59.90
					170.00	46.16	0.3131	0.0924	60.68
140.00	19.56	0.3532	0.0785	58.99	170.00	47.52	0.3318	0.0896	61.91
140.00	20.44	0.3813	0.0848	60.31	170.00	50.92	0.3694	0.0945	63.96
140.00	21.94	0.4191	0.0784	62.52	170.00	52.01	0.3817	0.0902	63.48
140.00	23.43	0.4442	0.0806	63.65					
140.00	24.32	0.5076	0.0866	70.33					
140.00	25.54	0.5295	0.0907	71.64					
L_1-L_2-V					L_1-L_2-V				
150.00	28.20	0.3550	0.0847	60.27	175.00	43.92	0.1511	0.1019	54.69
150.00	28.61	0.3617	0.0913	60.33	175.00	44.12	0.1634	0.1049	55.62
150.00	31.87	0.4215	0.0817	64.01	175.00	46.44	0.2333	0.0843	57.91
150.00	32.69	0.4304	0.0852	64.03	175.00	47.04	0.2426	0.0874	58.27
150.00	35.14	0.5042	0.0945	71.29	175.00	48.07	0.2611	0.0828	59.21
150.00	35.48	0.5150	0.0940	72.29	175.00	48.14	0.2632	0.0751	58.43
150.00	37.72	0.5510	0.1002	74.38	175.00	49.15	0.2756	0.0839	59.17
					175.00	49.97	0.2865	0.0826	59.36
					175.00	50.99	0.2993	0.0856	60.50
					175.00	52.28	0.3087	0.0942	60.68
L_1-L_2-V					L_1-L_2-V				
					180.00	48.27	0.1584	0.0913	56.78
					180.00	48.75	0.1751	0.0856	57.66
					180.00	52.57	0.2448	0.0802	59.14
					180.00	52.62	0.2550	0.0837	60.47
					180.00	54.54	0.2822	0.0830	61.97

As error analysis for the study was performed. The results of the error analysis indicate that the maximum error for the solute composition is $\pm 3.57\%$ in the L_1 phase and $\pm 3.03\%$ in the L_2 phase. The second solvent compositions have a maximum error of $\pm 8.85\%$ in the L_1 phase and $\pm 2.93\%$ in the L_2 phase. The molar volumes have maximum errors of $\pm 4.12\%$ and $\pm 2.12\%$ in the L_1 and L_2 phases, respectively.

Remarks

The nitrogen-containing systems presented in this study display much wider immiscibility regions than those seen earlier. The methane + *n*-pentane + nitrogen system extends over a much greater area than the methane + *n*-pentane + *n*-octane system reported previously (3). The methane + *n*-pentane + *n*-octane system extends from a Q-LCST point at 188.55 K and

40.10 atm to a tricritical point at 203.30 K and 60.22 atm. The methane + *n*-pentane + nitrogen system runs from a Q-LCST point at 131.18 K and 7.70 atm to a tricritical point at 194.22 K and 59.39 atm. The triangular L_1-L_2-V region for the present system is much wider than that of the purely hydrocarbon system.

Similarly, the methane + *n*-hexane + nitrogen system extends over a much wider area than that of the methane + *n*-hexane + *n*-octane system. These two systems are topologically similar, sharing the same sort of boundaries (K-point, Q-point, LCST, and binary L_1-L_2-V loci). The purely hydrocarbon system is extremely narrow, undoubtedly due to the molecular similarity of *n*-hexane and *n*-octane. The immiscibility region of the methane + *n*-hexane + nitrogen system is much wider than that of the methane + *n*-hexane + *n*-octane system.

Table IV. Raw Data for the *n*-Pentane-Lean Liquid Phase, L_2 , of the System Methane + Nitrogen + *n*-Pentane

temp, K	press., atm	[<i>n</i> -pentane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)	temp, K	press., atm	[<i>n</i> -pentane], mole fraction	[nitrogen], mole fraction	molar vol, mL/(g-mol)
K ($L_1-L_2 = V$)					L_1-L_2-V				
153.83	46.84	0.0090	0.6232	98.86	160.00	34.32	0.0469	0.1987	50.03
171.77	53.31	0.0042	0.3762	93.58	160.00	36.57	0.0322	0.2378	51.50
173.07	53.85	0.0063	0.3436	85.26	160.00	37.32	0.0287	0.2545	51.71
174.15	53.72	0.0045	0.3578	96.93	160.00	40.66	0.0186	0.3066	53.99
174.49	54.19	0.0081	0.3040	75.33	L_1-L_2-V				
174.85	54.60	0.0043	0.3414	95.59	165.00	39.77	0.0373	0.2135	52.42
175.41	53.79	0.0117	0.3387	101.60	165.00	43.03	0.0239	0.2607	54.66
176.02	54.60	0.0081	0.2979	80.66	165.00	43.38	0.0224	0.2677	55.77
177.44	55.01	0.0059	0.3000	88.81	165.00	48.61	0.0104	0.3564	61.88
179.19	55.29	0.0164	0.2468	73.58	L_1-L_2-V				
183.03	56.03	0.0253	0.2230	89.84	170.00	42.35	0.0458	0.1787	53.70
187.19	57.25	0.0127	0.1779	86.61	170.00	44.73	0.0325	0.2124	55.01
187.75	57.59	0.0167	0.1576	76.87	170.00	45.35	0.0297	0.2221	55.83
188.26	57.66	0.0100	0.1655	86.31	170.00	48.07	0.0188	0.2609	59.44
188.83	57.72	0.0098	0.1576	85.97	170.00	48.48	0.0189	0.2694	59.85
188.86	58.00	0.0165	0.1457	76.35	170.00	50.58	0.0170	0.2791	59.60
192.18	58.27	0.0028	0.1244	92.70	170.00	51.27	0.0117	0.3195	65.60
Q ($S-L_1-L_2-V$)					L_1-L_2-V				
132.28	12.01	0.1206	0.1835	56.61	175.00	47.25	0.0384	0.1773	57.21
132.64	12.62	0.0718	0.1612	44.63	175.00	48.14	0.0330	0.1909	57.13
133.26	14.05	0.0508	0.1943	44.17	175.00	48.48	0.0320	0.1913	58.21
135.67	22.76	0.0052	0.4194	45.90	175.00	50.38	0.0226	0.2214	60.45
L_1-L_2-V					L_1-L_2-V				
140.00	16.98	0.0744	0.1626	46.07	175.00	51.06	0.0197	0.2355	61.81
140.00	18.34	0.0551	0.1966	45.67	175.00	51.68	0.0182	0.2428	62.89
140.00	18.88	0.0488	0.2140	45.95	175.00	51.74	0.0178	0.2404	62.57
140.00	24.39	0.0093	0.3591	47.17	L_1-L_2-V				
140.00	26.63	0.0004	0.4265	48.32	180.00	49.70	0.0467	0.1414	58.27
L_1-L_2-V					180.00	51.00	0.0364	0.1644	60.90
150.00	24.53	0.0614	0.1632	48.59	180.00	51.20	0.0364	0.1611	59.63
150.00	26.57	0.0427	0.2180	48.58	180.00	53.03	0.0245	0.1929	64.34
150.00	26.98	0.0368	0.2211	47.90	180.00	53.04	0.0264	0.1900	62.66
150.00	35.48	0.0101	0.3912	51.43	180.00	53.10	0.0249	0.1878	63.44
150.00	36.91	0.0042	0.4290	52.65					

The slope (dP/dT) of the K-point locus is much steeper in the hydrocarbon systems than in the nitrogen systems. The Q-point locus is less steep in the hydrocarbon systems. We believe this is due to the affinity (or lack of affinity) of the components for each other. Nitrogen does not penetrate the liquid phases as thoroughly as does *n*-octane. Hence, the nitrogen stays concentrated in the vapor phase. This means that the critical phase compositions do not vary as much in the nitrogen systems as they do in the hydrocarbon systems. This in turn causes a "flat" K-point locus. Similarly, the concentration of nitrogen in the vapor phase prevents it from affecting the freezing point depression of the solute to any great degree.

Glossary

C	critical point
K	the K point or upper critical end point of an L_1-L_2-V region occurs when the L_2 phase becomes critically identical with the vapor phase
L_1	liquid phase rich in solute
L_2	liquid phase lean in solute
LCST	lower critical solution temperature—occurs when the L_1 and L_2 phases become critically identical with each other
Q	quadruple point—occurs whenever there is equilibrium coexistence of four phases, in this case L_1 , L_2 , V, and S phases
t	tricritical point—occurs under conditions at which three phases are in critical identity

S solid phase
T temperature
V vapor phase

Registry No. Methane, 74-82-8; nitrogen, 7727-37-9; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3.

Literature Cited

- Hottovy, J. D.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data* **1981**, *26*, 135.
- Hottovy, J. D.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data* **1982**, *27*, 298.
- Merrill, R. C.; Kohn, J. P.; Luks, K. D. *J. Chem. Eng. Data* **1983**, *28*, 210.
- Chang, S. D.; Lu, B. C.-Y. *Chem. Eng. Prog., Symp. Ser.* **1967**, *63*, 18.
- Lu, B. C.-Y.; Yu, P.; Poon, D. P. L. *Nature (London)* **1969**, *222*, 768.
- Yu, P.; Elshayal, I. M.; Lu, B. C.-y. *Can. J. Chem. Eng.* **1969**, *47*, 495.
- Stroud, L.; DeVaney, W. E.; Miller, J. E. *Soc. Pet. Eng. J.* **1961**, *1*, 137.
- Chu, T.-C.; Chen, R. J. J.; Chapplelear, P. S.; Kobayashi, R. J. *Chem. Eng. Data* **1978**, *21*, 41.
- Lin, Y.-N.; Chen, R. J. J.; Chapplelear, P. S.; Kobayashi, R. J. *Chem. Eng. Data* **1977**, *22*, 402.
- Kidnay, A. J.; Miller, R. C.; Parrish, W. R.; Hiza, M. J. *Cryogenics* **1975**, *15*, 531.
- Graboski, M. S.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 443.
- Graboski, M. S.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 448.

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