J. Chem. Eng. Data **1985**, *30*, 435-438

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

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The phase equilibria behavior of the binary mixtures nitrogen + ethane and nitrogen + propane is studied along their three-phase liquid–liquid–vapor loci at temperatures greater than 117 K. Data presented are pressure, and L_1 and L_2 liquid-phase compositions and molar volumes as a function of temperature. Comparisons with literature data are made.

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) (*1–6*). Many of these ternary systems have exhibited L–L–V immiscibility without having an immiscible constituent binary pair. An example would be the system methane + ethane + *n*-octane (*1*), whose three-phase thermodynamic phase space is bounded by loci of K points [L_1–L_2 = V), LCST points (L_1 = L_2–V), and Q points (S–L_1–L_2–V).

By comparison, the systems methane + *n*-hexane + *n*-octane (*3*) and methane + *n*-hexane + nitrogen (*5*) had a constituent binary pair, methane + *n*-hexane, which exhibited L–L–V immiscibility. The third species in these systems created the three-phase thermodynamic space as a surface extending out of the binary locus. The number of binary systems relevant to LNG that exhibit L–L–V immiscibility are few.

We have recently become interested in nitrogen-containing prototype LNG systems that exhibit multiphase L–L–V behavior. Nitrogen is sometimes used as a pressurizing gas in enhanced oil recovery processs, and processes for the separation of the LNG components from nitrogen-rich streams have been developed. This paper presents results on the two binary systems nitrogen + ethane and nitrogen + propane, both of which are L–L–V immiscible in themselves. These systems have been studied earlier by other investigators, but in this present study molar volumes of the L_1 and L_2 phases are reported as a function of temperature, in addition to the phase compositions and system pressure.

Table I. Smoothed Data for the Three-Phase Liquid–Liquid–Vapor Locus of the Binary System Nitrogen + Ethane

		mole fraction nitrogen		molar volume, mL/(g mol)	
temp, K	press., bar	L_1 phase	L_2 phase	L_1 phase	L_2 phase
132.38[a]	40.71	0.3247	0.9635	45.50	74.10
132.00	40.04	0.3232	0.9604	45.40	67.80
131.00	38.48	0.3193	0.9543	45.12	56.90
130.00	36.93	0.3158	0.9515	44.90	52.10
129.00	35.32	0.3122	0.9497	44.80	50.01
128.00	33.86	0.3085	0.9480	44.75	48.60
127.00	32.44	0.3048	0.9462	44.70	47.65
126.00	31.04	0.3018	0.9445	44.75	46.80
125.00	29.70	0.2965	0.9432	44.80	46.05
124.00	28.35	0.2923	0.9418	44.90	45.40
123.00	27.05	0.2878	0.9404	45.00	44.80
122.00	25.84	0.2831	0.9388	45.02	44.30
121.00	24.62	0.2784	0.9373	45.10	43.85
120.00	23.50	0.2738	0.9348	45.12	43.45
119.00	22.40	0.2695	0.9317	45.15	43.15
118.00	21.29	0.2653	0.9275	45.18	42.90

[a] K point.

Table II. Smoothed Data for the Three-Phase Liquid–Liquid–Vapor Locus of the Binary System Nitrogen + Propane

		mole fraction nitrogen		molar volume, mL/(g mol)	
temp, K	press., bar	L_1 phase	L_2 phase	L_1 phase	L_2 phase
126.62[a]	34.77	0.1383	0.9921	59.65	87.50
126.00	33.79	0.1381	0.9916	58.80	69.25
125.00	32.07	0.1378	0.9907	58.30	62.00
124.00	30.55	0.1373	0.9896	57.75	58.20
123.00	29.13	0.1367	0.9879	57.75	55.50
122.00	27.76	0.1359	0.9858	57.51	53.50
121.00	26.50	0.1352	0.9836	57.35	51.80
120.00	25.24	0.1343	0.9812	57.35	50.50
119.00	23.96	0.1330	0.9788	57.25	49.25
118.00	22.71	0.1312	0.9760	57.30	48.00
117.00	21.53	0.1282	0.9727	57.49	47.40

[a] K point.

Experimental Section

The study was carried out in an apparatus described in detail in earlier papers (*1–3*). The equipment is used to measure accurately the chemical species added to the glass visual equilibria cell. Measurements of temperature, pressure, volume, and input compositions permit the stoichiometric computation of the equilibrium composition and molar volume of each liquid phase.

The equilibrium temperature was measured with a platinum resistance thermometer, calibrated to the IPTS-1968 standards and was estimated to be accurate to ±0.03 K. The cell pressure was measured with a Heise bourdon tube gauge, which was accurate to ±0.07 bar. The equilibrium phase volumes were measured from the calibrated cell markings and are good to ±0.02 cm^3. The extremely low vapor-phase mole fraction for both ethane and propane in the ethane + nitrogen and propane + nitrogen binary liquid–vapor (*7*) and liquid–liquid–vapor system studies (*8*, *9*) led to the assumption that the gas phase is predominantly nitrogen. The error brought about by this assumption was minimized by minimizing the vapor space present in the cell.

The nitrogen used was Linde "High Purity" grade with a stated purity of 99.9 mol %. The propane used in this study was Linde "Instrument" grade with a stated purity of 99.5%. The materials were used without further purification. The ethane was purchased as Linde "CP" grade with a stated purity of 99.0%. It was passed through consecutive beds of molecular sieves (13 Å) and activated charcoal and then liquefied at 0 °C. The vapor phase was flashed for a period of time until

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0021-9568/85/1730-0435$01.50/0

about $^1/_3$ of the liquefied material was gone. The difference in the bubble and dew point pressures of the remaining ethane at 25 °C (77 °F) was 10 psia.

Experimental Results

The smoothed data for the ethane + nitrogen and propane + nitrogen binary systems are presented in Tables I and II. Raw data for these systems are presented in Appendix A. Figures 1 and 2 are plots of the L_1 and L_2 compositions (mole fraction nitrogen) of Tables I and II, respectively, to which some literature data are compared. There seems to be a good agreement between our work and that of Lu (*9*) and Kremer and Knapp (*10*) for the ethane + nitrogen system. However, the data of Kremer and Knapp (*10*) and Schindler et al. (*11*) do not agree that well with ours for the propane + nitrogen system studied. Kremer and Knapp's upper critical end points for the ethane + nitrogen system appear to be too high compared to those from both our work and Lu's. As mentioned above, it was assumed that the vapor phases are pure nitrogen, since ref 8 and 9 report nitrogen concentrations of about 99%. The quantity of vapor was kept small in the equilibria cell to minimize the effect of any assumptions made about its compositions.

The average absolute deviations (AAD) of the raw data from the smoothed data were computed and are typically 0.076 bar for the pressure vs. temperature data. The molar volumes have AAD's of 0.42 mL/(g mol) for the L_1 phase and 0.67 mL/(g mol) for the L_2 phase. The AAD's of the mole fractions of nitrogen are 0.0028 for the L_1 phase and 0.0027 for the L_2 phase.

Remarks

Studies are now underway by us on ternary systems composed of the binary systems described herein plus methane. Since methane is completely miscible with the species nitrogen, ethane, and propane, the resulting ternary three-phase regions should extend from the binary L–L–V locus upward in temperature (*6*).

Appendix A

***Tables of Raw Data*.** Raw data from which Tables I and II were constructed are presented in Tables III–VI. Tables III and IV correspond to Table I and Tables V and VI to Table II.

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
L	liquid phase
L_1	liquid phase rich in solute
L_2	liquid phase lean in solute
LCST	lower critical solution temperature, occurring when the L_1 and L_2 phases becomes critically identical with each other
Q	quadruple point, the equilibrium coexistence of four phases, in this case L_1, L_2, V, and S phases
S	solid phase
T	temperature
V	vapor phase

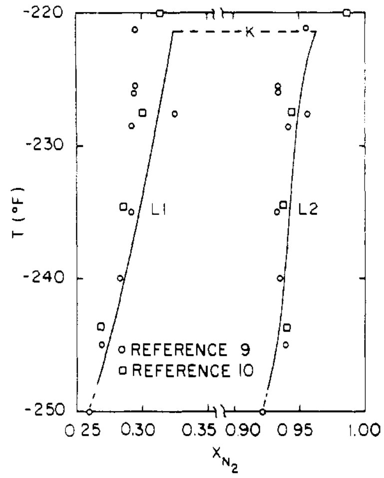

Figure 1. Temperature vs. nitrogen mole fraction for the binary system nitrogen + ethane.

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

temp, K	press., bar	[nitrogen], mole fraction	molar vol, mL/(g mol)
		K (L_1-L_2 = V)	
132.36	40.71	0.3246	45.00
132.36	40.71	0.3226	45.15
132.37	40.71	0.3215	45.26
132.37	40.71	0.3227	45.14
132.39	40.70	0.3278	45.60
132.39	40.70	0.3244	45.94
132.39	40.70	0.3277	45.57
		L_1-L_2-V	
130.80	37.95	0.3241	45.50
	37.95	0.3296	45.23
	38.03	0.3208	44.86
	38.03	0.3226	44.66
		L_1-L_2-V	
129.75	36.47	0.3243	44.97
	36.47	0.3171	45.55
	36.65	0.3191	44.75
	36.65	0.3165	44.94
		L_1-L_2-V	
128.71	34.77	0.3198	44.99
	34.78	0.3135	44.69
	34.78	0.3107	44.93
		L_1-L_2-V	
127.66	33.26	0.3130	45.08
	33.26	0.3071	45.60
	33.23	0.3096	44.69
	33.23	0.3072	44.88
		L_1-L_2-V	
125.58	30.54	0.3151	44.90
	30.39	0.3033	45.13
	30.39	0.2989	45.59
	30.51	0.3000	44.68
	30.51	0.2980	44.88
		L_1-L_2-V	
123.48	27.68	0.3020	45.11
	27.47	0.2917	45.00
	27.54	0.2911	44.48
		L_1-L_2-V	
120.33	23.89	0.2849	43.54
	23.75	0.2746	45.09
	23.75	0.2750	44.42
		L_1-L_2-V	
118.22	21.54	0.2776	45.21
	21.47	0.2665	44.89
	21.75	0.2662	44.32

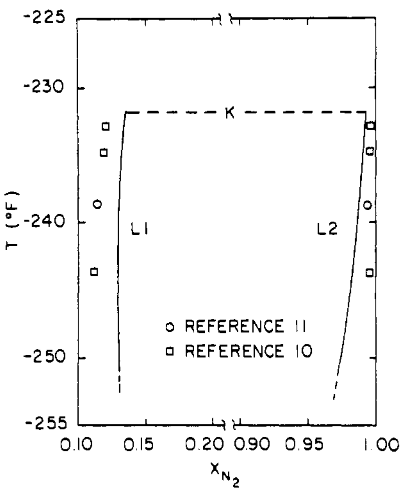

Figure 2. Temperature vs. nitrogen mole fraction for the binary system nitrogen + propane.

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

temp, K	press., bar	[nitrogen], mole fraction	molar vol, mL/(g mol)
		K (L_1-L_2 = V)	
132.34	40.70	0.9616	74.06
132.38	40.71	0.9602	73.92
132.34	40.70	0.9634	74.24
132.38	40.71	0.9637	74.15
132.34	40.70	0.9652	74.35
		L_1-L_2-V	
130.80	38.02	0.9326	50.41
	38.02	0.9348	50.48
	38.25	0.9457	48.34
	38.26	0.9527	55.39
	38.25	0.9488	48.50
	38.26	0.9539	55.39
		L_1-L_2-V	
129.75	36.50	0.9509	51.08
	36.74	0.9458	46.93
	36.50	0.9518	51.11
	36.74	0.9480	47.08
		L_1-L_2-V	
128.71	34.95	0.9479	49.76
	34.95	0.9492	49.70
	34.95	0.9502	49.73
		L_1-L_2-V	
127.66	33.53	0.9465	48.30
	33.53	0.9475	48.26
	33.61	0.9400	45.17
	33.53	0.9484	48.30
	33.61	0.9423	45.34
		L_1-L_2-V	
125.58	30.70	0.9433	46.49
	30.70	0.9441	46.46
	30.61	0.9334	44.07
	30.70	0.9450	46.51
	30.61	0.9357	44.22
		L_1-L_2-V	
123.48	27.81	0.9395	45.01
	27.81	0.9404	45.02
	27.81	0.9411	45.06
		L_1-L_2-V	
120.33	24.02	0.9349	43.54
	24.02	0.9358	43.56
	24.02	0.9365	43.60
		L_1-L_2-V	
118.22	21.67	0.9270	42.93
	21.67	0.9279	42.95
	21.67	0.9284	42.98

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

temp, K	press., bar	[nitrogen], mole fraction	molar vol, mL/(g mol)
		K (L_1-L_2 = V)	
126.54	34.77	0.1356	58.65
126.54	34.77	0.1383	58.46
126.54	34.77	0.1344	58.71
126.54	34.77	0.1300	59.03
126.54	34.77	0.1341	58.76
		L_1-L_2-V	
125.00	32.04	0.1305	59.08
	32.05	0.1375	58.30
		L_1-L_2-V	
123.00	29.11	0.1330	58.46
	29.29	0.1384	57.94
	29.11	0.1380	58.87
		L_1-L_2-V	
121.00	26.50	0.1378	57.52
	26.46	0.1321	58.08
	26.50	0.1351	57.83
		L_1-L_2-V	
120.00	25.19	0.1337	57.79
	25.08	0.1310	57.80
		L_1-L_2-V	
119.00	24.29	0.1326	57.80
	24.07	0.1338	57.56
		L_1-L_2-V	
118.00	22.71	0.1306	57.72
		L_1-L_2-V	
117.00	21.53	0.1279	57.72

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

temp, K	press., bar	[nitrogen], mole fraction	molar vol, mL/(g mol)
		K (L_1-L_2 = V)	
126.62	34.78	0.9899	86.68
126.52	34.71	0.9913	89.29
126.61	34.78	0.9921	85.91
126.62	34.71	0.9909	88.97
126.61	34.78	0.9917	85.58
		L_1-L_2-V	
125.00	32.07	0.9850	62.10
	32.07	0.9813	58.21
		L_1-L_2-V	
123.00	29.21	0.9846	55.64
	29.21	0.9844	55.59
	29.28	0.9900	58.62
		L_1-L_2-V	
121.00	26.56	0.9908	55.54
	26.56	0.9910	55.38
		L_1-L_2-V	
120.00	25.21	0.9779	50.52
	25.21	0.9779	50.50
		L_1-L_2-V	
119.00	23.97	0.9770	49.22
	23.97	0.9771	49.23
		L_1-L_2-V	
118.00	22.67	0.9761	47.97
		L_1-L_2-V	
117.00	21.49	0.9728	46.88

Registry No. Nitrogen, 7727-37-9; ethane, 74-84-0; propane, 74-98-6.

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Received for review September 10, 1984. Revised manuscript received February 4, 1985. Accepted March 10, 1985. We are grateful for the support of this work provided by the Gas Processors Association Research Project 795), Tulsa, OK. The apparatus was assembled under research grants from the National Science Foundation.

Densities of Molten Cobalt Chloride and Potassium Chloride Mixtures

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Density measurements of the molten $CoCl_2$–KCl mixtures of high $CoCl_2$ composition with an open vessel are very difficult or almost impossible because of their high volatility. The densities of $CoCl_2$ and KCl mixtures sealed in a quartz cell have been measured by a dilatometric method. The excess molar volume was positive around 30 mol % and around 70 mol % of $CoCl_2$. The results of the present investigation suggested that the title system contains the tetrahedral configuration, $CoCl_4^{2-}$, at the composition $X(CoCl_2) = 0.30$ and the other unknown species at $X(CoCl_2) = 0.70$.

Introduction

In the mixture of cobalt chloride and alkali chloride systems, the volatility of $CoCl_2$ was appreciable even at the melting points (*1*). Many workers studied the emf (*2*), enthalpy of mixing (*3*, *4*), and visible spectra (*5*, *6*) of molten cobalt chloride and the mixtures with alkali chlorides.

Dutt and Østvold (*7*) reported emf of molten alkali chlorides and cobalt chloride mixtures on the lower composition range of cobalt chloride ($X(CoCl_2)$, 0–0.6). They suggested that all systems except LiCl–$CoCl_2$ contain the divalent cobalt ion in the tetrahedral configuration, $CoCl_4^{2-}$, and that the tendency for "complex" formation increased with increasing size of the alkali metal ion. On the basis of visible spectral observation, Trutia and Musa (*8*) reported a change in the coordination symmetry about the Co^{2+} ion from octahedral in the solid state into tetrahedral in the liquid state for pure cobalt chloride.

In this paper we tried to measure on the whole composition range from $X = 0.0$ to $X = 1.0$ and a wide temperature range (from melting point up to 1000 °C). Similar studies on the density and refractive index in the molten $MnCl_2$–KCl system (*9*) and $ZnCl_2$–KCl system (*10*) with the same experimental technique were reported by us.

Experimental Section

Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$) was dehydrated under vacuum at 200 °C for a day. The dehydrated cobalt chloride and potassium chloride were mixed and melted at a temperature 50 °C higher than the melting point in a quartz refining cell, cleaned by bubbling dry HCl gas, and then sealed off after evacuation into a quartz ampule. The ampule was made up of a tank of volume 1.80–2.80 cm^3 and a neck of uniform bore, 4 mm in diameter. In this tube was made a horizontal mark on the upper part, and the volume below the mark and cross section of the tube were previously calibrated with distilled water.

The sample tube was then mounted on the electrical furnace which has a window (20 mm × 35 mm) of optically flat silica glass. The temperature measured by a Pt–Pt13%Rh thermocouple touching sample cell. Temperature measurement calibration was previously done by using another Pt–Pt13%Rh thermocouple inserted into the empty sample cell. This reference thermocouple was already calibrated with the melting points of ice, Sn, Pb, and Cu as references.

Figure 1 shows the density measurement apparatus. The subheater was necessary to avoid the condensation of sample vapor on the inner wall of the upper part of the sample cell. The lamp was useful at lower temperature to light the meniscus of the sample melt. The distance between the meniscus and the mark of the sample cell was measured with the cathetometer. At high temperature, sometimes the meniscus level disappeared from the window area, and then the jack was used to control the meniscus level back into the observation window.

The experimental error in this density measurement method came from four points mainly. First, the reproducibility of a particular composition and temperature was measured. This maximum error was calculated as 0.0065 g/cm^3. Second, the meniscus shape changes from the reference liquid. This error was obviously significant at high temperature and at high KCl content. For example, at 1000 °C, the meniscus of pure KCl melt was almost completely flat. In this case the error was calculated as 0.0064 g/cm^3. Third, the error in temperature measurement produces the error in calculated density. The maximum temperature irregularity in this furnace was about ±5 °C at the lower temperature (about 500 °C), and this leads to a density error of about ±0.002 g/cm^3. Fourth, the meniscus and the level measurement inevitably cause some error. The cathetometer used in this measurement has an accuracy of ±0.01 cm. Even if the level-measuring error was half of the accuracy (±0.005 cm), the error of the obtained density was ±0.0044 g/cm^3 in this case.

The first and the fourth points were not related to the temperature or the composition of the samples, but the second was significant at high temperature and at high KCl content, while the third was observable at lower temperature and at lower KCl content. Then, the experimental error in density measurement

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