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Three-Phase Liquid–Liquid–Vapor Equilibria in the Nitrogen + Methane + Ethane and Nitrogen + Methane + Propane Systems

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The phase equilibria behavior of the ternary systems nitrogen + methane + ethane and nitrogen + methane + propane in their three-phase liquid–liquid–vapor (L_1–L_2–V) regions is presented, with special attention directed toward identifying the boundaries of the regions. The temperature range studied for both systems was approximately 116–160 K. Liquid-phase compositions and molar volumes are reported as functions of temperature and pressure within the three-phase regions and at their boundaries. Each ternary system has a constitutent binary system (nitrogen + ethane and nitrogen + propane, respectively) which exhibits L_1–L_2–V immiscibility. The presence of the third species methane in each case creates a three-phase region extending upward in temperature from the binary L_1–L_2–V locus. These three-phase regions are bounded from above by a K point (L_1–L_2=V) locus and from below by an LCST (L_1=L_2–V) locus; these two critical end point loci intersect at a tricritical point (L_1=L_2=V).

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) (*1*–*5*). More recently, we studied two binary systems containing nitrogen, with ethane and propane, respectively, that exhibit L_1–L_2–V immiscibility (*6*). There is an interest in the phase equilibria of LNG systems containing nitrogen since nitrogen is sometimes used as the 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 for sometime been known to induce L_1–L_2–V behavior in LNG systems (*7*–*12*).

In this paper, we present results for the L_1–L_2–V phase equilibria of the ternary systems nitrogen + methane + ethane and nitrogen + methane + propane. Three-phase liquid–liquid–vapor data have been earlier reported on the system nitrogen + methane + ethane by Lu's group (*8*). Their study was limited to several isotherms within the three-phase region. This present study additionally addresses the determination of the nature of the boundaries of the three-phase regions. Liquid-phase compositions and molar volumes are reported for L_1 and L_2 in the three-phase region including its boundaries. In each of these systems, there is a binary constituent pair that exhibits L_1–L_2–V immiscibility, and the role of the third species methane is to create a three-phase L_1–L_2–V surface in thermodynamic phase space, extending from the binary L_1–L_2–V locus upward in temperature. The resulting three-phase space in each case is bounded by (1) the binary L_1–L_2–V locus, (2) a locus of K points (L_1–L_2=V), and (3) a locus of LCST points (L_1=L_2–V). The intersection of the K point and LCST point loci is a tricritical point (L_1=L_2=V) and marks the upper temperature limit of the three-phase surface. For a more comprehensive discussion of the L_1–L_2–V topography for typical ternary systems, one should consult ref *13*.

Experimental Section

The experimental study was performed using an apparatus developed by Kohn and co-workers. The experimental procedures are described in ref *1* and *2*.

The phenomena reported were observed in glass cells marked and calibrated to permit direct visual inspection. Stoichiometric and volumetric measurements were made, which permitted the computation of the composition and molar volume of each liquid phase. The temperature of the system was measured with a Pt resistance thermometer, calibrated to the IPTS-1968 scale and estimated to be accurate to ±0.03 K. The system's pressure was measured with a Heise Bourdon tube gauge, accurate to ±0.07 bar. Volumes of the different phases with the visual cell (total volume of about 10 cm^3) could be read to ±0.02 cm^3.

In order to calculate the properties of the two liquid phases accurately, the amount of vapor phase present in the cell was always minimized. In addition, the vapor phase was assumed to have negligible ethane or propane in it, an assumption supported reasonably well by previous data in the literature (*6*, *7*), wherein vapor–liquid equilibria typically demonstrated vapor compositions of 99+% nitrogen from mixtures of nitrogen + ethane and nitrogen + propane. The remaining mixture of nitrogen + methane composing the vapor phase was assumed to have the composition consistent with the nitrogen + methane binary vapor–liquid system reported by Kidnay et al. (*14*). Using this information, we estimated the vapor-space compressibility factor with the Soave–Redlich–Kwong equation of state, as modified by Graboski and Daubert (*15*, *16*).

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 ethane was purchased as Linde CP grade with a stated purity of 99.0%. It was passed through consecutive beds of molecular sieves (13A) and activated charcoal and then liquefied at 0 °C. The vapor phase was flashed off until about $^1/_3$ of the liquefied material was gone. The remaining ethane was then used for the study. At 25 °C the difference between the bubble and dew point pressures was 10 psi. The propane was Linde "Instrument" grade with a stated purity of 99.5 mol %. The methane, nitrogen, and propane were used without further purification.

Experimental Results

Each system has a binary L_1–L_2–V locus extending from a Q(S–L_1–L_2–V) point to a K(L_1–L_2=V) point. The topographical nature of the regions of immiscibility for the two ternary systems studied is illustrated schematically in Figure 1. The addition of the third component methane extends the domain of the three-phase phase behavior upward in temperature and pressure from the binary locus. The three-phase region would be bounded from below by an LCST (L_1=L_2–V) locus and a Q-

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

temp, K	press, bar	[nitrogen], mole fraction	[methane], mole fraction	molar vol, mL/(g-mol)
		K (L_1–L_2=V)		
160.32	61.12			
159.51	60.06			
158.83	59.37			
158.19	58.68			
157.28	57.73			
154.94	55.74	0.334	0.442	50.71
154.57	55.53	0.332	0.448	51.48
153.66	54.56	0.325	0.426	51.47
152.97	53.86	0.311	0.418	50.31
136.01	40.57	0.178	0.202	53.57
129.97	36.85	0.152	0.096	57.31
		LCST (L_1=L_2–V)		
152.79	51.12	0.520	0.429	54.73
151.68	49.47	0.471	0.437	50.70
142.11	37.60	0.501	0.417	46.68
140.05	35.19	0.485	0.424	46.36
138.28	32.91	0.392	0.443	48.37
130.29	24.20	0.424	0.405	41.31
129.04	22.92	0.420	0.410	41.03
123.73	18.27	0.408	0.422	40.26
118.86	14.45	0.358	0.465	43.41
		L_1–L_2–V		
138.00	40.29	0.189	0.266	54.51
	39.05	0.204	0.287	52.11
	38.22	0.206	0.306	53.00
	36.91	0.227	0.331	50.27
134.00	35.95	0.190	0.234	52.21
	32.43	0.224	0.310	52.85
	31.81	0.225	0.330	49.94
	31.40	0.228	0.342	49.56
	30.99	0.230	0.358	51.12
	30.02	0.250	0.386	49.85
	29.26	0.275	0.409	47.80
127.01	34.23	0.122	0.021	59.46
	33.05	0.131	0.060	58.21
	32.91	0.143	0.077	57.70
	32.04	0.141	0.109	56.29
	24.04	0.192	0.351	52.08
	23.35	0.221	0.366	50.43
125.00	30.58	0.139	0.026	59.16
	29.67	0.140	0.074	57.75
	28.94	0.142	0.105	56.38
	27.68	0.151	0.149	54.52
	26.52	0.157	0.182	52.83
123.00	27.53	0.149	0.056	58.29
	26.91	0.133	0.055	57.75
	26.58	0.136	0.083	56.43
	26.39	0.146	0.085	57.06
	19.93	0.206	0.364	50.12
	19.34	0.197	0.389	49.14
	19.07	0.233	0.397	48.44
121.00	25.23	0.142	0.048	56.25
	24.92	0.134	0.074	57.71
	24.84	0.130	0.055	57.44
	24.18	0.129	0.111	55.99
	17.75	0.229	0.397	48.25
	17.55	0.237	0.412	47.75
120.00	23.33	0.154	0.010	59.06
	16.45	0.213	0.423	48.26
	16.45	0.220	0.421	47.71
118.00	21.33	0.142	0.053	58.05
	20.17	0.126	0.115	54.20
	14.89	0.222	0.407	47.95
117.00	20.30	0.155	0.033	58.53
	19.01	0.138	0.073	57.72
	14.10	0.220	0.407	47.81

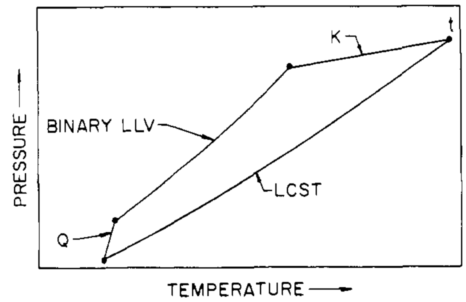

Figure 1. Schematic diagram of the topography of the thermodynamic phase space of the three-phase L_1–L_2–V regions of the systems studied: Projection in pressure–temperature space.

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

temp, K	press., bar	[nitrogen], mole fraction	[methane], mole fraction	molar vol, mL/(g-mol)
		K (L_1–L_2=V)		
154.57	55.64	0.578	0.387	63.56
154.28	55.33	0.594	0.379	64.66
140.11	43.47	0.758	0.218	77.37
137.05	41.33	0.809	0.149	80.13
129.64	36.59	0.936	0.050	83.10
128.38	35.79	0.964	0.028	86.20
		L_1–L_2–V		
138.00	40.37	0.746	0.228	62.87
	38.16	0.683	0.285	56.86
	37.13	0.689	0.311	54.65
	36.37	0.629	0.335	51.99
134.00	35.05	0.775	0.224	57.02
	33.43	0.722	0.271	53.59
	32.09	0.666	0.325	51.05
	31.56	0.647	0.342	50.33
	30.99	0.629	0.353	50.00
	30.64	0.618	0.363	48.54
	29.95	0.588	0.384	48.35
127.01	33.28	0.949	0.051	60.92
	33.00	0.940	0.046	60.18
	33.00	0.939	0.045	60.23
	32.04	0.929	0.069	57.74
	30.24	0.873	0.106	52.31
	23.95	0.694	0.281	41.37
125.00	29.28	0.927	0.072	54.01
	28.38	0.894	0.091	52.94
	26.17	0.818	0.163	49.62
	24.82	0.762	0.213	48.30
	22.16	0.629	0.327	44.32
123.00	23.89	0.819	0.162	48.33
	20.30	0.630	0.327	43.86
	19.20	0.569	0.366	43.10
121.00	24.32	0.926	0.071	49.83
	21.91	0.825	0.175	46.10
	20.03	0.712	0.266	43.59
120.00	19.34	0.712	0.267	43.40
	17.88	0.630	0.325	42.98
118.00	18.80	0.810	0.190	44.40
	17.07	0.711	0.269	42.75
	16.16	0.630	0.325	42.37
	14.52	0.524	0.411	41.85
117.00	16.24	0.710	0.267	42.06
	16.24	0.710	0.268	42.05
	13.83	0.524	0.414	41.58

point locus and from above a K-point locus and the binary L_1–L_2–V locus. The LCST and K-point loci intersect at a tricritical point, in these cases the highest temperature and pressure at which three-phase behavior occurs. Figure 2 plots the boundaries of the three-phase regions of the two ternary systems. Limitations of the apparatus prevented detailing the regions in the vicinity of their Q-point loci.

Tables I and II present raw data for the boundaries and interior of the three-phase region of the system nitrogen + methane + propane; Tables III and IV report the system nitrogen + methane + ethane. Tables I and III are data for the L_1 phases that are propane- and ethane-rich, respectively. Tables II and V are data for the L_2 phases (propane and eth-

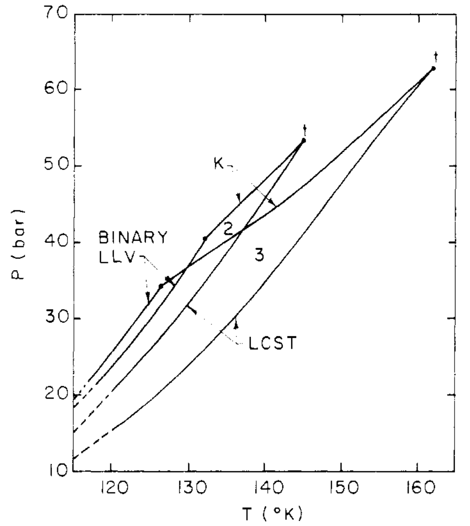

Figure 2. Projections in the pressure-temperature space of the boundaries of the three-phase L_1-L_2-V regions for the systems nitrogen + methane + ethane (labeled "2") and nitrogen + methane + propane (labeled "3").

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

temp, K	press., bar	[nitrogen], mole fraction	[methane], mole fraction	molar vol, mL/(g-mol)
		K (L_1-L_2=V)		
143.71	51.75			
142.00	50.07			
140.87	48.98	0.480	0.120	45.36
138.81	46.63	0.428	0.101	45.34
134.99	43.05	0.375	0.054	44.42
133.97	42.57	0.355	0.043	44.78
132.85	41.67			
		LCST (L_1=L_2-V)		
138.44	43.46	0.627	0.114	49.14
136.20	40.17			
135.29	38.70	0.666	0.118	46.68
131.54	34.16			
131.29	33.41	0.636	0.136	42.62
125.86	26.48	0.525	0.148	41.94
125.42	27.75			
123.94	24.31	0.535	0.151	41.61
115.91	16.57	0.443	0.164	41.41
		L_1-L_2-V		
135.00	42.09	0.388	0.075	43.86
	41.13	0.400	0.090	44.34
	40.50	0.431	0.106	44.77
	39.51	0.457	0.123	45.12
129.00	35.19	0.300	0.012	46.50
	34.61	0.315	0.034	46.10
	33.68	0.344	0.064	44.72
	32.92	0.365	0.082	44.53
	32.30	0.380	0.101	44.48
	31.67	0.409	0.117	44.00
125.00	29.33	0.310	0.014	44.48
	28.78	0.316	0.053	43.65
	28.09	0.340	0.077	43.33
	27.20	0.370	0.099	43.07
	26.78	0.401	0.118	42.79

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

temp, K	press., bar	[nitrogen], mole fraction	[methane], mole fraction	molar, vol, mL (g-mol)
		K (L_1-L_2=V)		
141.80	49.74	0.856	0.084	66.33
138.44	46.49	0.959	0.037	75.48
136.76	45.60			
136.03	44.22			
134.72	42.84	0.965	0.015	73.68
134.38	42.50	0.963	0.014	73.14
		L_1-L_2-V		
135.00	40.71	0.867	0.042	62.32
	40.44	0.840	0.037	62.02
	39.74	0.789	0.063	59.62
	40.03	0.768	0.102	51.81
129.00	34.64	0.929	0.018	54.67
	34.10	0.896	0.025	52.91
	33.81	0.888	0.026	52.91
	32.02	0.803	0.074	47.97
125.00	28.99	0.903	0.016	48.42
	28.30	0.867	0.039	47.14
	27.06	0.810	0.087	45.26
	26.30	0.761	0.118	43.94
	26.15	0.742	0.126	43.60

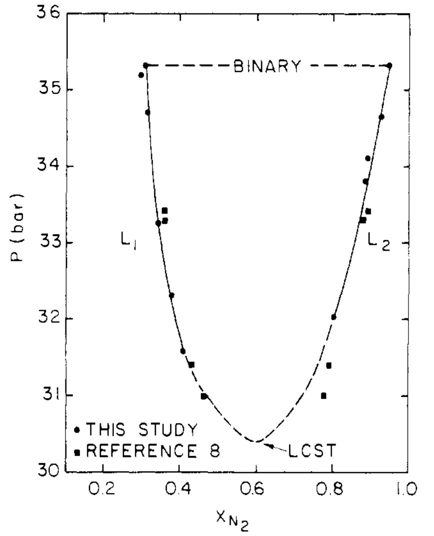

Figure 3. Comparison of L_1 and L_2 compositional data at 129 K for the system nitrogen + methane + ethane: nitrogen mole fractions.

ane lean, respectively). Binary L_1-L_2-V data for the systems nitrogen + propane and nitrogen + ethane were reported earlier by the investigators (*6*).

The solvent (nitrogen) compositions are believed to be accurate to ±2.7% for the L_1 phase and ±3.4% for the L_2 phase. The molar volumes should be accurate to ±1.7% for the L_1 phase and ±2.1% for the L_2 phase. These error estimates are based on comparing smoothed data representations with raw data and are considered to be conservative.

Remarks

The extent of the domain of three-phase behavior of the ternary system nitrogen + methane + ethane is considerably less than that of the system nitrogen + methane + propane. This latter system has a three-phase region extent comparable to that of the system nitrogen + methane + *n*-butane (*5*). In turn, extent in temperature-pressure space diminishes somewhat as *n*-butane is replaced by the heavier species *n*-pentane and *n*-hexane (*4*). It seems apparent therefore that propane and *n*-butane are prime contributors to L_1-L_2-V immiscibility in nitrogen-rich LNG mixtures.

Limited comparison can be made with data in the literature for the system nitrogen + methane + ethane. Figures 3 and 4 compare data of this present study with some of Yu et al. (*8*) at 129 K. As can be seen, there is reasonable agreement between the two studies, except near the LCST point where the properties of L_1 and L_2 converge (*5*). The LCST locations are based on interpolations of the raw data.

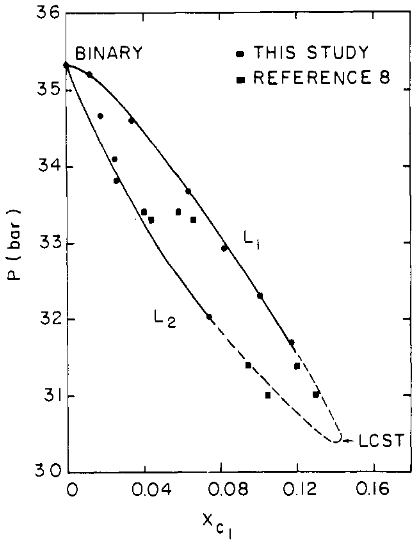

Figure 4. Comparison of L_1 and L_2 compositional data at 129 K for the system nitrogen + methane + ethane: methane mole fractions.

Glossary

K	the K point or upper critical end point of an L_1-L_2-V region, occurring when the L_2 phase becomes critically identical with the vapor phase V
L_1	liquid phase rich in solute (ethane or propane)
L_2	liquid phase lean in solute (ethane or propane)
LCST	lower critical solution temperature, occurring when the L_1 and L_2 phases become critically identical
Q	quadruple point, or four-phase point, herein an S-L_1-L_2-V point
S	solid phase
T	tricritical point, the intersection of an LCST and a K-point locus, whereby one has L_1=L_2=V criticality
V	vapor phase

Registry No. N_2, 7727-37-9; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6.

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Excess Gibbs Energies and Excess Volumes of Some Alcohol–Methyl Ester Binary Mixtures

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Isothermal vapor–liquid equilibrium data for the mixtures 1-butanol–methyl propanoate and 1-butanol–methyl butanoate have been measured by using a recirculating still. The excess molar volumes of the same mixtures and those of the system 1-pentanol–methyl butanoate were obtained from measurements of the density with an Anton Paar densimeter. The vapor–liquid equilibrium data were reduced according to the maximum likelihood principle. The parameters of the NRTL, Wilson, and UNIQUAC equations were calculated.

Introduction

This paper can be considered as a continuation of our previous studies on the excess thermodynamic properties of the binary systems formed by methyl ester and alcohol (*1*, *2*). In the present paper we report the results of vapor–liquid equilibrium measurements for the system 1-butanol–methyl propanoate at 348.15 K and for 1-butanol–methyl butanoate at 348.15 and 368.19 K. We also report the excess volume measurements at 298.15 and 308.15 K for the former system and at 298.15 K for the latter. The excess volumes of the system 1-pentanol–methyl butanoate at 298.15 K are also presented.

Experimental Section

Materials. The 1-butanol and 1-pentanol employed were Merck "zur analyse" products with a stated minimum purity of 99.5% and 99%, respectively. The esters were supplied by Fluka with a purity of 99%. The reagents were purified by distillation at atmospheric pressure, in a 60 real plate Oldershaw column. In Table I, we compare the measured densities and vapor pressures of the purified products with the literature values.

Apparatus and Procedure. Vapor–liquid equilibrium data were determined at constant temperature by using a still de-

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