Multiphase and Volumetric Equilibria of the Ethane-Methanol System at Temperatures between $-40°$ and 100°C.

YI HUA MA and JAMES P. KOHN
University of Notre Dame, Notre Dame, Ind.

The two-phase (vapor-liquid) *P-V-T-X* behavior and the three-phase (vapor-liquid 1, liquid 2) *P-V-T-X* behavior are presented at temperatures between $-40°$ and 100° C.

PARTIAL MISCIBILITY behavior in binary systems in which one or both components are gases has not been extensively studied. Mixtures of ethane and methanol have been investigated by Kuenen (*5, 6*). Two liquid phases were observed by Kuenen in a certain temperature range but concentration data were not reported.

The volumetric behavior of the pure components has been extensively studied. Ethane has been investigated by several groups of investigators (*1, 2, 11, 13*). Barkelew (*1*) evaluated the thermodynamic properties from the *P-V-T* data previously mentioned (*2, 11, 13*).

The properties of methanol have been established by several studies (*4, 15*).

EXPERIMENTAL

The equipment employed in this study was described by Kohn (*9*). The apparatus and techniques have been used in other studies of binary systems (*10, 14*). The one minor change in experimental technique came in obtaining compositional data in the three-phase region.

The compositions of the liquid (L_1) phase and liquid (L_2) phase were determined by using a conventional type borosilicate glass bubble point cell. In determining the composition of the (L_1) phase, the cell was initially charged with methanol to a level such that the saturated liquid (L_1) phase would fill the body of the cell simultaneously with the appearance of the second liquid (L_2) phase. The composition of the (L_2) phase was determined by initially charging the cell with a small amount of methanol. After the second liquid phase (L_2) appeared, sufficient ethane was added to cause the disappearance of the (L_1) phase.

The ethane used in this study was Matheson Co. "pure grade" material of 99 mole % minimum purity. Its impurities were listed as methane, nitrogen, carbon dioxide and propane. The unit was charged by passing the ethane through a pressure bomb packed with silica gel. The ethane was then liquified in a stainless steel bomb which was maintained at -40° C. in a bath of dry ice and acetone. To remove methane and nitrogen, about ⅓ of the liquified ethane was boiled away by slowly venting the vapor phase to the atmosphere. The purity of the processed ethane was at least 99.4 mole %.

The methanol used was J.T. Baker, 99.8% minimum purity, containing less than 0.09% water. A gas chromatograph run on the methanol verified that it contained less than 0.09% water in the alcohol. The methanol was used without further purification.

RESULTS

Selected representative isotherms are presented in Figure 1. Six experimental bubble point isotherms from $-25°$ to 100° C. and three experimental dew point isotherms from 50° to 100° C. were determined in borosilicate glass bubble point and dew point equilibrium cells, respectively. The temperatures, pressures, and compositions for the two liquid phase region are shown in Figure 1 by dashed lines. The average deviation of the experimental bubble point isotherms at 50° C. and higher is ± 0.0017 mole fraction, $\pm 0.07°$ C. and ± 0.10 atm. At lower temperatures it is ± 0.004 mole fraction, $\pm 0.1°$ C. and ± 0.10 atm. For the dew point isotherms, the average deviation is ± 0.006 mole fraction, $\pm 0.07°$ C. and ± 0.10 atm.

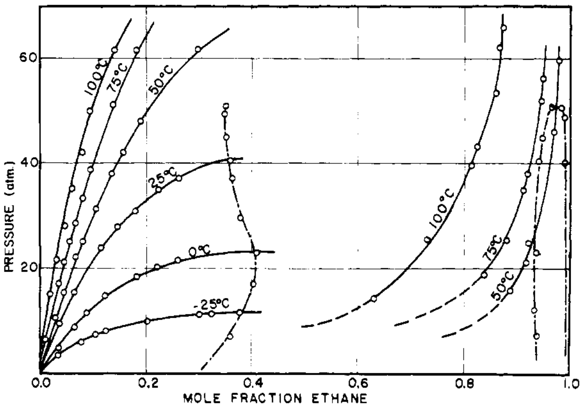

Figure 1. Experimental isotherms

At temperatures above 36.42° C. the isotherms of Figure 1 are similar to those of other binary systems which contain ethane (*7, 8*). The phase behavior for the temperatures below 36.42° C. is exactly the same as that observed in systems which have two liquid phases which extend into the vapor-liquid critical locus.

Figures 2*A* and 2*B*, which present the phase behavior at 20 and 40 atm., respectively, show that a region of two liquid phases exists as a miscibility gap intersecting the vapor-liquid region. Since it was impossible with the equipment used in this study to investigate the two-phase equilibria of L_1–L_2, these equilibria are indicated by dashed lines in the region indicated as $L_1 + L_2$.

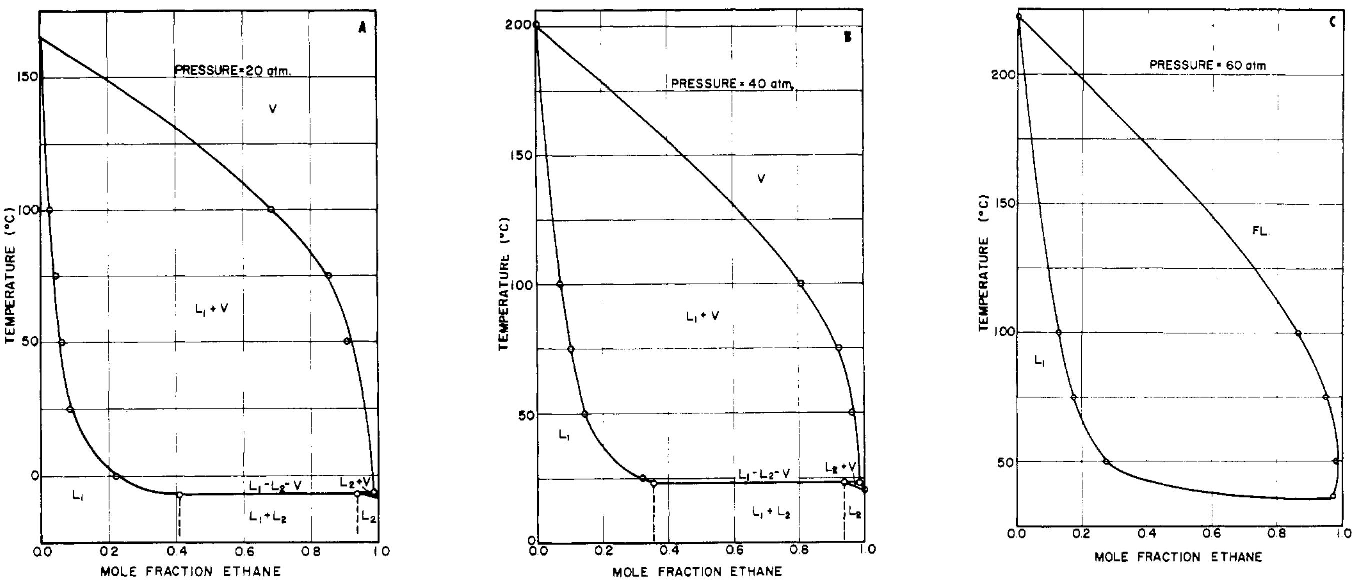

Figure 2. Isobaric temperature–composition diagram

A: 20 atm. pressure, *B*: 40 atm. pressure, *C*: 60 atm. pressure

Figure 2*C* shows the phase behavior at 60 atm. This pressure is above the pressure of the type *k* singular point of the system. Only two phases exist at this pressure.

Figure 3 shows that the locus of three-phase points is very close to the vapor pressure curve for pure ethane. The locus of this curve ends at the type *k* singular point (51.08 atm. and 36.42° C.). At this point, the L_2 phase is in critical identity with the vapor phase in the presence of the L_1 phase.

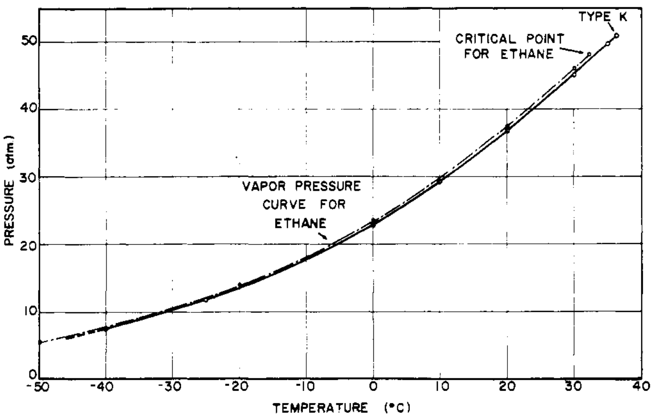

Figure 3. Locus of the three phase points (L_1–L_2–V)

The smoothed values of composition and molar volume of the bubble point and dew point states are presented in Table I at even values of pressure for each temperature studied. The bubble point molar volumes are believed accurate to ±0.2% at temperature of 50° C. and higher; at lower temperatures, the accuracy is ±0.3%. Accuracy of the dew point molar volumes is dependent on pressure—below 40 atm., accuracy is ±0.1%, above 40 atm., accuracy is ±0.5%.

Table I. Smoothed Values of Composition and Molar Volume of the Bubble Point and Dew Point States

	Bubble Point		Dew Point[a]	
Press., Atm.	Mole fraction ethane	Molal volume, ml. /gram mole	Mole fraction ethane	Molal volume, ml. /gram mole
		100° C.		
3.452[b]	0.0000	44.88		
10	0.0085	45.32		
20	0.0284	46.27	0.687	1357
30	0.0510	47.27	0.756	1046
40	0.0719	48.15	0.808	797
50	0.0967	49.08	0.842	613
60	0.1290	49.95	0.864	462
		75° C.		
1.492[b]	0.0000	43.26		
10	0.0181	43.95		
20	0.0433	44.86	0.855	1162
30	0.0718	45.88	0.897	807
40	0.1015	46.90	0.926	550
50	0.1332	47.91	0.944	380
60	0.1738	48.99	0.949	333
		50° C.		
0.534[b]	0.0000	41.89		
10	0.0270	42.76		
20	0.0619	43.92	0.907	1200
30	0.0990	45.13	0.943	805
40	0.1454	46.64	0.960	590
50	0.2045	48.48	0.970	457
60	0.2753	50.55	0.978	343
		25° C.		
0.168[b]	0.0000	40.72		
10	0.0370	42.01		
20	0.0871	43.59		
30	0.1665	45.98		
40	0.3210	50.78		
40.74[c]	0.3528	51.61		
		0° C.		
0.0389[b]	0.0000	39.48		
10	0.0764	41.53		
20	0.2225	45.69		
23.1[c]	0.4068	50.79		
		-25° C.		
	0.0000			
10	0.2085	44.07		
11.94[c]	0.3850	48.63		

[a] Dew point compositions and molar volumes at 25° C. and lower temperatures are accurately given by properties of pure ethane. [b] Vapor pressure of pure methanol. [c] Composition of liquid 1 along liquid 1– liquid 2–vapor phase line.

The composition and molar volume values for the dew point state were not determined for the temperature below 25° C. The determination of dew points below 25° C. could not be justified because of the difficulty of measuring accurately a few tenths of a mole per cent methanol and the initial limited purity of the material used. Since the dew point states, at the lower temperatures, contain ethane in excess 0.99 mole fraction except at very low pressures,

Table II. Smoothed Values of Composition of Three-Phase Region

Press., Atm.	Temp., ° C.	Mole Fraction Ethane Comp., liquid 1	Comp., liquid 2	Comp., vapor phase
7.18	−40.00	0.360	0.957	0.992
10	−30.07	0.376	0.936	0.991
20	−5.65	0.410	0.934	0.990
30	10.80	0.357	0.936	0.989
40	23.78	0.354	0.941	0.988
50	35.25	0.348	0.962	0.986
51.08[a]	36.42	0.351	0.979	0.979

[a] Critical temperature and pressure of the liquid 2 and vapor phase.

the equilibrium properties at these states are regarded as identical to those of pure ethane.

The smoothed three-phase data (L_1-L_2-V) are shown at even pressures in Table II. In comparing those smoothed values presented in Table II with values of Kuenen (*5*), the average deviation of the pressure is 1% for temperatures below the critical point. At the critical point, the deviation is 3% and −3% in temperature and pressure, respectively. Kuenen's system contained air, which raised the critical pressure and lowered the critical temperature of the system.

From the compositions along the three-phase line given in Table II and illustrated by the dashed lines in Figure 1, there definitely does not seem to be a lower critical solution point for the system (L_1 = L_2 in the presence of a vapor phase). Rather it would appear that at a temperature in the region of −97.8° C. that the three-phase line terminates at a quadruple point. At this point solid methanol should be in equilibrium with the (L_1), (L_2) and vapor phases.

NOMENCLATURE

L_1 = liquid phase rich in methanol
L_2 = liquid phase rich in ethane
V = vapor phase

LITERATURE CITED

(1) Barkelew, C.H., Valentine, J.L., Hurd, C.O., *Trans. A.I.Ch.E.* **43**, 25 (1947).
(2) Beattie, J.A., Hadlock, C., Poffenberger, N., *J. Chem. Phys.* **3**, 93 (1935).
(3) International Critical Tables, Vol. **III**, pp. 115 to 116 McGraw-Hill, New York, 1928.
(4) *Ibid.*, pp. 290.
(5) Kuenen, J.P., *Phil. Mag.* [VI], **6**, 637 (1903).
(6) Kuenen, J.P., Robson, W.G., *Ibid.*, **48**, 180 (1899).
(7) Kay, W.B., *Ind. Eng. Chem.* **30**, 459 (1938).
(8) *Ibid.*, **32**, 253 (1940).
(9) Kohn, J.P., *A.I.Ch.E.J.* **7**, 514 (1961).
(10) Kohn, J.P., Kurata, F., *Petroleum Processing* **11**, No. 12, 57 (1956).
(11) Pitzer, K.S., Brewer, L., "Thermodynamics," pp. 207, McGraw-Hill, New York, 1961.
(12) Porter, A.W., *J. Am. Chem. Soc.* **48**, 2055 (1926).
(13) Ricci, J.E., "The Phase Rule and Heterogeneous Equilibrium," pp. 169–185, D. Van Nostrand, New York.
(14) Sage, B.H., Webster, D.C., Lacey, W.N., *Ind. Eng. Chem.* **29**, 658 (1937).
(15) Shim, J., Kohn, J.P., J. CHEM. ENG. DATA **7**, 3 (1962).
(16) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," pp. 302–06, 1950.

RECEIVED for review November 5, 1963. Accepted August 8, 1963. Sincere appreciation is expressed for the financial support of the Esso Education Foundation and to the University of Notre Dame whose teaching assistantship made this study possible.

Multiphase and Volumetric Equilibria of the Methane–*n*-Octane System at Temperatures between −110° and 150°C.

JAMES P. KOHN and WILLIAM F. BRADISH
University of Notre Dame, Notre Dame, Ind.

Vapor-liquid compositions and molar volumes were determined at eight temperatures between −50° and 150° C. Temperature, pressures, and compositions along the three phase (vapor-liquid-solid) lines are reported at temperatures between −107.6° and −56.7° C.

THIS STUDY was undertaken in view of the scarcity of information on the low temperature phase and volumetric behavior of the methane-*n*-octane system. Such information is desirable for its use in low temperature theoretical studies and for its value in assessing the economic feasibility of employing low temperature separation processes in systems involving light hydrocarbon mixtures.

No studies of the vapor-liquid behavior of the methane-*n*-octane system were found in the literature. Brewer (*1*) reported a study of the three phase (solid-liquid-vapor) locus and reported compositions of the liquid phase.

The *P-V-T* behavior of the pure components has been studied. Methane has been investigated by several groups of investigators (*3, 6, 8, 9, 10*). Matthews (*7*) evaluated the thermodynamic properties of methane from selected *P-V-T* data previously mentioned.

Young (*15, 16*) presented vapor pressures, specific volumes, and critical constants of *n*-octane from −3° to 296° C. Felsing (*2*) reported the compressibility of liquid *n*-octane at temperatures from 100° to 275° C. at pressures to 300 atm. Data on the liquid density, vapor pressures, critical constants, and heat of fusion of *n*-octane were