Vapor–Liquid Equilibria in the Ternary System Methyl Alcohol–Ethyl Alcohol–Isopropyl Alcohol at Atmospheric Pressure

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Vapor–liquid equilibrium data for the ternary system MeOH–EtOH–*i*-PrOH were determined at atmospheric pressure in an Ellis and Froome equilibrium still. Activity coefficients were calculated by assuming nonidealities in the vapor and liquid phases. The results showed the existence of slight nonidealities among alcohols. The thermodynamic consistency of the data was considered by the McDermott and Ellis test. The ternary results were predicted satisfactorily by the use of the Wilson model.

Introduction

During an efficiency study of distillation of binary and multicomponent primary alcohol systems, experimental data for the system MeOH–EtOH–*i*-PrOH were not found in the available literature. These vapor–liquid equilibria data are important in the design and operation of separation equipment. In the absence of these data, the use of the exact thermodynamic relations to predict vapor–liquid equilibrium data requires a correlating equation which describes the nonidealities of the liquid phase and an equation of state to describe the nonidealities in the vapor phase. Numerous equations are presented in the literature to describe the nonidealities (*1–3*), but for the liquid phase most of these equations require parameters which are evaluated from a consistent set of vapor–liquid equilibrium data. An example is the use of binary sets in the Wilson equation for miscible multicomponent systems. The objective of this study was to obtain a fairly complete set of equilibrium data for the system MeOH–EtOH–*i*-PrOH at atmospheric pressure and to use these data as a check on the predictions of the Wilson model which is used in the efficiency study.

Experimental Section

Purity of Materials. The materials used for the experiments were purchased from Fisons Ltd. and were used without further purification after gas-chromatographic analysis failed to show any significant impurities. The results showed that the purities were better than (99.9%). The results of the chromatographic analysis are shown in Table I. Some physical quantities determined for the material were also compared with values from the literature as shown in Table I.

Apparatus and Procedure. The experimental equilibrium data were measured by using the original Ellis and Froome (*6*) apparatus which has been described previously in detail. The recommended procedure and operation of the apparatus described by Ellis and Froome were followed closely. Equilibrium temperatures were measured by using a sensitive thermometer with an accuracy of ±0.05 °C. The analysis of the liquid and condensed vapor was carried out by using a gas chromatograph provided with thermal conductivity detector. The current supplied to the detector was 100 mA. The column was 290 cm long supplied ready packed with Porapak Q and was operated isothermally at 175 °C and 3-bar column pressure. The injector and detector temperatures were 190 and 175 °C, respectively. Helium was used as the carrier gas. Calibration analysis was carried out with 28 samples of known compositions; two to three injections for each sample were made, peak heights for each component being measured. Methyl alcohol was selected as the base component, the ratios of m_i/m_s and h_i/h_s were found, and finally a least-squares method was adopted to find the best correlating equations. The ratio of the areas and peak heights has been shown to work equally well (*7–9*). With this method the sample measurements were accurate to better than 0.45 mol %.

Results

The experimental equilibrium data for the ternary system are presented in Table II. For the small variation in the atmospheric pressure, ±10 mmHg, the Clapeyron equation was used to give a close approximation of the effect of pressure on the boiling point

$$\Delta T = KT_b\Delta P \tag{1}$$

Hala (*2*) and Weissberger (*10*) recommended a value of 0.000 10 for K in the case of alcohols. Delzenne (*11*) measured vapor–liquid equilibrium data in the system MeOH–EtOH–H_2O and used a value of 0.000 12 for K. In this work the relatively recent values of dP/dT at the normal boiling point measured by Ambrose and Sprake (*5*) for all the alcohols were used. The estimated value of K for each alcohol was found to be approximately equal to 0.000 10, agreeing well with Hala and Weissberger, and so this value has been used in eq 1.

The corrected temperatures are shown in Table II. The equilibrium vapor–liquid compositions are shown in Figure 1. The activity coefficient values were calculated from the experimental vapor–liquid equilibrium data by using the following thermodynamic formula:

$$\gamma_i = \frac{y_iP}{x_iP_i^\circ}\,\frac{\phi_i}{\phi_i^\circ\exp[V_i^L(P-P_i^\circ)/RT]} \tag{2}$$

The vapor-phase fugacity coefficients are obtained by the virial equation truncated after the second term.

$$\ln\phi_i = \frac{2}{V_i}\sum_{j=1}^{C} y_jB_{ij} - \ln Z \tag{3}$$

The compressibility factor and the molar volume of the vapor mixture are related by

$$Z = 1 + \frac{\sum_{i=1}^{C}\sum_{j=1}^{C} y_iy_jB_{ij}}{V} \tag{4}$$

For the second virial coefficients B_{ij}, the correlation of Tsonopoulos (*12*) was used. The Antoine equation was used to represent the vapor pressure data of pure components.

$$\log P_i^\circ = \alpha_i - \beta_i/(T+\delta_i) \tag{5}$$

The constants used were those determined by Boublik (*13*) and based on the measured data of Ambrose and Sprake (*5*). (See Table III.)

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Table I. Physical Properties of Pure Materials

		$d^{20}{}_4{}^a$		refractive index at 20 °C		bp at 760 mmHg, °C	
component	purity, wt %	exptl	lit.^{b}	exptl	lit.^{b}	exptl	lit.
MeOH	99.92	0.7942	0.791 31	1.329	1.328 40	64.77	64.70 (*4*) 64.55 (*5*)
EtOH	99.94	0.7892	0.789 39	1.361	1.361 43	78.30	78.29 (*4*) 78.29 (*5*)
i-PrOH	99.91	0.7839	0.785 47	1.377	1.377 20	82.45	82.26 (*4*) 82.24 (*5*)

^{a} Specific gravity. ^{b} Reference *4*.

Table II. Vapor–Liquid Equilibria in the Ternary System MeOH–EtOH–*i*-PrOH at Atmospheric Pressure^a

expt	P, mmHg	T, °C	T_n, °C	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
1	760.10	68.20	68.20	0.7467	0.0967	0.8851	0.0444	1.0139	0.6695	0.7792
2	760.10	69.00	69.00	0.6897	0.1030	0.8401	0.0540	1.0116	0.7399	0.8546
3	760.00	70.00	70.00	0.6251	0.1072	0.7898	0.0616	1.0116	0.7788	0.8902
4	758.80	70.55	70.60	0.5912	0.1070	0.7586	0.0625	1.0051	0.7728	0.9270
5	751.50	69.25	69.55	0.5846	0.2918	0.7362	0.2056	1.0231	0.9705	0.7679
6	751.50	70.65	70.95	0.5369	0.3356	0.6811	0.2539	0.9794	0.9850	0.7840
7	758.80	71.55	71.60	0.5366	0.1243	0.7027	0.0856	0.9893	0.8754	0.9364
8	758.30	72.45	72.50	0.4973	0.1193	0.6666	0.0874	0.9803	0.8985	0.9272
9	770.00	72.15	71.80	0.4914	0.3191	0.6466	0.2461	0.9886	0.9745	0.8440
10	764.10	71.45	71.25	0.4770	0.4078	0.6300	0.3128	1.0123	0.9907	0.7572
11	751.50	71.15	71.45	0.4765	0.2968	0.6380	0.2285	1.0151	0.9825	0.8869
12	758.30	72.85	72.90	0.4761	0.0986	0.6521	0.0688	0.9867	0.8417	0.9320
13	762.20	73.60	73.52	0.4554	0.0772	0.6261	0.0535	0.9701	0.8171	0.9507
14	770.00	73.35	73.00	0.4330	0.3244	0.5871	0.2627	0.9757	0.9757	0.8782
15	764.10	72.45	72.30	0.4322	0.4285	0.5794	0.3399	0.9882	0.9814	0.8447
16	762.20	74.05	73.97	0.4161	0.0396	0.5916	0.0211	0.9875	0.6172	0.9688
17	751.50	72.90	73.20	0.3990	0.2860	0.5511	0.2388	0.9834	0.9942	0.9345
18	763.20	73.20	73.09	0.3846	0.4449	0.5331	0.3642	0.9936	0.9820	0.8505
19	767.10	73.45	73.20	0.3822	0.4969	0.5230	0.4083	0.9795	0.9842	0.8011
20	767.00	73.50	73.25	0.3769	0.4606	0.5216	0.3839	0.9835	0.9905	0.8131
21	760.20	73.60	73.60	0.3383	0.5486	0.4724	0.4593	0.9818	0.9832	0.8340
22	769.60	75.00	74.67	0.3371	0.3464	0.4895	0.2940	0.9854	0.9585	0.9070
23	763.50	74.60	74.48	0.3131	0.4381	0.4560	0.3772	0.9936	0.9780	0.8944
24	769.90	74.95	74.60	0.3119	0.4856	0.4471	0.4167	0.9745	0.9710	0.8936
25	757.90	76.15	76.22	0.2605	0.2734	0.3996	0.2500	0.9833	0.9697	0.9338
26	763.50	75.70	75.58	0.2525	0.4404	0.3894	0.3921	1.0120	0.9690	0.9081
27	769.90	76.40	76.05	0.2310	0.5018	0.3523	0.4530	0.9852	0.9655	0.9131
28	760.20	75.30	75.30	0.2300	0.6391	0.3491	0.5662	1.0049	0.9736	0.8340
29	770.00	77.00	76.65	0.2299	0.3509	0.3583	0.3242	0.9862	0.9659	0.9269
30	770.10	77.65	77.30	0.1999	0.2782	0.3223	0.2635	0.9957	0.9640	0.9446
31	769.50	77.20	76.85	0.1989	0.4342	0.3220	0.3983	1.0169	0.9513	0.9252
32	760.20	76.15	76.15	0.1775	0.6434	0.2830	0.5854	1.0245	0.9675	0.9152
33	769.50	78.05	77.70	0.1532	0.4323	0.2611	0.4118	1.0401	0.9570	0.9266
34	758.10	76.05	76.12	0.1480	0.5956	0.2452	0.5594	1.0658	0.9999	0.9503
35	760.10	78.40	78.40	0.1367	0.2825	0.2321	0.2761	1.0091	0.9535	0.9646
36	757.90	76.85	76.90	0.1346	0.6466	0.2277	0.6075	1.0582	0.9699	0.9097
37	761.90	79.90	79.87	0.1239	0.0157	0.2255	0.0171	1.0302	1.0071	0.9484
38	769.50	78.20	77.87	0.1172	0.5101	0.2110	0.4918	1.0923	0.9623	0.9300
39	760.20	77.25	77.25	0.1020	0.7239	0.1767	0.6901	1.0713	0.9717	0.9120
40	769.50	79.05	78.71	0.1000	0.4127	0.1798	0.4085	1.0598	0.9569	0.9532
41	761.90	79.30	79.23	0.0837	0.2656	0.1538	0.2757	1.0618	0.9817	0.9671
42	761.90	78.85	78.78	0.0828	0.3837	0.1534	0.3894	1.0868	0.9759	0.9616
43	758.10	76.90	76.97	0.0823	0.6899	0.1462	0.6804	1.1090	1.0157	0.9166
44	760.20	77.45	77.45	0.0635	0.7799	0.1102	0.7751	1.0659	1.0053	0.8661
45	759.30	79.65	79.68	0.0558	0.2446	0.1143	0.2844	1.1652	1.0808	0.9310

^{a} P is the barometric pressure, T the boiling temperature at this pressure, T_n the boiling temperature at 760.00 mmHg, x_i the liquid-phase mole fraction, y_i the vapor-phase mole fraction, and γ_i the activity coefficient.

Table III. Constants of the Antoine Equation

component	α	β	δ
MeOH	8.080 97	1582.271	239.726
EtOH	8.112 2	1592.866	226.184
i-PrOH	7.740 21	1359.517	197.527

Liquid molar volumes at three different temperatures were correlated by using a quadratic equation for purposes of interpolation. Liquid molar volume data, critical constants, and other physicochemical quantitites were available (*4*, *14*–*16*).

Experimental ternary isotherms are shown in Figure 2. The end points of each isotherm were located by using the binary data of Delzenne for the system methyl alcohol–ethyl alcohol and those of Van Winkle (*17*) for the systems methyl alcohol–isopropyl alcohol and ethyl alcohol–isopropyl alcohol.

The experimental results indicate that slight nonidealities exist in this ternary system, especially in the regions of low concentration.

The thermodynamic consistency of the data was tested by the McDermott and Ellis (*18*) method. The method examines the experimental data points in pairs by using the equation

$$D = \sum_{i=1}^{c} (x_{ic} + x_{id})(\log \gamma_{id} - \log \gamma_{ic}) \qquad (6)$$

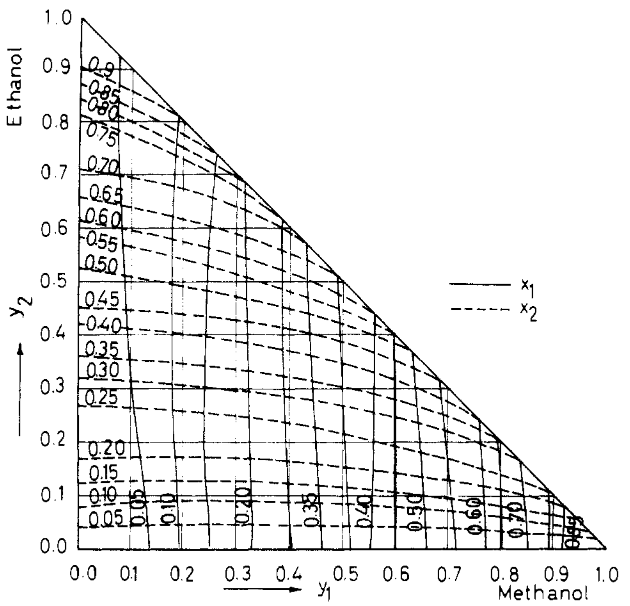

Figure 1. Ternary x-y: (—) x_1, (---) x_2.

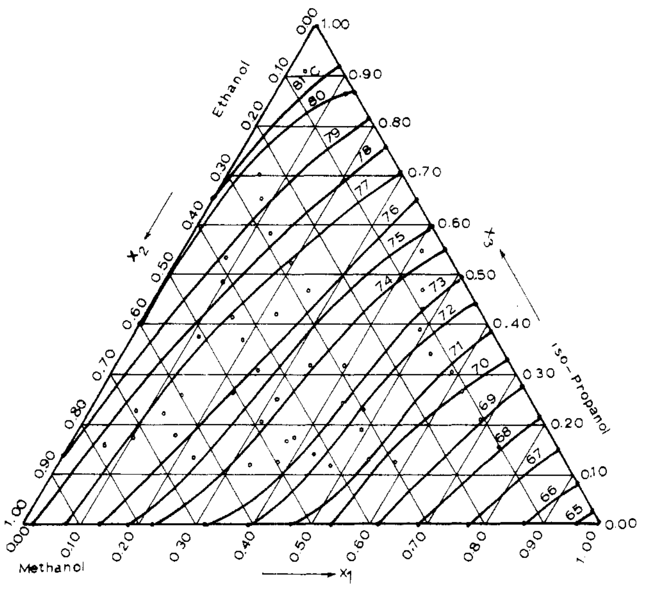

Figure 2. Ternary isotherms.

by which two experimental points c and d are consistent if the absolute value of D lies between 0.0 and 0.01. The tests have been applied widely in the literature even for isobaric data with the absence of heat of mixing data. In fact, McDermott and Ellis stated that the test has been applied for isobaric data along isotherms and between experimental results that had a temperature difference of less than 3 °C. In this work, the test applied in such a way that the boiling point differences between the two points were kept as small as possible. The mole fractions were kept as close to each other as possible to minimize the error in the numerical integration. All the data points satisfied the test except experimental runs 1, 2, 16, 37, and 45 which had a deviation of D much greater than 0.01. These five points were considered to be thermodynamically inconsistent and other points are likely to be consistent.

Prediction of Results. For the purpose of our efficiency studies in distillation, the results of this ternary system were used as a check on the prediction of the Wilson model from binary data. The Wilson model requires a consistent set of binary data. The data of Delzenne for the system MeOH–EtOH and the data of Ballard and Van Winkle for the system MeOH–*i*-PrOH and EtOH–*i*-PrOH were used. These data were shown

Table IV. Wilson Parameters and the Mean Deviation in the Vapor Mole Fraction and the Bubble Point Temperature, $\Delta y = \sum |y_{\text{calcd}} - y_{\text{exptl}}|/(\text{Data Points})$ and $\Delta T = \sum |T_{\text{calcd}} - T_{\text{exptl}}|/(\text{Data Points})$

system	parameters of Wilson eq		Δy	ΔT
MeOH-EtOH	326.951	−284.643	0.0049	0.26
MeOH-*i*-PrOH	449.545	−537.986	0.0044	0.20
EtOH-*i*-PrOH	389.690	−417.677	0.0051	0.22

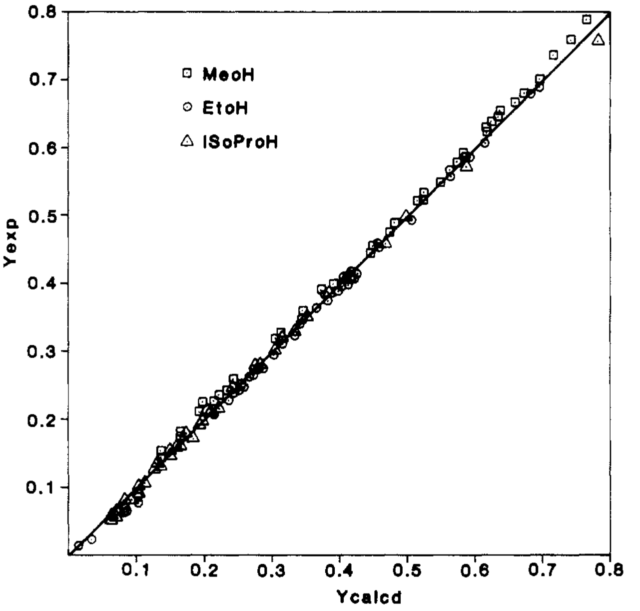

Figure 3. Comparison of experimental vapor compositions with values predicted by the Wilson equation.

to be consistent by Gmehling (*1*).

The Wilson parameters were determined by a nonlinear least-squares method coupled with the use of the Q fraction as an objective function. The method is described in detail by Hirata et al. (*19*). The method was implemented with a computer program to minimize the following objective function:

$$F = \sum_{i=1}^{N} (Q_{\text{exptl}} - Q_{\text{calcd}})_i^2 \quad (7)$$

where

$$Q_{\text{exptl}} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (8)$$

and

$$Q_{\text{calcd}} = -x_1 \ln (x_1 + \Lambda_{12}x_2) - x_2 \ln (\Lambda_{21}x_1 + x_2) \quad (9)$$

where N is the number of data points.

The activity coefficients were calculated by using eq 2. The final results of the parameters for each set of binary data are shown in Table IV. These parameters were found to predict the vapor composition and the bubble point temperature with a good degree of accuracy for each binary system. Table IV shows the mean deviation in the vapor mole fraction and the bubble point temperature. For the ternary system, comparisons between the experimental and predicted vapor composition for each component are shown in Figure 3. A good agreement was obtained. The mean deviation in the vapor mole fraction is 0.0071 and in the bubble point temperature is 0.44 K.

Glossary

B_{ij}	second virial coefficient, cal/mol
C	number of components
D	deviation of pair of points c and d
h_0	height of the peak
K	constant defined by eq 1
m	weight, g
N	number of data points
P_i	vapor pressure of pure component, atm
P	total pressure, atm
Q	defined by eq 8
R	gas constant, 1.987 cal/(mol K)
T	temperature, K
V	molar vapor volume of the mixture mL/mol
V_i	molar vapor volume of component i, mL/mol
V_i^L	molar liquid volume of pure component i, mL/mol
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
Z	compressibility
Λ_{ij}	parameters in Wilson equation
γ_i	liquid-phase activity coefficient of component i
ϕ_i	vapor-phase fugacity coefficient of component i
ϕ_i°	vapor-phase fugacity coefficient of pure saturated component i at P_i° and system temperature
a_i, β_i, δ_i	constants in eq 5

Subscripts

b	boiling point
c, d	pair of data points
i	component i
j	component j
l	data point
s	base component

Registry No. MeOH, 67-56-1; EtOH, 64-17-5; *i*-PrOH, 67-63-0.

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Kinetics and Equilibrium Data of the Dehydration–Hydration Reaction between Diacetone Alcohol and Mesityl Oxide in Phosphoric Acid

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The velocities of dehydration of diacetone alcohol and hydration of mesityl oxide were studied in regions of 8.6–85.2% phosphoric acid. Because the reactions are acid-catalyzed, the reaction velocities in both directions were increased as the acid concentration increased. The reaction kinetics fit the reversible first-order model with respect to the concentration of reactants, including the activity of water. These results are consistent with the mechanisms proposed by a previous investigator in which the rate-determining step is addition or removal of protons. Equilibrium constants were derived from solution composition and specific rate constants which agreed with each other. The equilibrium constant did not change with acid concentration in the dilute range, but increased slightly at higher acid concentrations. The reaction velocities and the equilibrium constants increased with increasing temperature, and the activation energies were 18.8 and 12.7 kcal/mol for the dehydration and hydration reactions, respectively.

The condensation of acetone in strong acid produces mesityl oxide through the dehydration of diacetone alcohol (*1–3*). The dehydration kinetics have been investigated in the presence of catalysts such as ion-exchange resins (*4*), polymers (*5*, *6*), and dimethyl sulfoxide (*7*). The velocity of the reverse reaction, hydration, also has been investigated in different acids of modest concentration (*8*, *9*).

A recent study in this laboratory of the purification of wet-process phosphoric acid with acetone extraction (*10*) showed that small amounts of mesityl oxide were formed in removing the acetone from the purified acid by distillation at atmospheric pressure. The amount of mesityl oxide present was affected by the concentration of the acid and the temperature of the reaction.

During the analysis for mesityl oxide by gas chromatography, it also was found that the mesityl oxide was unstable in H_3PO_4 solution and gradually changed to another compound which had a different boiling point and gave a different peak in the gas chromatogram. This new peak position corresponds to that of diacetone alcohol, and the new compound was positively