Vapor-Liquid Equilibrium Measurements for the Propane-Ethanol System at Elevated Pressures

Vapor-liquid equilibrium measurements have been carried out for the propane-ethanol system at 325°, 350°, 375°, 400°, and 425°K. The pressures corresponding to these temperatures ranged from 569.5 kPa (82.6 lb/in.^{2}abs) to 5 618.5 kPa (814.9 lb/in.^{2}abs). Altogether, nineteen experimental determinations were made; one of these determinations at 425°K approached the critical state, and this measurement assisted in establishing the entire critical temperature and critical pressure profiles for this binary system. The information associated with these measurements enabled the construction of isothermal bubble point-dew point relationships up to 500°K. These results made possible the establishment of isothermal relationships of K values vs. pressure for the components of the propane-ethanol system. Calculated K values for this system using the BWR method and the SRK method were found to be in fair agreement with corresponding experimental values.

MATEO GÓMEZ-NIETO
and
GEORGE THODOS
Northwestern University
Evanston, Illinois 60201

SCOPE

Current interest in the accessibility of information on the physical properties of polar-nonpolar mixtures has prompted an experimental study dealing with the vapor-liquid equilibrium behavior of the binary system, propane-ethanol, at elevated pressures. This study was conducted in a high pressure vapor-liquid equilibrium facility of the static type for temperatures ranging from 325° to 425°K and pressures up to 5 618.5 kPa (814.9 lb/in.^{2}abs), measured with a pressure transducer. Studies of this type for polar-nonpolar mixtures at elevated pressures are essentially non-existent (McCracken et al., 1960; Cherry, 1967), and therefore the present study aims to provide information needed to formulate a background in this direction. Information derived from this investigation should provide a needed background for the theoretical development of the vapor-liquid equilibrium behavior for polar-nonpolar mixtures.

CONCLUSIONS AND SIGNIFICANCE

Vapor-liquid equilibrium measurements at high pressures have been established for the propane-ethanol system. The temperatures, 325°, 350°, 375°, 400°, and 425°K, investigated in this study permitted the establishment of the vapor-liquid equilibrium behavior up to the critical state of this system. This experimental investigation presents information that should assist in the theoretical development of methods capable of predicting fluid phase behavior for polar-nonpolar mixtures.

The vapor-liquid equilibrium behavior of nonpolar compounds has been estensively investigated over the last 40 yrs and during this period has kept pace with the technological development of the petroleum industry. In this regard, an abundance of experimental information related to hydrocarbon mixtures has been presented in the literature. Along these lines, it is noteworthy to point out the comprehensive studies of Kay (1938, 1940, 1941) on the binary systems associated with the hydrocarbons ethane, *n*-butane and *n*-heptane, and the extensive work of Sage and Lacey who contributed so much to the development of the general discipline associated with the physical property behavior of a host of hydrocarbons. Their work is monumental and dates back to 1934 when Sage, Lacey, and Schaafsma (1934) investigated the behavior of the methane-propane system, and thereafter continued with further experimental studies for a host of binary and multicomponent hydrocarbon systems. Largely due to the efforts of these investigators, and also those of Katz and Hachmuth (1937) and Price and Kobayashi (1959), abundant information associated with the vapor-liquid equilibrium behavior of simple and complex hydrocarbon mixtures has been compiled.

In general, information available in the literature for polar-nonpolar compounds has been limited to low pressures. Nagahama et al. (1971) present bubble point measurements for a number of propane binary systems at 19.9°C, including the propane-ethanol system from 1.69 to 9.38 atm. Kretschmer and Wiebe (1951) determine the solubility of propane in ethanol at 0°, 25°, and 50°C for propane concentrations up to 0.04054 mole fraction and pressures up to 764.4 mm. No vapor-liquid equilibrium measurements for the propane-ethanol system are available in the literature at elevated temperatures and pressures. More specifically, no information is available for this binary system in the critical region. Therefore, it is appropriate at this time to undertake an experimental study for the establishment of the vapor-liquid equilibrium behavior of the propane-ethanol system at elevated temperatures. In this connection, an experimental facility, originally used by Din-

---

Mateo Gomez-Nieto is presently with the Institute Politecinco Nacional, Mexico City, Mexico.

0001-1541-78-1237-0672-$00.95.

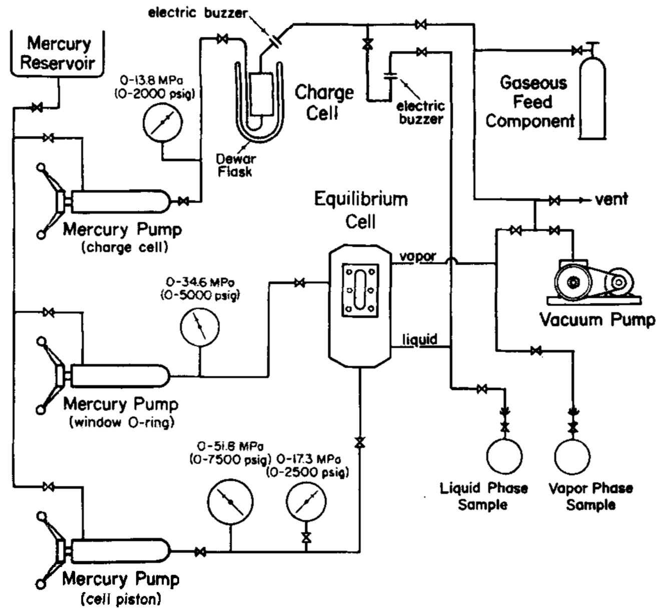

Fig. 1. Schematic diagram of vapor-liquid equilibrium facility.

grani and Thodos (1977), has been used to obtain the information needed for establishing this needed background on this binary system.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The propane was of research grade and was claimed to be 99.99 pure. The ethanol, claimed by the manufacturer to be of 99.99 purity, with a reported normal boiling point of 78.5°C and a liquid density of 0.7893 g/cm^3 at 25°C, was stored in a desiccator provided with anhydrous calcium chloride. In addition, granules of molecular sieves, predried at 400°C, were introduced into this liquid to eliminate any possibility of water contamination. The ethanol was pipetted, using a rubber bulb, into a charging glass bulb over a dry nitrogen atmosphere.

The vapor-liquid equilibrium cell included in Figure 1 represents the nucleus of the experimental facility. This equilibrium cell was electrically heated with air baths that surrounded it. The outer bath was manually controlled to within a few degrees of the temperature prescribed for the inner bath, which was electronically controlled. The temperature within the inner air bath was kept constant with the aid of an iron constantan thermocouple whose signal was utilized by a controller recorder. The iron constantan thermocouples used in this facility were calibrated using as references, the melting point of ice at 0°C, the normal boiling point of water at 100°C, and the freezing point of tin, certified by the National Bureau of Standards as having a melting point of 231.90°C. A Leeds and Northrup potentiometer (Model No. 9834-1), capable of accuracy within 10^{-8}V, was used with the five iron constantan thermocouples placed in the different thermowells of the body of the cell. The temperature within the air bath, surrounding the equilibrium cell, was kept constant within 0.05°C, as indicated by one of the calibrated iron constantan thermocouples. The basic features of this facility are essentially those described by Dingrani and Thodos (1977) who used this equipment to investigate the vapor-liquid equilibrium behavior of the ternary system consisting of ethane, *n*-butane, and *n*-hexane. However, in this study a new vapor-liquid equilibrium cell was involved in order to accommodate a higher compression ratio than that attainable with the cell used previously by Dingrani and Thodos (1977). Figure 2 presents a cross-sectional view of the cell facility used but does not include the piston and mercury chamber accessories, the details of which can be found elsewhere (Gomez-Nieto, 1977). The experimental layout and procedure used are identical to those described by the previous investigators, except for the replacement of the new equilibrium cell.

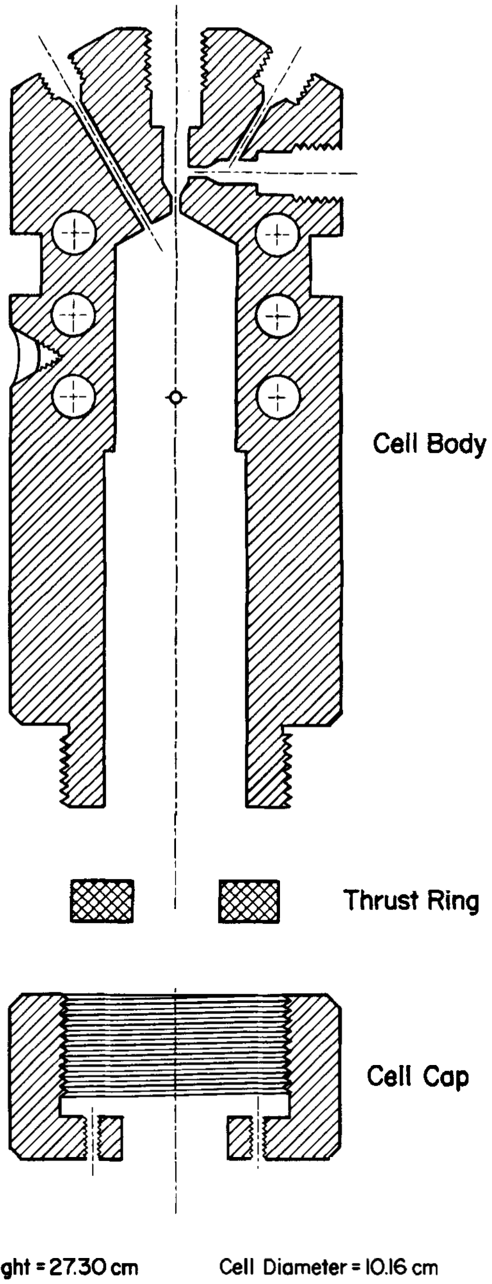

Fig. 2. Cross-sectional view of vapor-liquid equilibrium cell.

The cell was charged by introducing a prescribed amount of ethanol into a glass bulb which was then immersed into liquid nitrogen to freeze it. A line leading to the vapor sampling port of the equilibrium cell was then connected to this glass bulb. The system, including the glass bulb, was evacuated with the ethanol still in its frozen state. To expel any residual air from the ethanol, the frozen alcohol was allowed to melt. This liquid sample was again solidified, and the system was again evacuated. To insure complete removal of any residual air, the freezing-thawing process was repeated two or three times. Water, as brought to a boil with an electric heater, surrounded the glass bulb containing the deaerated liquid charge thus enabling this charge to be introduced into the equilibrium cell via the vapor sampling port. The entire liquid sample was transferred by this approach into the equilibrium cell where it condensed. Liquid propane was then added to the liquid ethanol via the liquid sampling port. To accomplish this, it became necessary to first condense and solidify propane in the charge cell, shown in Figure 1, by surrounding it with liquid nitrogen after properly evacuating the system to avoid contamination with air. With the removal of liquid nitrogen, the propane within the charge cell was allowed to reach room temperature and was then compressed with the mercury pump to a pressurized liquid state. Once the propane was completely liquefied, the mercury pump forced it into the equilibrium cell through the liquid sampling port to establish a predesignated binary composition.

The cell was allowed to reach thermal equilibrium at a prescribed temperature by electrically heated and controlled inner and outer air baths which surrounded the cell. At least 8 hr were required to establish thermal equilibrium as a consequence of the relatively large cell mass. Vapor and liquid equilibrium within the cell was expedited by means of a magnetic agitator that was actuated by an electromagnetic field generated externally near the top of the cell. This magnetic agitator consisted of a thin hollow iron cylinder which was forced to rise into the vapor phase and then allowed to fall into the liquid phase once every 30 s by turning on and off the magnetic field. This mixing phenomenon was observable owing to the visual capability of the cell. The system was allowed to set an hour or two after thermal equilibrium had been established in order to make certain that the system pressure had also attained a state of equilibrium.

The pressure within the equilibrium chamber was measured with a pressure transducer of the strain gauge type (Standard Controls, model No. 210-40-010-02). This transducer was claimed by the manufacturer to withstand temperatures up to 600°K (327°C) and pressures up to 200 atm. The indicator (BLH Electronics, Inc., model 450H) used produced controlled excitation voltages for the transducer coils and amplified and displayed the differential response signal of the transducer to account for the pressure existing within the equilibrium chamber. This pressure measuring facility was calibrated to account for both pressure and temperature variations prevalent within the chamber of the equilibrium cell. This was accomplished by mounting the transducer onto the equilibrium cell, located within the air bath. The chamber of the equilibrium cell was also connected to a Heise gauge that had been precalibrated against a dead-weight gauge (Aminco, model 47-12111). Pressurized nitrogen, introduced into the chamber of the cell, produced both signal responses from the transducer and pressure readings from the Heise gauge. The pressure of nitrogen within the chamber was then varied from 0 to 137 atm for each of the temperature levels of 25°, 50°, 100°, 150°, 200°, and 250°C. The transducer response signals and corresponding pressures resulting from the Heise gauge were correlated to produce for the transducer the temperature dependent relationship

$$P = 1.677 r_z - 1.4 r_z^{1/2}$$

where r_z corrected for temperature

$$r_z = r + 7.1815 - 0.108t - 0.8963t^{1/2}$$

The measurement of pressures with this pressure transducer over the range of pressures encountered in this study (570 to 5 618 kPa) introduces an uncertainty of ± 13.8 kPa (± 2.0 lb/in.^{2}). Periodic checks on the response of this transducer facility at room temperature and elevated temperatures exhibited good reproducibility over the course of this study. Further details and information associated with the calibration of this facility can be found elsewhere (Gomez-Nieto, 1977).

The capability of this experimental facility to account for the combined contribution of temperature and pressure was tested by measuring with this facility the vapor pressure of acetone. These measurements were then compared with values calculated using a vapor pressure equation based primarily on the measurements of Ambrose, Sprake, and Townsend (1974). The comparison of these vapor pressure measurements and calculated values are as follows:

t, °C	Vapor pressure, kPa Expt'l	 Calc'd	ΔP kPa
76.96	206.7	196.7	10.0
102.81	395.2	400.3	−5.1
127.80	723.0	723.1	0.1
149.41	1 139.9	1 135.4	4.5

For this limited pressure variation of 206.7 to 1 139.9 kPa, the maximum pressure departure was 10.0 kPa (1.45 lb/in.^{2}).

Microsamples of about 0.05 cm^3 for both the vapor and liquid phases were transferred from the cell and condensed with liquid nitrogen into specially designed glass bulbs. To increase the pressure to slightly above 760 mm, helium was introduced into these bulbs by means of a gas mixing facility. These condensed microsamples were then allowed to reach room temperature, with vaporization occurring within the glass bulbs into the helium environment. Small portions of the samples were withdrawn after the samples were allowed to mix thoroughly. These portions were then withdrawn and syringed into a gas chromatographic unit (Beckman GC72-5) to obtain chromatograms using a recorder-integrator facility. These responses were translated into compositions through the usual lines of interpretation (McNair and Bonnelli, 1969). The composition of the vapor and liquid phases associated with the combined involvement of the sampling procedure, preparation for analysis, and injection into the gas chromatograph is estimated to produce an uncertainty in composition of 0.005 mole fraction. Details associated with the calibration and interpretation of the chromatograms can be found elsewhere (Gómez-Nieto, 1977).

This investigation experienced a number of difficulties because of the chemical attack of propane and ethanol on the gaskets, seals, and stem valve packings of the equilibrium cell. The most reliable means of operation were possible if Teflon were used only for packing the valve stems. However, this packing material was found to be satisfactory for temperatures not higher than 425°K. Because of its flow characteristics for temperatures above 425°K, Teflon proves inadequate as a valve packing material above this temperature. For the glass-window seal and piston rings, Viton proved adequate in resisting the chemical attack of propane and ethanol and in addition maintained its resilient characteristics at these elevated temperatures.

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

The isothermal vapor-liquid equilibrium measurements established at 325°, 350°, 375°, 400°, and 425°K are presented in Table 1 and extend in pressure up to 5 618.5 kPa (814.9 lb/in.^{2}abs). It is worth noting that the measurements at 425.00°K and 5 618.5 kPa (814.9 lb/in.^{2}abs) were associated with an opalescence phenomenon, indicating the proximity of a critical state for this mixture. The coexisting compositions of propane in the liquid and vapor phases were found to be 0.648 and 0.727 mole fraction, respectively, indicating that this set of conditions did not represent an exact critical point. However, this behavior and this close proximity of composition are indicative of an approach to this terminal state. In Table 1 are also presented the vapor pressures of propane and ethanol at each temperature level. These values have been calculated from the comprehensive vapor pressure studies of Gómez-Nieto and Thodos (1977*a*, 1977*b*) who present the following vapor pressure relationships for propane and ethanol:

$$\ln P_R = 4.22669 - \frac{4.36761}{T_R^{1.27762}} + 0.14092\, T_R^7 \text{ (propane)} \tag{1}$$

$$\ln P_R = 5.98366 - \frac{5.99505}{T_R^{1.37030}} + 0.01139\, T_R^7 \text{ (ethanol)} \tag{2}$$

In Equations (1) and (2), the reduced temperature $T_R = T/T_c$ and the reduced pressure $P_R = P/P_c$. The critical values $T_c = 369.975$°K, $P_c = 4\,256.7$ kPa (42.01 atm) for propane, and $T_c = 513.92$°K, $P_c = 6\,148.4$ kPa (60.68 atm) for ethanol were used. The information presented in Table 1 has been applied to develop the isothermal relationships of Figure 3. Since the critical state of the propane-ethanol system is not reached until $T = 369.975$°K, the isotherms 325° and 350°K are subcritical and therefore extend over the complete range of compositions up to pure propane. However, for the remaining isotherms, the bubble point-dew point relationships terminate on the critical

TABLE 1. EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM MEASUREMENTS FOR THE PROPANE-ETHANOL SYSTEM

Pressure		Liquid, mole fraction		Vapor, mole fraction		Equilibrium constant	
kPa	lb/in.²abs	x_3	x_e	y_3	y_e	K_3	K_e
$T = 325.00$°K (51.85°C)		$P_3° = 1\,782.3$ kPa (258.5 lb/in.²abs)			$P_e° = 32.34$ kPa (4.69 lb/in.²abs)		
1 439.6	208.8	0.628	0.372	0.979	0.021	1.559	0.0564
1 195.5	173.4	0.412	0.588	0.964	0.036	2.340	0.0612
997.0	144.6	0.283	0.717	0.955	0.045	3.374	0.0628
569.5	82.6	0.105	0.895	0.921	0.079	8.771	0.0883
$T = 350.00$°K (76.85°C)		$P_3° = 2\,950.3$ kPa (427.9 lb/in.² abs)			$P_e° = 95.56$ kPa (13.86 lb/in.²abs)		
2 064.3	299.4	0.582	0.418	0.948	0.052	1.629	0.124
1 628.5	236.2	0.374	0.626	0.926	0.074	2.476	0.118
1 372.1	199.0	0.278	0.722	0.917	0.083	3.299	0.115
841.2	122.0	0.139	0.861	0.868	0.132	6.245	0.153
$T = 375.00$°K (101.85°C)		$P_3°$ = supercritical			$P_e° = 238.9$ kPa (34.65 lb/in.²abs)		
3 088.2	447.9	0.614	0.386	0.919	0.081	1.497	0.210
2 503.5	363.1	0.435	0.565	0.887	0.113	2.039	0.200
1 965.0	285.0	0.293	0.607	0.852	0.148	2.908	0.244
1 130.0	163.9	0.118	0.882	0.760	0.240	6.441	0.272
$T = 400.00$°K (126.85°C)		$P_3°$ = supercritical			$P_e° = 522.2$ kPa (75.74 lb/in.²abs)		
4 685.0	679.5	0.702	0.298	0.859	0.141	1.224	0.473
3 633.5	527.0	0.451	0.549	0.816	0.184	1.809	0.335
2 990.2	433.7	0.336	0.664	0.778	0.222	2.315	0.334
1 654.7	240.0	0.132	0.868	0.631	0.369	4.780	0.425
$T = 425.00$°K (151.85°C)		$P_3°$ = supercritical			$P_e° = 1\,025.2$ kPa (148.7 lb/in.²abs)		
5 618.5	814.9	0.648	0.352	0.727	0.273	1.122	0.776
4 768.4	691.6	0.447	0.553	0.713	0.287	1.595	0.519
2 487.6	360.8	0.161	0.839	0.504	0.496	3.130	0.591

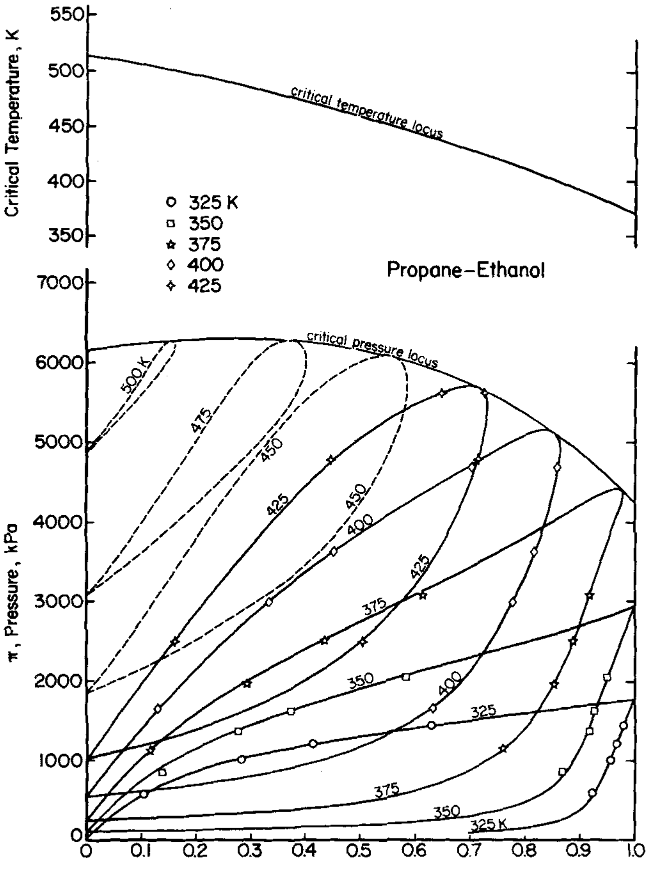

Fig. 3. Isothermal relationships for bubble point-dew point behavior of the propane-ethanol system.

pressure locus of the system. The single point at 425°K and 5 618.5 kPa (814.9 lb/in.²abs) has permitted a good estimation of the critical pressure and composition corresponding to this temperature of 425°K. This critical point at 425°K was established to be $P_c = 5\,681.3$ kPa (824 lb/in.²abs) at $n_3 = 0.716$ mole fraction. This single value, in conjunction with the critical state behavior of propane and ethanol, provided the necessary information to permit the establishment of the critical temperature and critical pressure profiles of this binary system. In this connection, the method outlined by Ekiner and Thodos (1965, 1966) has been applied to produce the critical state behavior of this system as follows:

$$T_c = T_c' + n_3\,n_e\,(66.29 + 3.358\,n_3) \tag{3}$$

and

$$P_c = P_c' + n_3\,n_e\,(2\,757.9 + 2\,220.1\,n_3) \tag{4}$$

where T_c' and P_c' are the corresponding pseudocritical values. From Equations (3) and (4), the critical temperature and the critical pressure profiles presented in Figure 3 were calculated. Once these limiting state relationships were produced, it became possible to establish the critical state values corresponding to 375° and 400°K. The information obtained for the complete isotherms of this study, included between 325° and 425°K, was then cross plotted to produce isobaric temperature-composition relationships. Pressure-temperature relationships corresponding to constant vapor and constant liquid compositions were then obtained from these isobaric relationships and expressed as log π vs. $1/T$. This cross-plotting approach enabled the establishment of the isotherms at 450°, 475°, and 500°K, presented as dotted lines in Figure 3. The bubble point-dew point relationships of this figure describe the complete vapor-liquid equilibrium behavior of the propane-ethanol system between 325° and 513.92°K, the critical temperature of ethanol.

TABLE 2. VAPOR-LIQUID EQUILIBRIUM COMPOSITIONS AND K CONSTANTS FROM SMOOTHED RELATIONSHIPS OF THE PROPANE-ETHANOL SYSTEM

Pressure		Liquid, mole fraction		Vapor, mole fraction		Equilibrium constant	
kPa	lb/in.^{2}abs	x_3	x_e	y_3	y_e	K_3	K_e
$T = 325.00°K$ (51.85°C)							
32.34	4.69	0.000	1.000	0.000	1.000	—	1.000
137.9	20	0.015	0.985	0.776	0.224	51.7	0.227
275.8	40	0.0435	0.9565	0.883	0.117	20.3	0.122
413.7	60	0.072	0.928	0.914	0.086	12.7	0.093
551.6	80	0.104	0.896	0.926	0.074	8.90	0.083
689.5	100	0.143	0.857	0.937	0.063	6.55	0.074
827.4	120	0.193	0.807	0.946	0.054	4.90	0.067
965.3	140	0.260	0.740	0.952	0.048	3.662	0.065
1 103.2	160	0.340	0.660	0.960	0.040	2.824	0.061
1 241.1	180	0.450	0.550	0.969	0.031	2.153	0.056
1 379.0	200	0.565	0.435	0.976	0.024	1.727	0.055
1 516.8	220	0.715	0.285	0.982	0.018	1.373	0.063
1 654.3	240	0.850	0.150	0.991	0.009	1.166	0.060
1 782.3	258.5	1.000	0.000	1.000	0.000	1.000	—
$T = 350.00°K$ (76.85°C)							
95.56	13.86	0.000	1.000	0.000	1.000	—	1.000
344.7	50	0.035	0.965	0.740	0.260	21.1	0.269
689.5	100	0.093	0.907	0.856	0.144	9.20	0.159
1 034.2	150	0.169	0.831	0.892	0.108	5.28	0.130
1 379.0	200	0.282	0.718	0.917	0.083	3.258	0.116
1 723.7	250	0.415	0.585	0.932	0.068	2.246	0.116
2 068.4	300	0.582	0.418	0.950	0.050	1.632	0.120
2 413.2	350	0.760	0.240	0.969	0.031	1.275	0.129
2 757.9	400	0.925	0.075	0.990	0.010	1.070	0.133
2 950.3	427.9	1.000	0.000	1.000	0.000	1.000	—
$T = 375.00°K$ (101.85°C)							
238.9	34.65	0.000	1.000	0.000	1.000	—	1.000
689.5	100	0.056	0.944	0.638	0.362	11.39	0.383
1 378.9	200	0.161	0.839	0.800	0.200	4.969	0.238
2 068.4	300	0.308	0.692	0.860	0.140	2.792	0.202
2 757.9	400	0.502	0.498	0.901	0.099	1.795	0.199
3 447.4	500	0.700	0.300	0.937	0.063	1.339	0.210
3 792.1	550	0.800	0.200	0.952	0.048	1.190	0.240
4 136.8	600	0.882	0.118	0.968	0.032	1.098	0.271
4 405.7	639	0.976	0.024	0.976	0.024	1.000	1.000
$T = 400.00°K$ (126.85°C)							
522.2	75.74	0.000	1.000	0.000	1.000	—	1.000
689.5	100	0.019	0.981	0.205	0.795	10.79	0.810
1 378.9	200	0.100	0.900	0.570	0.430	5.700	0.478
2 068.4	300	0.191	0.809	0.695	0.305	3.639	0.377
2 757.9	400	0.295	0.705	0.760	0.240	2.576	0.340
3 447.4	500	0.415	0.585	0.808	0.192	1.947	0.328
4 136.8	600	0.560	0.440	0.841	0.159	1.502	0.361
4 481.6	650	0.645	0.355	0.855	0.145	1.326	0.408
4 826.3	700	0.729	0.271	0.861	0.139	1.181	0.513
5 115.9	742	0.854	0.146	0.854	0.146	1.000	1.000

(Continued on opposite page)

Equilibrium compositions for the liquid and vapor states for each isotherm were obtained from an enlarged plot of Figure 3 for a series of pressures ranging from the vapor pressure of ethanol to the corresponding vapor pressure of propane for subcritical temperatures or to the critical state for temperatures exceeding $T_c = 369.975°K$, the critical temperature of propane. This information is presented in Table 2 and was used to establish the K values of propane and ethanol also shown in this table. These K values have been plotted against pressure to produce the isothermal relationships presented in Figure 4. The relationships for ethanol appear to follow a conventional behavior characteristic of the heavy component of a binary system; however, the corresponding relationships for propane exhibit a curvature that increases with temperature. At 325°K, the relationship for propane in Figure 4 exhibits a trend that becomes more nonlinear with increasing pressure. With increasing temperature, these propane relationships continue to be nonlinear and progressively exhibit this trend to extend at infinite dilution. This pattern of behavior is more so accentuated for the propane isotherms at 450°, 475°, and 500°K which become essentially independent of pressure in the proximity of the infinite dilution point. This mode of behavior for these isotherms might be the result of interaction between propane and the polar compound ethanol, or it might follow from any possible inaccuracies associated with establishment of these extrapolated isotherms. The resolution of their behavior at these elevated temperatures deserves a further study capable of producing accurate experimental measurements for this system at these elevated temperatures which approach the vicinity of the critical temperature of ethanol. The be-

Table 2 (Continued)

Pressure		Liquid, mole fraction		Vapor, mole fraction		Equilibrium constant	
kPa	lb/in.^{2}abs	x_3	x_e	y_3	y_e	K_3	K_e
$T = 425.00$°K (151.85°C)							
1 025.2	148.7	0.000	1.000	0.000	1.000	—	1.000
1 378.9	200	0.040	0.960	0.202	0.798	5.050	0.831
2 068.4	300	0.115	0.885	0.419	0.581	3.643	0.656
2 757.9	400	0.192	0.808	0.543	0.457	2.828	0.566
3 447.4	500	0.270	0.730	0.625	0.375	2.315	0.514
4 136.8	600	0.358	0.642	0.680	0.320	1.899	0.498
4 826.3	700	0.460	0.540	0.717	0.283	1.559	0.524
5 171.1	750	0.529	0.471	0.728	0.272	1.376	0.577
5 518.8	800	0.612	0.388	0.730	0.270	1.193	0.696
5 681.3	824	0.716	0.284	0.716	0.284	1.000	1.000
$T = 450.00$°K (176.85°C)							
1 834.0	266.0	0.000	1.000	0.000	1.000	—	1.000
2 068.4	300	0.030	0.970	0.080	0.920	2.667	0.948
2 757.9	400	0.101	0.899	0.255	0.745	2.525	0.829
3 447.4	500	0.168	0.832	0.400	0.600	2.381	0.721
4 136.8	600	0.237	0.763	0.490	0.510	2.068	0.668
4 826.3	700	0.312	0.688	0.548	0.452	1.756	0.657
5 171.1	750	0.352	0.648	0.569	0.431	1.616	0.665
5 515.8	800	0.400	0.600	0.582	0.418	1.455	0.697
5 860.5	850	0.460	0.540	0.582	0.418	1.265	0.774
6 067.4	880	0.558	0.442	0.558	0.442	1.000	1.000
$T = 475.00$°K (201.85°C)							
3 075.1	446.0	0.000	1.000	0.000	1.000	—	1.000
3 447.4	500	0.045	0.955	0.071	0.929	1.578	0.973
4 136.8	600	0.119	0.881	0.189	0.811	1.588	0.921
4 826.3	700	0.181	0.819	0.290	0.710	1.602	0.867
5 171.1	750	0.219	0.781	0.338	0.662	1.543	0.848
5 515.8	800	0.252	0.748	0.374	0.626	1.484	0.837
5 860.5	850	0.288	0.712	0.398	0.602	1.382	0.846
6 205.3	900	0.340	0.660	0.392	0.608	1.153	0.921
6 274.2	910	0.380	0.620	0.380	0.620	1.000	1.000
$T = 500.00$°K (226.85°C)							
4 853.9	704	0.000	1.000	0.000	1.000	—	1.000
5 171.1	750	0.037	0.963	0.047	0.953	1.270	0.990
5 515.8	800	0.072	0.928	0.091	0.909	1.264	0.980
5 860.5	850	0.109	0.891	0.131	0.869	1.202	0.975
6 205.3	900	0.140	0.860	0.161	0.839	1.150	0.976
6 274.2	910	0.158	0.842	0.158	0.842	1.000	1.000

havior of the ethanol relationships follows a normal pattern for all the isotherms included between 325° and 500°K. For 325° and 350°K, these subcritical isothermal relationships properly terminate at the point of infinite dilution for ethanol, while for the remaining isotherms the terminal point of these relationships becomes the critical point of the corresponding propane-ethanol mixtures.

COMPARISON OF RESULTS WITH EQUATION OF STATE APPROACH

An attempt has been made to compare K constants calculated from an equation of state approach, with corresponding values obtained from the experimental measurements of this study. In this connection, the Benedict, Webb, Rubin equation of state (1951) and also the modification of Soave (1972) of the Redlich-Kwong equation of state (1949) have been applied to this study. In this context, the BWR constants needed in these calculations were obtained from the literature for propane (Das and Eubank, 1973) and ethanol (Gómez-Nieto and Thodos, 1976). For the SRK method, the following values were used:

	a atm (l/mole)^2	b l/mole	m dimensionless
Propane	9.378	0.062611	0.71183
Ethanol	12.527	0.060209	1.38204

These methods have been applied to establish corresponding calculated K values using the fugacity coefficient approach. This approach utilizes the relationship

$$K_i = \frac{\varphi_i^l}{\varphi_i^v} \tag{5}$$

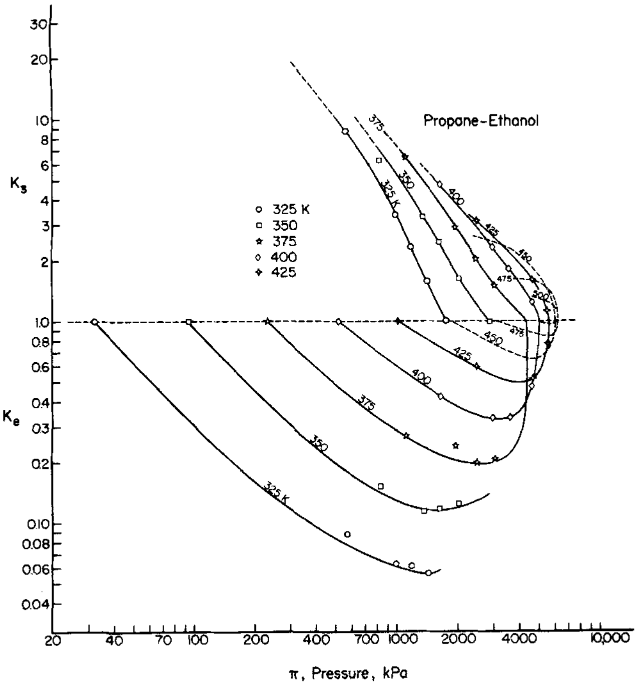

Fig. 4. Isothermal relationships of K constants vs. pressure for the propane-ethanol system.

where $\varphi_i^l = \bar{f}_i^l/x_i$ and $\varphi_i^v = \bar{f}_i^v/y_i$. From the appropriate equations of state, K constants were calculated using, for their corresponding mixing rules, the experimental vapor and liquid compositions of this study. The resulting calculated K values were then compared with corresponding values obtained from the experimental measurements. In general, the agreement between these comparisons was fair for both methods. The BWR method failed to converge for one point and yielded for the eighteen remaining points an average deviation of 6.94% for propane and 28.9% for ethanol. The SRK method accounted for all nineteen points, yielding corresponding deviations of 14.2% for propane and 10.7% for ethanol.

Both methods are known to produce relatively small deviations for mixtures of hydrocarbons, and these somewhat more significant departures may be attributed to the interaction encountered between propane and ethanol or mixing rules for polar-nonpolar mixtures that are not available to these methods of calculation.

ACKNOWLEDGMENT

The authors are grateful to R. A. Findlay of the Phillips Petroleum Company for making available the propane used in these experimental studies.

NOTATION

a, b = Soave-Redlich-Kwong parameters
$\bar{f}_i$ = fugacity of component i in mixture, kPa
K = vapor-liquid equilibrium constant, y/x
m = Soave parameter
n = mole fraction
P = pressure, kPa
P_c = critical pressure, kPa
P_c' = pseudocritical pressure of mixture, kPa
P_R = reduced pressure, P/P_c
r = direct transducer response
t = temperature of transducer, °C
T = temperature, °K
T_c = critical temperature, °K
T_c' = pseudocritical temperature, °K
T_R = reduced temperature, T/T_c
x = liquid composition, mole fraction
y = vapor composition, mole fraction
φ_i = fugacity coefficient, $\bar{f}_i/n_i$

LITERATURE CITED

Ambrose, D., C. H. S. Sprake, and R. Townsend, "Thermodynamic Properties of Organic Compounds: The Vapour Pressure of Acetone," *J. Chem. Thermodynamics*, **6**, 693 (1974).

Benedict, M., G. B. Webb, and L. C. Rubin, "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures, Fugacities and Vapor-Liquid Equilibria," *Chem. Eng. Progr.*, **47**, 449 (1951).

Cherry Jr., R. H., "Azeotropic Behavior in the Critical Region: The System Acetone-n-Pentane," Ph.D. dissertation, The Ohio State Univ., Columbus (1967).

Das, T. R., and P. T. Eubank, "Thermodynamic Properties of Propane: The Vapor-Liquid Coexisting Curve," *Adv. Cryog. Eng.*, **18**, 208 (1973).

Dingrani, J. G., and G. Thodos, "Vapor-Liquid Equilibrium Behavior of the Ethane-n-Butane—n-Hexane System," *Can. J. Chem. Eng.*, to be published.

Ekiner, O., and G. Thodos, "Interaction Model for Critical Temperatures of Multicomponent Mixtures of Methane-Free Aliphatic Hydrocarbons," *AIChE J.*, **11**, 897 (1965).

————, "Interaction Model for Critical Pressures of Multicomponent Methane-Free Aliphatic Hydrocarbon Mixtures," *Chem. Eng. Sci.*, **21**, 353 (1966).

Gómez-Nieto, M., "High Pressure Vapor-Liquid Equilibria: The Propane-Ethanol Acetone System," Ph.D. dissertation, Northwestern Univ., Evanston, Il. (1977).

———, and G. Thodos, "A New Vapor Pressure Equation and Its Application to Normal Alkanes," *Ind. Eng. Chem. Fundamentals*, **16**, 254 (1977*a*).

————, "Benedict-Webb-Rubin Parameters for Ethanol," *Can. J. Chem. Eng.*, **54**, 438 (1976).

————, "Generalized Treatment for the Vapor Pressure Behavior of Polar and Hydrogen Bonding Compounds," *ibid.*, **55**, 445 (1977*b*).

Katz, D. L., and K. H. Hachmuth, "Vaporization Equilibrium Constants in a Crude-Oil—Natural-Gas System," *Ind. Eng. Chem.*, **29**, 1072 (1937).

Kay, W. B., "Liquid-Vapor Phase Equilibrium Relations in the Ethane—n-Heptane System," *ibid.*, **30**, 459 (1938).

———, "Liquid-Vapor Equilibrium Relations in Binary Systems: The Ethane—n-Butane System," *ibid.*, **32**, 353 (1940).

———, "Liquid-Vapor Equilibrium Relations in Binary Systems: n-Butane—n-Heptane System," *ibid.*, **33**, 590 (1941).

Kretschmer, C. B., and R. Wiebe, "The Solubility of Propane and the Butanes in Ethanol," *J. Am. Chem. Soc.*, **73**, 3778 (1951).

McCracken, P. G., T. S. Storvick, and J. M. Smith, "Phase Behavior From Enthalpy Measurements Benzene-Ethyl Alcohol and n-Pentane-Ethyl Alcohol Systems," *J. Chem. Eng. Data*, **5**, 130 (1960).

McNair, H. M., and E. J. Bonnelli, *Basic Gas Chromatography*, Consolidated Printers, Berkeley, Calif. (1969).

Nagahama, K., S. Suda, T. Hakuta, and M. Hirata, "Determination of Vapor-Liquid Equilibrium from Total Pressure Measurement: C_3-Hydrocarbon∼Solvent," *Sekiyu Gakkai Shi*, **14**, 252 (1971).

Price, A. R., and R. Kobayashi, "Low Temperature Vapor-Liquid Equilibrium in Light Hydrocarbon Mixtures: Methane-Ethane-Propane System," *J. Chem. Eng. Data*, **4**, 40 (1959).

Redlich, O., and J. N. S. Kwong, "On the Thermodynamics of Solutions. V. An Equation of State. Fugacities of Gaseous Solutions," *Chem. Rev.*, **44**, 233 (1949).

Sage, B. H., W. N. Lacey, and J. G. Schaafsma, "Phase Equilibria in Hydrocarbon Systems: Methane-Propane System," *Ind. Eng. Chem.*, **26**, 214 (1934).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Manuscript received August 11, 1977; revision received February 1, and accepted February 22, 1978.