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Three-Phase Liquid–Liquid–Vapor Equilibria in the Methane + Ethane + *n*-Hexane and Methane + Ethane + *n*-Heptane Systems

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The three-phase L_1–L_2–V equilibria behavior of the ternary systems methane + ethane + *n*-hexane and methane + ethane + *n*-heptane is studied. Also presented are the results for the binary system methane + *n*-heptane. The compositions and molar volumes of the liquid phases are reported as functions of temperature and pressure within the immiscibility regions. The two ternary systems have constituent binaries that exhibit L_1–L_2–V immiscibility (methane + *n*-hexane and methane + *n*-heptane, respectively). The addition of the third component, ethane, promotes three-phase behavior in a region extending upward in temperature. The three-phase regions of both systems are bounded from above by a K-point (L_1–L_2 = V) locus and from below by a LCST (L_1 = L_2–V) locus. The system of methane + ethane + *n*-heptane, however, has a fourth boundary of Q points (S–L_1–L_2–V). For both systems, the K point and LCST 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*). Many of these ternary system studies have exhibited L–L–V immiscibility without having an immiscible constituent pair. Some of the nitrogen-rich ternary systems studied, however, contained either the immiscible pair nitrogen + propane (*6*) or nitrogen + ethane (*7*).

Only a few binary prototype LNG hydrocarbon systems exhibit L–L–V three-phase behavior, almost always very near the critical point of the more volatile component. For example, the binary system of methane + *n*-hexane exhibits L–L–V immiscibility terminating with a critical end point of type K (L_1–L_2 = V) at the high-temperature end and an LCST (L_1 = L_2–V, lower critical solution temperature) at the low-temperature end (*8*). The L–L–V locus of the binary system methane + *n*-heptane extends from a K point at the high-temperature end to a four-phase S–L_1–L_2–V point, or Q point (quadruple point), at the low-temperature end (*9*).

This paper presents the results of the L_1–L_2–V phase equilibria of the ternary systems of methane + ethane + *n*-hexane and methane + ethane + *n*-heptane. The liquid-phase compositions and molar volumes are reported for the L_1 and L_2 phases within the three-phase region including the critical boundaries. The addition of the ethane component to each of the two binary immiscible pairs extends their respective multiphase behavior upward in temperature and pressure from the binary three-phase locus, in the direction of the ethane pure component critical point. These two ternary systems are bounded by (1) the binary L_1–L_2–V locus; (2) a locus of K points (L_1–L_2 = V); (3) a locus of LCST points (L_1 = L_2–V). There is also a fourth boundary for the system of methane + ethane + *n*-heptane, a locus of Q points (S–L_1–L_2–V), where S is a solid *n*-heptane phase. For both systems, the intersection of the loci of K points and LCST points is an invariant point, the tricritical point. For a more complete discussion of the three-phase topography, the reader is directed to ref *10*.

Experimental Section

The experimental work was performed with the aid of an apparatus of the type similar to the one developed by Kohn (*11*), designed to measure accurately pressure, temperature, volume, and input compositions of the chemical species added to a glass equilibria visual cell. The details of the experimental procedures are discussed in ref *1* and *2*. Volumetric calibration of the visual cell permits accurate accounting of the phase volumes of the multiphase behavior under study. Combination of the stoichiometric and volumetric measurements allows the computation of the composition and molar volume of each liquid phase present.

Precise measurement of the amount of each chemical species introduced into the cell is essential in the stoichiometric procedure. This was achieved by accurate temperature, pressure, and input volume determination. The temperature was measured with a platinum resistance thermometer, calibrated to the IPTS-1968 standards and was estimated to be accurate ±0.03 K. The equilibrium cell pressure was monitored by means of a Heise bourdon tube gauge with an accuracy of about ±0.07 bar. The phase volumes of the equilibrium mixtures were measured from calibrated cell markings which can be read to about ±0.02 cm^3. The visual cell volumes are typically about 10 cm^3.

In order to account properly for the distribution of the input composition in the liquid phases present, the vapor space was assumed to be composed of only methane + ethane in both ternary systems. The vapor-phase mixture of methane + ethane was assumed to have a composition consistent with the methane + ethane binary vapor–liquid system reported by Wichterle and Kobayashi (*12*). With this information on com-

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

temp, K	press., bar	mole fraction of		molar vol, mL/mol
		methane	ethane	
		$K(L_1-L_2 = V)$		
201.61	56.81	0.7644	0.0786	72.64
198.08	54.07	0.7392	0.0331	71.27
197.27	53.41	0.7336	0.0274	70.21
197.20	53.30	0.7401	0.0249	64.94
197.13	53.33	0.7341	0.0240	65.76
196.07	52.67	0.7308	0.0080	54.62
		$LCST(L_1 = L_2-V)$		
202.20	56.64	0.8361	0.0800	61.66
200.54	54.78	0.8497	0.0730	63.47
200.06	54.09	0.8489	0.0725	63.37
198.78	52.56	0.8538	0.0642	65.41
198.46	52.23	0.8381	0.0642	60.05
197.08	50.54	0.8257	0.0600	64.78
196.15	49.44	0.8203	0.0573	62.61
187.22	39.40	0.8412	0.0207	56.56
186.67	39.12	0.8587	0.0187	58.31
186.57	39.19	0.8225	0.0108	58.18
		L_1-L_2-V		
198.00	53.93	0.7466	0.0258	66.23
	53.86	0.7421	0.0323	66.00
	53.31	0.7496	0.0343	65.99
	52.97	0.7612	0.0378	64.64
194.00	49.28	0.7459	0.0064	64.19
	49.22	0.7394	0.0094	64.79
	48.83	0.7490	0.0135	64.02
	48.49	0.7571	0.0292	63.34
	48.01	0.7754	0.0311	62.43
	47.52	0.7773	0.1899	61.06

position, the vapor space compressibility factor was estimated by means of the Soave–Redlich–Kwong equation of state, as modified by Graboski and Daubert (*13*, *14*). Knowledge of the vapor space compressibility and vapor space volume allowed proper determination of the proportion of the total input composition that was distributed in the remaining (liquid) phases. The possible error introduced by these assumptions was reduced by the minimization of the vapor phase present in the experimental runs.

The methane used was a Linde Ultra Purity grade with a stated purity of 99.97 mol %. The *n*-hexane and *n*-heptane were from Humphrey Chemical Co. of North Haven, CT. Both these chemicals have a stated purity of 99 mol %. The ethane gas used in the experiments was a Linde CP grade with a stated purity of 99 mol %. The ethane gas was purified further prior to use in the experimental runs by filtering it through consecutive beds of 13A molecular sieves and activated charcoal at ambient temperature and then placing it into a storage reservoir at about 0 °C. After liquefaction the vapor phase was then vented until a sufficient amount of the ethane was gone, usually about $^1/_3$ of the liquid phase. The difference between the bubble and dew point pressures at 25 °C was found to be about 10 psia. The rest of the chemicals and gases were used without further purification.

Experimental Results

The raw data for the methane + ethane + *n*-hexane system are presented in Tables I and II, while the raw data for the methane + ethane + *n*-heptane system are presented in Tables III and IV. Tables I and III are data for the L_1 phases that are *n*-hexane- and *n*-heptane-rich, respectively, while Tables II and IV are the data for the ethane-rich L_2 phases. The binary L_1–L_2–V data for the methane + *n*-hexane system were obtained from the literature. (*8*).

Analysis of our experimental procedure and the computational methods suggests that the liquid-phase volumes are accurate to ±1.5%. The hydrocarbon solute compositions should be reliable to ±2% in the L_1 phase and ±8% in the L_2 phase. The ethane compositions are reliable to ±3.5%. These estimates should be considered conservative.

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

temp, K	press., bar	mole fraction of		molar vol, mL/mol
		methane	ethane	
		$K(L_1-L_2 = V)$		
203.95	59.40	0.8193	0.0782	64.64
201.93	57.37	0.9173	0.0525	71.81
199.44	54.99	0.9413	0.0339	71.25
199.04	54.79	0.9678	0.0311	73.42
198.21	54.28	0.9737	0.0217	81.03
198.14	53.96	0.9691	0.0224	79.08
197.81	53.98	0.9698	0.0268	80.18
196.64	52.92	0.9867	0.0031	87.33
		L_1-L_2-V		
198.00	53.79	0.9719	0.0158	78.21
	53.25	0.9530	0.0259	75.23
	52.90	0.9397	0.0322	72.99
	51.94	0.9280	0.0506	68.83
194.00	48.90	0.9677	0.0098	66.03
	47.82	0.9318	0.0303	64.80
	47.66	0.9423	0.0355	63.62

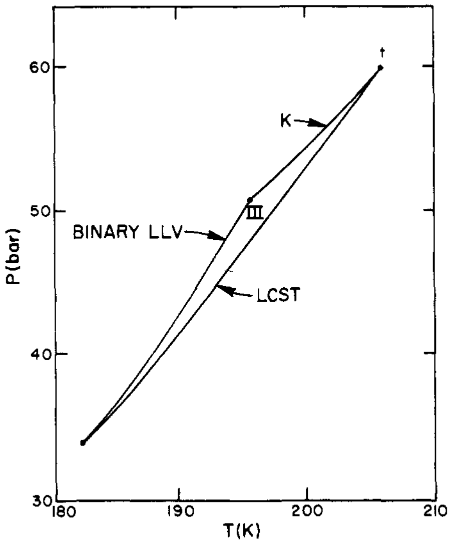

Figure 1. Projection in pressure–temperature space of the boundaries of the three-phase L_1–L_2–V region for the system methane + ethane + *n*-hexane.

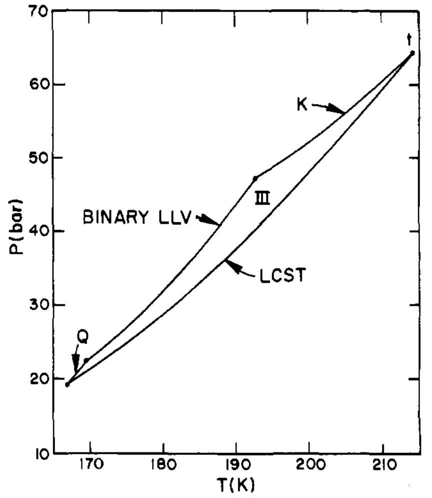

Figure 2. Projection in pressure–temperature space of the boundaries of the three-phase L_1–L_2–V region for the system methane + ethane + *n*-heptane.

Table III. Raw Data for the *n*-Hexane-Rich Liquid Phase, L_1, of the System Methane + Ethane + *n*-Heptane

temp, K	press., bar	mole fraction of		molar vol, mL/mol
		methane	ethane	
		$K(L_1–L_2 = V)$		
208.20	60.63	0.7053	0.1784	62.43
204.63	57.81	0.6805	0.1480	60.14
203.00	56.70	0.6685	0.1337	61.07
200.38	54.42	0.6571	0.1220	61.96
200.16	54.29	0.6472	0.1144	65.91
199.38	53.67	0.6539	0.1045	67.34
198.73	53.26	0.6406	0.1001	68.27
197.93	52.64	0.6352	0.0912	69.36
196.54	51.32	0.6216	0.0780	72.90
195.41	50.70	0.6218	0.0624	72.15
194.24	49.91	0.6338	0.0356	72.51
193.01	49.05	0.6402	0.0113	73.09
		$LCST(L_1 = L_2–V)$		
210.18	61.87	0.7636	0.1629	62.48
208.72	59.94	0.7742	0.1586	60.12
205.82	56.76	0.7583	0.1434	60.63
204.36	54.97	0.7707	0.1378	59.38
203.13	53.53	0.7811	0.1325	58.53
202.07	52.28	0.7904	0.1275	58.04
201.07	51.18	0.7983	0.1233	57.01
200.12	50.29	0.8053	0.1194	56.75
198.21	48.22	0.8187	0.1119	55.81
196.57	46.36	0.8281	0.1064	55.26
195.29	45.11	0.8385	0.0993	54.97
194.02	43.33	0.8342	0.0997	53.52
193.76	43.12	0.8383	0.0966	53.74
191.77	41.05	0.8496	0.0908	53.62
189.73	38.85	0.8239	0.0957	53.89
184.77	34.09	0.8074	0.0856	54.12
183.46	32.91	0.8144	0.0826	53.57
182.26	31.81	0.8211	0.0797	53.25
178.64	28.56	0.8329	0.0746	52.82
178.45	28.79	0.8309	0.0823	52.90
175.98	26.51	0.8420	0.0737	52.13
175.51	26.16	0.8400	0.0783	52.16
175.13	25.82	0.8439	0.0764	51.95
174.01	24.78	0.8490	0.0739	51.61
173.99	24.86	0.8506	0.0691	51.34
172.78	24.02	0.8562	0.0704	50.88
171.88	23.06	0.8597	0.0713	50.64
		$L_1–L_2–V$		
200.00	53.39	0.6683	0.1025	67.94
	53.04	0.6657	0.1062	68.81
	52.01	0.6860	0.1104	64.82
195.00	49.60	0.6224	0.0577	73.52
	48.08	0.6459	0.0786	68.53
	45.94	0.6891	0.1039	62.71
190.00	44.26	0.6485	0.0144	72.52
	42.43	0.6573	0.0462	69.48
	41.19	0.6756	0.0665	66.24
180.00	31.89	0.6828	0.0491	66.93
	30.85	0.7055	0.0680	62.87
	30.51	0.7253	0.0711	59.54
		$Q(S–L_1–L_2–V)$		
168.93	22.16	0.6836	0.0231	66.47
167.94	21.06	0.7130	0.0578	60.58

Table IV. Raw Data for the *n*-Hexane-Lean Liquid Phase, L_2, of the System Methane + Ethane + *n*-Heptane

temp, K	press., bar	mole fraction of		molar vol, mL/mol
		methane	ethane	
		$K(L_1–L_2 = V)$		
205.82	58.71	0.8685	0.1227	79.96
202.94	56.40	0.8759	0.1128	81.84
200.97	54.91	0.8913	0.1060	81.74
199.28	53.60	0.9106	0.0827	82.25
197.69	52.36	0.9395	0.0520	82.72
195.47	50.84	0.9834	0.0128	83.94
194.21	49.84	0.9697	0.0247	85.81
		$L_1–L_2–V$		
200.00	53.87	0.9105	0.0892	80.67
	52.50	0.8980	0.0894	69.00
	50.98	0.8729	0.1055	62.07
195.00	50.08	0.9640	0.0345	80.70
	48.22	0.9391	0.0485	66.89
	46.36	0.9022	0.0716	60.15
	44.70	0.8701	0.0945	54.14
190.00	43.74	0.9766	0.0129	62.64
	42.71	0.9620	0.0269	60.30
	40.99	0.9314	0.0485	56.92
	39.95	0.9079	0.0707	54.93
	39.22	0.8681	0.0875	53.93
180.0	32.09	0.9475	0.0263	54.24
	30.99	0.9089	0.0532	53.14
	30.02	0.8646	0.0729	53.59
		$Q(S–L_1–L_2–V)$		
168.55	21.75	0.9338	0.0206	49.32

Table V. Raw Data for the Binary System Methane + Ethane + *n*-Heptane along with the $L_1–L_2–V$ Locus

		L_1		L_2	
temp, K	press., bar	methane mole fracn	molar vol, mL/mol	methane mole fracn	molar vol, mL/mol
		$K(L_1–L_2 = V)$			
192.59	48.78	0.6419	74.7		
192.61	48.78			0.9946	89.9
		$L_1–L_2–V$			
190.00	45.04	0.6470	73.7		
	45.02			0.9915	67.3
185.00	38.67	0.6576	72.1		
	38.82			0.9870	59.0
180.0	33.13	0.6640	70.9		
	33.00			0.9844	55.0
175.00	27.86	0.6696	69.8		
	27.85			0.9800	52.8
170.00	23.38	0.6722	68.9		
				0.9766	50.5
		$Q(S–L_1–L_2–V)$			
169.78	23.16	0.6703	68.8		
169.77	23.20			0.9762	50.1

Figures 1 and 2 present the boundaries of the immiscibility regions of the two ternary systems in pressure–temperature space. Each system exhibits the binary L_1–L_2–V locus intrusion. The main difference between the two binary system loci is the lower temperature termination. As previously mentioned, the lower end point of the L_1–L_2–V locus for the methane + *n*-heptane system is a Q point (S–L_1–L_2–V), while for the system methane + *n*-heptane it is an LCST point (L_1 = L_2–V). The addition of the ethane component extends the three-phase behavior upward in temperature and pressure from the binary immiscibility loci. Both ternary systems are basically bounded from below by an LCST locus and from above by a K-point locus. The methane + ethane + *n*-hexane system has a triangular immiscibility region, while the methane + ethane + *n*-heptane system has a fourth boundary which is a locus of Q points. For both systems, the LCST and K-point loci intersect at a tricritical point.

The binary L_1–L_2–V data for the methane + *n*-heptane system were studied herein in more compositional detail than previously reported in the literature by Kohn (*9*) and Chang et al. (*15*). Results are presented in Table V. These data agree well with the literature except for the K-point terminus, which was reported in ref *9* and *15* to be 191.71 K and 47.85 bar. The discrepancy with our location of 192.59 K and 48.78 bar may be due to difference in the purity of methane used. Kohn (*9*) estimated the purity of his methane to be 99.5 mol %.

The extent of the three-phase behavior of the ternary system methane + ethane + *n*-hexane is considerably less than that of the system of methane + ethane + *n*-heptane. The latter system in turn has a larger immiscibility region than the system of methane + ethane + *n*-octane (*1*). Considering the projection of these immiscibility regions in pressure–temperature space when the solvent pair is that of methane + ethane, the extent of the three-phase behavior starts with the *n*-hexane-containing system and diminishes with the *n*-octane system.

Glossary

K	K point or upper critical end point of an L–L–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 become critically identical with each other
Q	quadruple point, the equilibrium coexistence of four phases, for this case the L_1, L_2, V, and S phases
S	solid phase
t	tricritical point
T	temperature
V	vapor phase

Registry No. Methane, 74-82-8; ethane, 74-84-0; hexane, 110-54-3; heptane, 142-82-5.

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Solubility of Ethane in *n*-Decane at Pressures to 8.2 MPa and Temperatures from 278 to 411 K

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The solubility of ethane in liquid *n*-decane has been measured as a function of pressure at five temperatures (4.4, 37.8, 71.1, 104.4, and 137.8 °C) by two separate experimental techniques. Liquid-phase molar volumes are also reported at 4.4 and 37.8 °C. The compositional data of the two experiments display minor systematic differences at 37.8 °C; however, both data sets exhibit significant systematic differences at all temperatures from the earlier study of Reamer and Sage.

Introduction

The viability of using rich gases (e.g., mixtures of methane, ethane, and propane) as drive gases for enhancing the recovery of crude oils from reservoirs is being investigated actively by the petroleum production industry. Rich-gas enhanced recovery is an attractive option particularly in remote locations where reinjection of reservoir gases would be an alternative to flaring. The computer simulation of such recovery processes usually requires use of an equation of state (EOS) to describe the local phase equilibria in the reservoir. Parameters for the EOS are generally determined from pure-component thermodynamic data and binary phase equilibria data. Data on the phase equilibria of a binary mixture of ethane + *n*-decane would constitute a prominent contribution to such a data base.

Reamer and Sage (*1*) reported the properties and phase equilibria of mixtures of ethane + *n*-decane at pressures to 69 MPa and temperatures from 40 to 460 °F. The two-phase isotherms were studied up to their critical points, with compositions and molar volumes being measured for both the vapor and liquid phases.

One of us (K.D.L.), while engaged in a study of the liquid-phase diffusion of rich-gas components in well-defined hydrocarbons such as *n*-decane, measured equilibrium solubilities of ethane in *n*-decane at 37.8 °C (100 °F) which were in significant disagreement with the data of Reamer and Sage. Consequently, we decided to undertake a joint study of the solubility of ethane in *n*-decane, using independent experimental apparatuses and procedures, in an attempt to resolve discrepancies with the literature data.

Experimental Section

A detailed description of the experimental apparatus at the University of Tulsa is given in an earlier paper (*2*). The procedures for performing vapor–liquid equilibrium studies are presented in the same reference and will be briefly summarized here. A known amount of *n*-decane is first placed in a 7.5-mL visual (glass) equilibrium cell. During an experimental run, measured amounts of ethane gas are added to the thermostated visual cell from a high-pressure bomb by means of a

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