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Three-Phase Liquid–Liquid–Vapor Equilibria in the Nitrogen + Ethane + *n*-Butane System

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The three-phase liquid–liquid–vapor (L_1–L_2–V) phase equilibria behavior of the ternary mixture nitrogen + ethane + *n*-butane is presented, with special attention directed toward identifying the boundaries of the three-phase region. Liquid-phase compositions and molar volumes are reported as a function of temperature and pressure within the three-phase region and along the boundaries over the temperature range 118–132 K. In addition, some limited data on the L_1–L_2–V immiscibility of the ternary systems nitrogen + ethane + *n*-hexane and nitrogen + ethane + *n*-octane are presented. All three of these ternary systems have a constituent binary mixture, nitrogen + ethane, which exhibits L_1–L_2–V immiscibility. The presence of the heavier hydrocarbon creates a four-sided L_1–L_2–V region extending in pressure–temperature space down in temperature from the binary L_1–L_2–V locus. The other three boundaries of the three-phase region are a type K point (L_1–L_2=V) and two different Q-point (S–L_1–L_2–V) loci, with solid phases of ethane and the heavier hydrocarbon, respectively.

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 processing systems. Additionally, we have studied two binary mixtures that exhibit L_1–L_2–V immiscibility, nitrogen + ethane and nitrogen + propane, the first of which is relevant to the systems reported herein (*8*).

In this paper, we present results for the L_1–L_2–V phase equilibria of the ternary mixture nitrogen + ethane + *n*-butane, as well as some limited data on the ternary mixtures nitrogen + ethane + *n*-hexane and nitrogen + ethane + *n*-octane. All three ternary mixtures contain the binary constituent mixture nitrogen + ethane that exhibits L_1–L_2–V immiscibility. The role of the heaviest species is to create a three-phase region (surface) in thermodynamic phase space, extending down in temperature from the binary L_1–L_2–V locus. In addition to the binary LLV locus, the three-phase region is bounded by a K-point (L_1–L_2=V) locus, and two Q-point (S–L_1–L_2–V) loci, as illustrated in Figure 1. The solid phases in the Q-point loci are the heavy hydrocarbon and ethane, respectively, with the ethane forming a solid only at very low temperatures, not documented herein. The two Q-point loci will intersect at a five-phase point S–S′–L_1–L_2–V, while the Q-point locus with the solid heavy hydrocarbon phase intersects the K-point locus at the point S–L_1–L_2–V, which is invariant in a ternary system. The extent of the ternary three-phase region from the binary LLV locus is governed by the degree to which the melting point of the heavy hydrocarbon species can be depressed, that is, the degree to which the solid heavy hydrocarbon will dissolve in the fluid phases of the nitrogen + ethane. This depression of the solid-phase formation diminishes with increasing carbon number of the *n*-paraffin heavy hydrocarbon.

A related study is that of the mixture nitrogen + methane + ethane (*7*). In this case, the methane as the third component causes the growth of the three-phase region upward in temperature from the binary LLV locus of nitrogen + ethane. This trend occurs because the methane is of intermediate volatility when compared to the components of the constituent immiscible binary mixture. Growth downward in temperature from the LLV locus of a constituent immiscible binary mixture is generally observed when the third component is either more or less volatile than both of the species of the binary mixture.

Liquid-phase compositions and molar volumes are reported herein for the ternary mixture nitrogen + ethane + *n*-butane for the L_1 and L_2 phases in the three-phase region including along its boundaries. Some limited data on the boundaries of the other two ternary mixtures, containing *n*-hexane and *n*-octane respectively in place of the *n*-butane, are also reported.

Experimental Section

The experimental study was performed by using an apparatus originally developed by Kohn and co-workers (*9*). 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 nitrogen only. This assumption appears justified given the very low vapor phase mole fraction of ethane in the phase equilibria of the binary mixture nitrogen + ethane at its three-phase temperatures (*8*). 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.

The nitrogen used in this study was Linde "High Purity" grade with a stated purity of 99.99 mol %. The *n*-butane was Linde "Instrument Grade", with a stated purity of 99.5 mol %. The *n*-hexane and *n*-octane were products of Humphrey Chemical Company, with stated purities of 99.0 mol %. These four materials were used without further purification.

The ethane was purchased as Linde "CP" grade with a stated purity of 99.0 mol %. It was passed through consecutive beds of molecular sieves (13A) and activated charcoal and then liquified at 0 °C. The vapor phase was flashed off until about one-third of the liquified ethane was gone. The difference in the bubble point and the dew point of the remaining ethane

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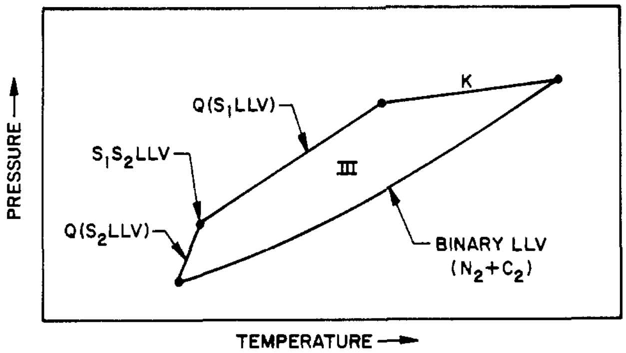

Figure 1. Schematic diagram in pressure–temperature space of the boundaries of the three-phase L_1–L_2–V regions for the three ternary systems studied.

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

temp, K	press., bar	[nitrogen], mole fracn	[ethane], mole fracn	mol vol, mL/(g·mol)
		K (L_1–L_2=V)		
126.85	34.45	0.0822	0.1259	70.13
127.01	34.51	0.1039	0.1202	72.01
127.31	34.72	0.1000	0.1804	67.16
127.42	34.92	0.1157	0.2163	64.16
127.45	35.12	0.1603	0.2477	63.10
128.09	35.61	0.1550	0.3339	57.30
129.34	36.85	0.1576	0.4980	58.83
129.48	36.99	0.1663	0.5174	56.12
129.56	37.06	0.1757	0.5175	54.72
129.65	37.27	0.1850	0.5260	53.11
130.23	38.30	0.2140	0.6243	53.11
131.06	38.72	0.2033	0.6565	53.72
131.83	39.55	0.2617	0.7102	51.86
		Q (S–L_1–L_2–V)		
126.69	33.96	0.1062	0.1257	67.80
125.98	32.93	0.0838	0.1486	69.09
125.10	31.41	0.0854	0.1780	68.00
124.00	29.61	0.0860	0.1800	67.69
123.73	29.20	0.0797	0.2115	65.75
123.04	28.23	0.0869	0.2270	65.21
122.15	27.13	0.0884	0.2338	65.37
121.72	26.58	0.0881	0.2482	65.17
120.83	25.34	0.0955	0.2658	64.32
120.17	24.44	0.0990	0.2832	63.48
119.02	22.99	0.0942	0.3073	63.35
118.33	22.17	0.0899	0.3285	62.62
		L_1–L_2–V		
129.16	36.30	0.1770	0.5171	53.72
	35.95	0.1784	0.5696	54.89
	35.88	0.2267	0.6468	51.49
	35.55	0.2079	0.6661	50.90
	35.21	0.2594	0.7065	49.91
125.19	31.40	0.1035	0.2849	66.53
	31.12	0.1349	0.2583	63.82
	30.30	0.1603	0.5281	54.36
	29.95	0.2086	0.6571	51.86
	29.69	0.2007	0.6697	51.36
	29.55	0.2487	0.7167	50.31
120.23	24.51	0.0872	0.3312	63.23
	24.51	0.0910	0.2850	66.94
	24.03	0.1478	0.5321	54.10
	23.75	0.1446	0.5874	55.65
	23.74	0.1927	0.6690	51.84
	23.48	0.1927	0.6748	51.14
	23.42	0.2376	0.7310	50.30

was typically 10 psia at 25 °C.

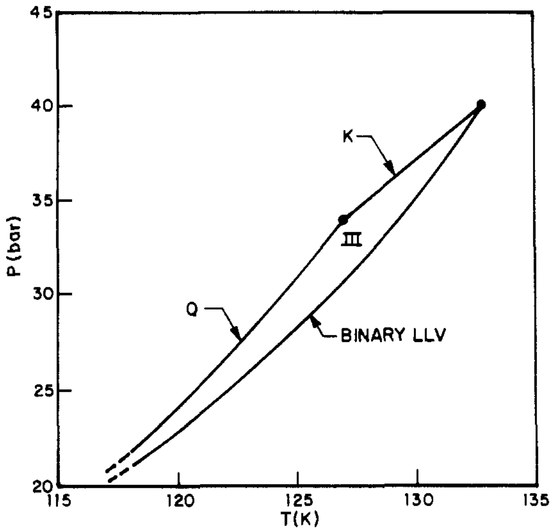

Figure 2. Projection in pressure–temperature space of the boundaries of the three-phase L_1–L_2–V region for the system nitrogen + ethane + *n*-butane.

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

temp, K	press., bar	[nitrogen], mole fracn	[ethane], mole fracn	mol vol, mL/(g·mol)
		K (L_1–L_2=V)		
127.01	34.45	0.9747	0.0116	95.86
127.59	35.14	0.9648	0.0277	93.16
129.08	36.65	0.9491	0.0316	88.28
129.55	37.07	0.9529	0.0459	86.56
129.99	37.76	0.9293	0.0257	82.79
130.33	38.03	0.9317	0.0303	80.80
130.57	38.24	0.9306	0.0370	77.62
131.81	39.48	0.9507	0.0175	79.39
		Q (S–L_1–L_2–V)		
126.45	33.61	0.9882	0.0041	68.51
126.25	33.27	0.9598	0.0298	64.96
124.55	30.50	0.9645	0.0305	54.47
123.49	28.99	0.9747	0.0206	56.12
123.10	28.36	0.9893	0.0050	56.00
122.85	27.96	0.9850	0.0064	55.71
122.69	27.75	0.9524	0.0335	53.58
121.62	26.43	0.9599	0.0324	52.58
120.51	24.92	0.9651	0.0189	50.71
118.91	22.85	0.9777	0.0159	50.29
		L_1–L_2–V		
129.16	36.77	0.9816	0.0077	72.22
	36.02	0.9652	0.0171	62.61
	35.21	0.9566	0.0359	55.81
125.19	31.27	0.9859	0.0002	60.97
	31.25	0.9813	0.0016	46.92
	30.86	0.9475	0.0500	56.01
	30.51	0.9748	0.0125	53.35
	30.29	0.9686	0.0110	55.43
	29.48	0.9464	0.0463	50.33
120.23	24.44	0.9675	0.0168	52.00
	24.17	0.9491	0.0492	49.82
	23.42	0.9283	0.0508	47.56

Experimental Results

The region of three-phase L_1–L_2–V immiscibility for the mixture nitrogen + ethane + *n*-butane is shown to scale in Figure 2. The surface as reported is bounded in pressure–temperature space by the binary nitrogen + ethane L_1–L_2–V locus, a K-point (L_1–L_2=V) locus, and a Q-point (S–L_1–L_2–V) locus, where the solid phase is pure *n*-butane. Not shown is the fourth side of the three-phase region, the Q-point locus with ethane as the solid phase, which would occur at temperatures lower than the 118 K temperature lower limit of the visual cell apparatus. Tables I and II present raw data for the L_1 and L_2 phases, respectively, for the K- and Q-point loci in Figure 2 and for three isotherms within the L_1–L_2–V region. The binary

Table III. Raw Data for the Liquid-Liquid-Vapor Region of the System Nitrogen + Ethane + *n*-Hexane

boundary	temp, K	press., bar
$S-L_1-L_2=V$	132.37	40.70
$L_1-L_2=V$	132.37	40.70
	132.44	40.77
	132.15	40.85
	131.72	40.67
$S-L_1-L_2-V$	131.74	39.87
	130.00	37.50
	130.00	37.39
	130.00	38.02
	128.00	34.50
	128.00	34.29
	128.00	34.78
	126.00	31.75
	124.00	28.65

Table IV. Raw Data for the Liquid-Liquid-Vapor Region of the System Nitrogen + Ethane + *n*-Octane

boundary	temp, K	press., bar
$S-L_1-L_2=V$	132.38	40.74
	132.38	40.71
$L_1-L_2=V$	132.38	40.74
	132.38	40.74
$S-L_1-L_2-V$	131.84	39.95
	131.84	39.95
	131.45	39.34
	130.80	38.23
	130.80	38.30
	130.06	36.98
	129.75	36.44
	129.75	36.37
	129.13	35.61
	128.71	34.99
	128.71	34.85
	128.20	34.16
	127.66	33.47
	127.66	33.27
	127.27	32.88
	126.62	31.89
	126.35	31.54
	125.58	30.37
	125.42	30.23
	124.53	29.13
	124.49	29.02
	123.57	27.74
	123.48	27.78
	122.64	26.54
	121.72	25.47
	120.79	24.34
	119.87	23.26
	118.95	22.30

L_1-L_2-V locus was constructed from data in ref *8*.

Noteworthy is the observation that the width of the three-phase region is less than 3 K when *n*-butane is the heavy hydrocarbon. With a heavier *n*-paraffin, the LLV region will be narrower. Tables III and IV present raw data for the location of the K-point and Q-point boundaries of the ternary LLV systems nitrogen + ethane + *n*-hexane and *n*-octane, respectively. Included are raw data for the invariant point $S-L_1-L_2=V$ (the intersection of the Q- and K-point loci) in each system. We were unable to obtain precise determinations of the properties of the liquid phases in these systems. We estimate that the L_1 phase composition does not exceed 0.047 for *n*-hexane and 0.006 for *n*-octane along the three phase boundaries reported; these estimates are based on overall mass of the components loaded into the visual cell during these experiments.

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 ±1.4% for the L_1 phase and ±0.3% for the L_2 phase. The ethane compositions are estimated to be good to ±0.5% for the L_1 phase and ±6.4% for the L_2 phase. The molar volumes should be good to ±1.8% for the L_1 phase and ±0.5% for the L_2 phase.

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

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	quadruple point, or four-phase point, herein, $S-L_1-L_2-V$
S	solid phase
V	vapor phase

Registry No. N, 7727-37-9; C_2H_6, 74-84-0; hexane, 110-54-3; butane, 106-97-8; octane, 111-65-9.

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