Registry No. CO_2, 124-38-9; styrene, 100-42-5.

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Three-Phase Liquid–Liquid–Vapor Equilibria in the Nitrogen + Methane + *n*-Heptane System

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The three-phase liquid–liquid–vapor (L_1–L_2–V) phase equilibria behavior of the ternary mixture nitrogen + methane + *n*-heptane is presented, with special attention directed toward identifying the boundaries of the three-phase region. This ternary system has a constituent binary mixture, methane + *n*-heptane, which exhibits L_1–L_2–V immiscibility. The presence of nitrogen creates a three-sided L_1–L_2–V region extending in pressure–temperature space down in temperature, over a range of 169–192 K, from the binary L_1–L_2–V locus. The other two boundaries of the three-phase region are type K point (L_1–L_2=V) and Q point (S–L_1–L_2–V) loci. Liquid-phase compositions and molar volumes are reported as a function of temperature and pressure within the three-phase region and along the boundaries.

Introduction

We have been engaged in an extensive study of liquid–liquid–vapor (L_1–L_2–V) phenomena in well-defined ternary prototype mixtures of liquefied natural gas (LNG) (*1*–*7*), in order to help understand the possible occurrence of multiphase equilibria in LNG process systems. To date, we have studied five ternary mixtures containing nitrogen + methane (*4*, *5*, *7*), with the third component being the solutes ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane, respectively.

In this paper, we present results for the L_1–L_2–V phase equilibria of the ternary mixture nitrogen + methane + *n*-heptane. The binary constituent mixture methane + *n*-heptane exhibits L_1–L_2–V immiscibility. *n*-Heptane is the largest *n*-paraffin that is partially miscible with methane. Since nitrogen is more volatile than methane, *n*-heptane is therefore the largest *n*-paraffin to be immiscible with mixtures of nitrogen + methane. The role of nitrogen is to create a three-phase L_1–L_2–V region (surface) in thermodynamic phase space, extending down in temperature from the binary L_1–L_2–V locus. Liquid-phase compositions and molar volumes are reported herein for the L_1 and L_2 phases in the three-phase region including along its boundaries.

Experimental Section

The experimental study was performed using and apparatus originally developed by Kohn and co-workers (*8*). The experimental procedures are detailed in ref *1* and *2*.

The multiphase equilibria phenomena were observed in a glass visual cell of approximately 12 mL internal volume, marked and calibrated so that phase volumes could be determined by direct visual inspection. Stoichiometric and phase volumetric measurements were made on the liquid phases in the cell which permitted the computation of the composition and molar volume of each of those phases. In order to calculate these properties accurately, the amount of the vapor phase was kept small during any run, and the composition of the vapor phase was assumed to be a mixture of nitrogen and methane only. This assumption appears justified given the very low vapor phase mole fraction of *n*-heptane in the phase equilibria of the binary mixture methane + *n*-heptane at comparable temperatures (*8*). Further justification for the assumption is found in Table II, where the composition of the L_2 phase at L_2=V in the presence of L_1 phase is given for several conditions. The maximum composition of *n*-heptane at any conditions given is 0.0044 mole fraction and generally averages asound 0.003 mole fraction. Since the composition of *n*-heptane in all of the noncritical vapor phases must be lower than that in the critical (L_2=V) phase and this composition of the critical vapor phase is obtained without invoking the simplifying assumption of zero *n*-heptane, the upper limit for composition of *n*-heptane in all the gas phases is clearly established. The vapor-phase nitrogen + methane composition was assumed to be the same as that for the nitrogen + methane binary vapor–liquid system as reported by Kidnay et al. (*9*) at the same temperature and pressure. Given this assumption, the vapor-phase compressibility factor, and then the amount of material in the vapor phase, was estimated by using the Soave–Redlich–Kwong equation of state as modified by Graboski and Daubert (*10*, *11*).

The temperature of the liquid bath housing the visual cell was measured with a Pt-resistance thermometer, calibrated to the IPTS-1968 scale; cell temperatures were estimated to be accurate to ±0.03 K. The system pressure was measured with a Heise bourdon tube gauge, accurate to ±0.07 bar. Liquid-phase volumes in the visual cell could be read to ±0.02 mL.

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

temp, K	press., bar	[nitrogen], mole fracn	[methane], mole fracn	molar vol, mL/(g·mol)
K (L_1–L_2=V)				
192.00	48.63	0.0054	0.6408	75.52
189.99	48.98	0.0121	0.6269	72.70
188.65	49.19	0.0141	0.6008	76.54
187.11	49.54	0.0194	0.5886	76.75
186.82	49.54	0.0130	0.5644	82.23
184.73	49.88	0.0094	0.5611	82.34
182.10	50.16	0.0777	0.4998	78.08
178.20	50.58	0.0422	0.4806	84.71
176.53	50.58	0.0421	0.4750	84.57
175.33	50.64	0.0486	0.4656	83.62
174.21	50.64	0.0682	0.4507	81.58
173.51	50.64	0.0508	0.4577	83.01
Q (S–L_1–L_2–V)				
172.73	48.99	0.0274	0.4640	86.33
172.64	47.61	0.0257	0.4733	85.77
172.35	45.40	0.0381	0.4890	81.81
172.33	43.75	0.0324	0.5054	80.74
171.59	39.55	0.0313	0.5295	79.03
171.56	37.07	0.0266	0.5457	78.15
170.74	35.13	0.0336	0.5524	76.85
170.74	33.95	0.0100	0.5714	78.37
170.72	33.12	0.0281	0.5686	75.93
170.65	30.85	0.0105	0.5912	76.51
170.03	30.02	0.0199	0.5923	74.95
170.47	29.26	0.0133	0.6192	71.63
170.04	27.20	0.0131	0.6196	73.34
170.50	27.20	0.0078	0.6259	73.42
170.56	24.91	0.0034	0.6452	72.73
170.02	24.78	0.0063	0.6442	71.92
L_1–L_2–V				
190.00	48.13	0.0177	0.5936	79.71
	46.92	0.0114	0.6018	79.35
	46.14	0.0010	0.6182	79.05
	45.33	0.0055	0.6315	75.59
185.00	47.82	0.0119	0.5870	77.89
	46.44	0.0278	0.5876	75.41
	45.68	0.0133	0.6078	74.57
	42.50	0.0158	0.6257	74.34
	39.60	0.0013	0.6404	74.69
180.00	49.41	0.0425	0.5175	80.09
	47.82	0.0917	0.5111	73.10
	45.88	0.0796	0.5263	73.29
	44.92	0.0413	0.5555	75.96
	43.20	0.0255	0.5638	78.39
	40.78	0.0180	0.5867	76.75
	40.24	0.0268	0.5930	74.29
	39.41	0.0137	0.6149	72.99
	36.64	0.0140	0.6244	72.95
	34.70	0.0012	0.6433	71.01
175.00	50.30	0.0480	0.4322	89.27
	48.58	0.0450	0.4876	81.34
	46.92	0.0373	0.5010	81.08
	43.27	0.0293	0.5334	79.10
	38.92	0.0361	0.5536	76.68
	37.89	0.0112	0.5710	78.94
	35.40	0.0121	0.5924	76.72
	34.86	0.0236	0.5987	73.51
	34.10	0.0117	0.6192	72.59
	31.13	0.0123	0.6249	73.13
	29.18	0.0027	0.6452	73.23

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

temp, K	press., K	[nitrogen], mole fracn	[methane], mole fracn	molar vol, mL/(g·mol)
K (L_1–L_2=V)				
190.65	48.78	0.0328	0.9649	96.88
188.42	49.34	0.0785	0.9181	91.68
185.87	49.68	0.1147	0.8824	87.47
183.96	49.95	0.1488	0.8480	83.95
181.86	50.30	0.1731	0.8242	89.63
180.43	50.43	0.2083	0.7885	85.42
179.07	50.43	0.2181	0.7813	93.86
179.00	50.50	0.2385	0.7584	81.82
177.48	50.64	0.2677	0.7288	78.49
176.15	50.64	0.2906	0.7054	76.02
175.49	50.63	0.2689	0.7284	86.83
175.20	50.64	0.3121	0.6835	73.70
173.49	50.63	0.2944	0.7027	83.79
Q (S–L_1–L_2–V)				
172.54	48.99	0.2884	0.7066	60.62
172.51	47.27	0.2685	0.7262	56.83
172.44	46.85	0.2505	0.7445	57.11
173.25	46.43	0.2569	0.7394	60.31
172.35	45.40	0.2373	0.7573	58.84
172.51	44.78	0.2377	0.7584	58.25
172.26	44.10	0.2081	0.7862	56.66
172.26	43.95	0.2288	0.7668	57.46
171.93	42.44	0.2001	0.7955	59.15
171.87	40.85	0.1760	0.8187	59.50
171.60	39.05	0.1672	0.8256	54.95
171.64	38.03	0.1559	0.8375	55.07
171.07	34.92	0.1266	0.8651	52.80
170.84	32.85	0.1043	0.8853	52.21
170.57	30.78	0.0855	0.9026	51.63
169.98	28.23	0.0584	0.9272	51.32
169.89	25.75	0.0336	0.9489	51.34
169.61	23.47	0.0132	0.9672	50.44
L_1–L_2–V				
190.00	47.60	0.0287	0.9643	76.72
	46.30	0.0207	0.9714	76.19
	44.91	0.0044	0.9880	67.25
185.00	46.15	0.0673	0.9252	66.76
	44.71	0.0525	0.9381	64.03
	43.12	0.0374	0.9293	61.49
	41.61	0.0228	0.9426	60.13
	39.88	0.0176	0.9700	60.23
180.00	48.43	0.1692	0.8265	68.36
	47.82	0.1354	0.8598	65.92
	45.82	0.1211	0.8727	64.65
	45.68	0.1349	0.8598	63.28
	44.44	0.1099	0.8832	62.58
	42.45	0.0922	0.9001	60.70
	40.44	0.0732	0.9117	59.16
	38.86	0.0585	0.9312	58.42
	36.65	0.0365	0.9515	56.99
	33.82	0.0144	0.9716	55.58
175.00	48.92	0.2415	0.7546	63.35
	47.20	0.2127	0.7820	60.35
	45.74	0.2223	0.7692	60.68
	44.71	0.2067	0.7852	60.02
	43.87	0.1952	0.7965	58.57
	42.77	0.1752	0.8163	59.25
	41.62	0.1593	0.8354	57.98
	41.53	0.1357	0.8550	55.72
	37.12	0.1130	0.8759	54.42
	35.88	0.0946	0.8933	54.10
	34.02	0.0728	0.9138	54.00
	31.88	0.0509	0.9346	53.25
	30.08	0.0308	0.9527	52.81
	28.29	0.0132	0.9684	52.46

The methane used in this study was Linde "Ultra Pure" grade with a stated purity of 99.97 mol %. The nitrogen was Linde "High Purity" grade with a stated purity of 99.99 mol %. The *n*-heptane was a product of Humphrey Chemical Co., with a stated purity of 99.0 mol %. All of the materials were used without further purification.

Experimental Results

The region of three-phase L_1–L_2–V immiscibility is shown to scale in Figure 1. The surface is bounded in pressure–temperature space by the binary methane + *n*-heptane three-phase locus, a K-point (L_1–L_2=V) locus, and a Q-point (S–L_1–L_2–V) locus. The intersection of the K-point and the Q-point loci, S–L_1–L_2=V, is an invariant point, not directly observed by us but estimated to be at 172.85 K and 50.64 bar. Tables I and II present raw data for the boundaries of the region and

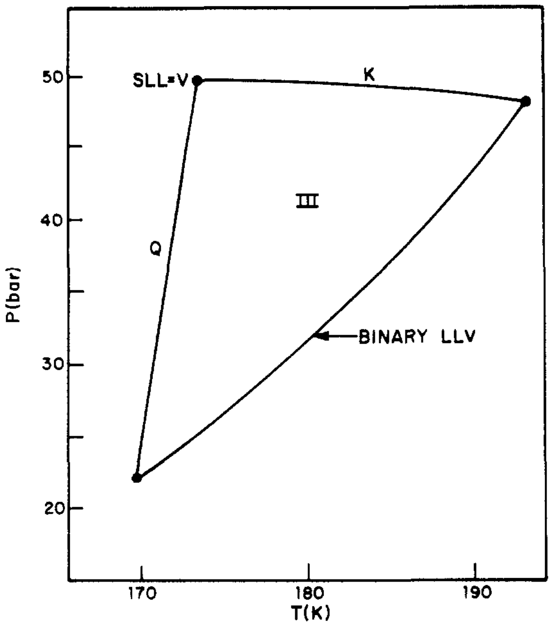

Figure 1. Projection in pressure–temperature space of the boundaries of the three-phase L_1–L_2–V region for the system nitrogen + methane + *n*-heptane.

four isotherms within the region for the L_1 ("heptane-rich") and L_2 ("heptane-lean") phases, respectively. Data on the binary methane + *n*-heptane three-phase locus are available from ref *6* and *8* and were used to help construct Figure 1.

Estimates of the reliability of the L_1–L_2–V data were made, based on the average absolute deviations of the raw data from smoothed curves. These estimates should be considered conservative. The nitrogen compositions are believed to be accurate to ±15.2% for the L_1 phase and ±0.6% for the L_2 phase. The methane compositions are estimated to be good to ±1.3% for the L_1 phase and ±0.3% for the L_2 phase. The molar volumes should be good to ±2.5% for the L_1 phase and ±3.5% for the L_2 phase.

The composition and molar volume data on the boundaries are less reliable than those within the L_1–L_2–V region, as these points by their nature are more difficult to reproduce in the laboratory.

Remarks

Nitrogen-containing mixtures generally exhibit larger LLV regions of immiscibility than those composed solely of hydrocarbons. The three-phase LLV region for methane + ethane + *n*-heptane, reported earlier by us (*6*), is much narrower than that reported herein.

Additionally, we have seen that the extent of the LLV region for ternary systems of nitrogen + methane + *n*-paraffin is a function of the *n*-paraffin. The largest LLV region is that of the ternary mixture with *n*-butane or *n*-pentane; the regions shrink with higher or lower *n*-paraffins (*4*).

Glossary

K	the K point, or upper critical end point L–L=V
L	liquid phase
L_1	liquid phase rich in solute
L_2	liquid phase lean in solute
Q	quadrupole point, or four-phase point, herein, S–L_1–L_2–V
S	solid phase
V	vapor phase

Registry No. N, 7727-37-9; CH_4, 74-82-8; heptane, 142-82-5.

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