Isothermal Vapor–Liquid Equilibria for the Ternary Ethanol–Acetonitrile–Chloroform System

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Vapor–liquid equilibrium data for the ethanol–acetonitrile–chloroform system were measured at 40 °C by using a vapor-recirculating equilibrium still. The experimental data were well correlated by the extended UNIQUAC equation with binary parameters alone.

Isothermal vapor–liquid equilibrium data for the three ternary systems containing ethanol have been reported from this laboratory (*1–3*). This work presents similar measurements for the system ethanol–acetonitrile–chloroform at 40 °C and compares the experimental results with those calculated by the extended UNIQUAC equation (*4*). Vapor–liquid equilibrium data for the three binary systems constituting the present ternary system are available in the literature: for ethanol–acetonitrile at 40 °C (*5*); for ethanol–chloroform at 35 °C (*6*); for acetonitrile–chloroform at 40 °C (*7*).

Experimental Section

All chemicals were purchased from Wako Pure Chemical Industries, Ltd. Guaranteed reagent grade acetonitrile was directly used. Chloroform (guaranteed reagent grade) was washed with concentrated sulfuric acid, diluted sodium hydroxide, and distilled water, and then dried over calcined sodium carbonate and distilled through a 1-m packed column in an atmosphere of nitrogen. C.P. ethanol was fractionally distilled after drying over calcium oxide. Densities, measured with an Anton Paar DMA40 densimeter, and vapor pressures of these compounds are compared with literature values as shown in Table I (*6, 8–10*). The still used is a Boublik vapor-recirculating one described previously (*3*).

Liquid and condensed vapor sample compositions were analyzed by a Shimadzu (GC-7A) gas chromatograph connected to an electronic integrator (Shimadzu Chromatopac C-E1B). The errors of the measured variables were 0.002 mole fraction for composition, 13.3 Pa for pressure, and 0.05 K for temperature.

Results and Correlations

Table II gives experimental vapor–liquid equilibrium results, activity coefficients γ, and fugacity coefficients ϕ calculated from the relations

$$\gamma_i = P\phi_i y_i/\{P_i^s\phi_i^s x_i \exp[v_i^L(P - P_i^s)/RT]\} \qquad (1)$$

$$\ln \phi_i = (P/RT)(2\sum_j y_j B_{ij} - \sum_i\sum_j y_i y_j B_{ij}) \qquad (2)$$

where the pure-liquid molar volumes v_i^L were calculated from the modified Rackett equation (*11*) and the second virial coefficients B_{ij} estimated from the method of Hayden and O'Connell (*12*). The values of v_i^L and B_{ij} are reported in Table II.

Table I. Densities and Vapor Pressures of Compounds

compd	density at 25 °C, g cm^{-3} this work	density at 25 °C, g cm^{-3} lit. (*8*)	vapor press. at 40 °C, kPa this work	vapor press. at 40 °C, kPa lit.
ethanol	0.7852	0.78504	17.879	17.905 (*9*)
acetonitrile	0.7766	0.7766	22.678	22.678 (*10*)
chloroform	1.4796	1.47988	48.023	48.023 (*6*)

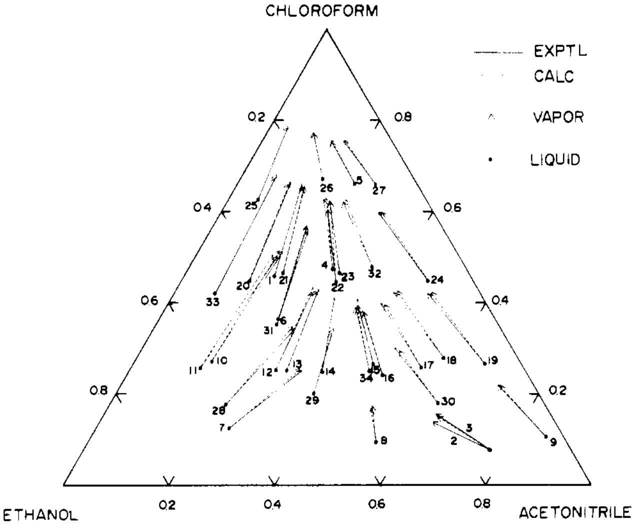

Figure 1. Equilibrium tie lines.

The ternary vapor–liquid equilibrium results were correlated with the extended UNIQUAC equation (*4*). The equation gives the activity coefficient of compound *i* in a multicomponent mixture by

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + 1 - \frac{\Phi_i}{x_i} - \frac{Z}{2}q_i\left[\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i}\right] - q_i^* \ln (\sum_j \theta_j \tau_{ji}) + q_i\sum_j \left(\frac{q_j^*}{q_j}\right)\theta_j - q_i\sum_j \frac{(q_j^*/q_j)\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \qquad (3)$$

where Z is the coordination number set as 10, and the segment fraction Φ, the area fraction θ, and adjustable parameters τ_{ij} related to energy parameters a_{ij} are given by

$$\Phi_i = r_i x_i/\sum_j r_j x_j \qquad (4)$$

$$\theta_i = q_i x_i/\sum_j q_j x_j \qquad (5)$$

$$\tau_{ij} = \exp(-a_{ij}/T) \qquad (6)$$

The pure-component molecular structural constants are as follows: for ethanol, $r = 2.11$, $q = 1.97$, $q^* = 0.92$; for acetonitrile, $r = 1.87$, $q = 1.72$, $q^* = q^{0.2}$; and for chloroform, $r = 2.70$, $q = 2.34$, $q^* = q^{0.2}$ (*4, 13*).

Table II. Vapor–Liquid Equilibrium Data for the Ethanol (1)–Acetonitrile (2)–Chloroform (3) System at 40 °C[a]

point	x_1	x_2	x_3	y_1	y_2	y_3	P, kPa	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.369	0.172	0.459	0.218	0.122	0.660	41.037	1.354	1.234	1.233	0.987	0.921	0.984
2	0.159	0.761	0.080	0.231	0.630	0.139	28.558	2.329	1.031	1.039	0.993	0.947	0.985
3	0.154	0.767	0.079	0.217	0.628	0.155	28.931	2.289	1.033	1.188	0.993	0.946	0.985
4	0.255	0.277	0.468	0.193	0.180	0.627	40.343	1.707	1.114	1.129	0.989	0.922	0.984
5	0.117	0.221	0.662	0.115	0.128	0.757	43.143	2.375	1.053	1.029	0.991	0.915	0.983
6	0.411	0.225	0.364	0.252	0.177	0.571	39.250	1.344	1.316	1.287	0.987	0.926	0.985
7	0.628	0.251	0.121	0.421	0.326	0.253	30.398	1.138	1.719	1.334	0.987	0.946	0.988
8	0.362	0.544	0.094	0.340	0.500	0.160	30.691	1.612	1.227	1.094	0.989	0.944	0.986
9	0.035	0.862	0.103	0.068	0.713	0.219	27.864	3.054	1.006	1.240	0.998	0.948	0.985
10	0.584	0.144	0.272	0.325	0.158	0.517	36.304	1.127	1.710	1.446	0.986	0.932	0.987
11	0.613	0.131	0.256	0.343	0.155	0.502	35.504	1.108	1.807	1.459	0.986	0.934	0.987
12	0.472	0.276	0.252	0.316	0.260	0.424	35.490	1.327	1.438	1.250	0.987	0.934	0.986
13	0.452	0.297	0.251	0.302	0.270	0.428	35.170	1.313	1.376	1.256	0.988	0.935	0.986
14	0.383	0.367	0.250	0.281	0.309	0.410	35.544	1.458	1.287	1.220	0.989	0.934	0.985
15	0.282	0.458	0.260	0.245	0.361	0.394	35.170	1.710	1.193	1.115	0.990	0.934	0.985
16	0.277	0.482	0.241	0.244	0.374	0.382	34.677	1.710	1.159	1.150	0.990	0.935	0.985
17	0.194	0.549	0.257	0.201	0.401	0.398	34.704	2.016	1.091	1.124	0.992	0.935	0.985
18	0.141	0.582	0.277	0.164	0.412	0.424	34.744	2.269	1.058	1.112	0.993	0.984	0.985
19	0.070	0.665	0.265	0.102	0.478	0.420	33.024	2.709	1.025	1.095	0.995	0.937	0.985
20	0.425	0.130	0.445	0.241	0.100	0.659	41.437	1.310	1.351	1.282	0.986	0.920	0.984
21	0.353	0.184	0.463	0.220	0.130	0.650	41.677	1.450	1.247	1.222	0.987	0.920	0.984
22	0.260	0.297	0.443	0.198	0.201	0.601	40.010	1.704	1.151	1.134	0.989	0.923	0.984
23	0.244	0.292	0.464	0.187	0.192	0.621	40.770	1.748	1.138	1.140	0.989	0.922	0.984
24	0.087	0.464	0.449	0.104	0.299	0.597	38.117	2.560	1.048	1.059	0.994	0.926	0.984
25	0.320	0.055	0.625	0.185	0.033	0.782	46.103	1.486	1.159	1.203	0.986	0.910	0.982
26	0.174	0.157	0.669	0.139	0.086	0.775	45.356	2.025	1.042	1.096	0.989	0.911	0.982
27	0.079	0.262	0.659	0.092	0.152	0.756	42.983	2.807	1.051	1.029	0.992	0.915	0.983
28	0.609	0.219	0.172	0.388	0.268	0.344	32.637	1.160	1.730	1.369	0.987	0.941	0.988
29	0.427	0.373	0.200	0.326	0.343	0.331	33.651	1.436	1.337	1.166	0.988	0.938	0.986
30	0.201	0.621	0.178	0.224	0.477	0.299	32.717	2.044	1.087	1.150	0.992	0.939	0.985
31	0.418	0.228	0.354	0.259	0.187	0.554	38.570	1.334	1.350	1.262	0.988	0.927	0.985
32	0.176	0.345	0.479	0.159	0.218	0.623	40.157	2.032	1.078	1.091	0.991	0.923	0.984
33	0.504	0.078	0.418	0.252	0.065	0.683	41.570	1.158	1.468	1.420	0.986	0.920	0.984
34	0.296	0.457	0.247	0.252	0.359	0.389	34.171	1.629	1.157	1.126	0.990	0.936	0.985

[a] $B_{11} = -1650$ cm^3 mol^{-1}; $B_{22} = -5016$ cm^3 mol^{-1}; $B_{33} = -1043$ cm^3 mol^{-1}; $B_{12} = -2527$ cm^3 mol^{-1}; $B_{13} = -719$ cm^3 mol^{-1}; $B_{23} = -3322$ cm^3 mol^{-1}; $\upsilon_1{}^L = 59$ cm^3 mol^{-1}; $\upsilon_2{}^L = 53$ cm^3 mol^{-1}; $\upsilon_3{}^L = 82$ cm^3 mol^{-1}.

Table III. Binary Parameters and Root-Mean Square (RMS) Deviations

			RMS deviations					
	temp, °C	no. of data points	ΔP, kPa	ΔT, K	compn, mol %		parameters, K	
					Δx	Δy	a_{12}	a_{21}
ethanol (1)–acetonitrile (2)	40	14	0.1267	0.02	0.05	0.43	286.07	171.03
ethanol (1)–chloroform (2)	35	15	0.3613	0.06	0.26	0.93	-62.53	769.73
acetonitrile (1)–chloroform (2)	40	6	0.1373	0.03	0.02		176.91	-47.95

Table IV. Ternary Calculated Results for the System Ethanol (1)-Acetonitrile (2)-Chloroform (3) at 40 °C

	Δy_1[a]	Δy_2[a]	Δy_3[a]	ΔP, kPa	$\Delta P/P$, %
mean deviation	0.52	0.32	0.43	0.3434	0.90
RMS deviation	0.59	0.40	0.58	0.4614	1.17

[a] In mol %.

Binary parameter estimation for the three binary systems which compose the ternary system was performed by using a computer program, based on the maximum likelihood principle, as developed by Prausnitz et al. (*13*). Standard deviations for the measured variables were 0.133 kPa for pressure, 0.05 K for temperature, 0.001 for liquid mole fraction, and 0.003 for vapor mole fraction. Table III reports the interaction energy parameters and the root-mean-square deviations between the calculated values and the corresponding experimental values obtained in binary vapor–liquid equilibrium data reduction. These binary parameters were used to calculate the ternary vapor–liquid equilibria of the system and good agreement is obtained between the calculated and measured variables as shown in Table IV.

Figure 1 shows the tie lines connecting the liquid and vapor mole fractions, demonstrating that there is no ternary azeotrope.

Glossary

a_{ij}	extended UNIQUAC binary interaction energy parameter related to τ_{ij}
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular geometric area parameter for pure component i
q_i^*	correction factor of interaction for pure component i
r_i	molecular geometric volume parameter for pure component i
R	universal gas constant
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid mole fraction of component i
y_i	vapor mole fraction of component i
Z	lattice coordination number, here equal to 10

Greek Letters

γ_i	activity coefficient of component i
θ_i	area fraction of component i
τ_{ij}	extended UNIQUAC binary parameter
ϕ_i	fugacity coefficient of component i at P and T
ϕ_i^s	fugacity coefficient of pure component i at P_i^s and T

Φ_i segment fraction of component i

Registry No. Ethanol, 64-17-5; acetonitrile, 75-05-8; chloroform, 67-66-3.

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Excess Volumes for 2-Methyl-2-propanol + Water at 5 K Intervals from 303.15 to 323.15 K

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Excess volumes of mixtures of 2-methyl-2-propanol (x_a) + water (x_w) have been measured at 5 K intervals from 303.15 to 323.15 K by using a dilution dilatometer. The partial molar excess volume of 2-methyl-2-propanol at infinite dilution in water is extremely temperature-dependent, becoming more negative as the temperature increases. The partial molar excess volume of 2-methyl-2-propanol in dilute solutions with water is very concentration-dependent and the dependence reduces as temperature increases. At $x_a = 0.019$, the partial excess volume of 2-methyl-2-propanol is independent of temperature, having a value of -9.83 cm^3 mol^{-1}, while the excess volume is independent of temperature at $x_a = 0.039$, having a value of -0.0376 cm^3 mol^{-1} over the temperature range measured. These unusual observations are explained in terms of the variation of the temperature of maximum density and hydrophobic interaction for dilute 2-methyl-2-propanol solutions.

Introduction

Volumetric properties of mixtures of alcohols with water have been investigated by numerous researchers. The nonideal behavior of these mixtures has been discussed on the basis of MacMillan-Mayer theory (*1*), scaled-particle theory (*2*), and the cosphere-solvation concept of Gurney (*3*, *4*).

2-Methyl-2-propanol is of particular interest since it is completely miscible in water, although other C_4 alcohol isomers are only partially miscible. Kenttamaa and co-workers (*5*) measured the densities of 2-methyl-2-propanol + water with an Oswald pycnometer from 288.15 to 323.15 K and reported the partial molar volumes covering the majority of the mole fraction range. Density measurements of 2-methyl-2-propanol + water were made by Nakanishi et al. (*6*) at 298.15 K with an accuracy of $\pm 1 \times 10^{-5}$ g cm^{-3} and the excess volumes were calculated over the whole composition range.

Frank and Smith (*7*) used a float technique to measure the densities of solution up to the molal concentration of 0.1 (x_a = 0.018) at 273.65, 278.15, 298.15, and 313.15 K with a precision of $\pm 1 \times 10^{-6}$ g cm^{-3}. They discussed various methods of extrapolating density results to obtain the partial molar volume at infinite dilution, V_a^∞, and suggested that, as x_a approaches zero, $(\partial V_a/\partial x_a)$ should approach zero rather than have the temperature-dependent finite slope usually observed. Hvidt et al. (*8*) measured the densities of 2-methyl-2-propanol + water up to $x_a = 0.4$ between 278.15 and 298.15 K with an accuracy of $\pm 1 \times 10^{-5}$ g cm^{-3}. They argued that the unusual apparent molar volumes at infinite dilution of alcohol were determined not only by an overlapping of hydrophobic cospheres but also by a shift in mobile equilibria between different structures in the water near the nonpolar groups. Jolicoeur et al. (*9*) measured densities of alcohol isomers using a flow densimeter and discussed the effect of alcohols on the structure of water. The variation of nonpolar group size and geometry of alcohols was not conclusively attributed to specific effects in the hydration of the alkyl groups.

Precise measurements of excess volumes over the whole composition range are necessary to understand the nature of interactions between nonpolar groups and water, the so-called hydrophobic solvation. However, there have been no direct measurements of the excess volumes of 2-methyl-2-propanol + water covering the whole composition range. Furthermore, there are insufficient measurements at high alcohol concentrations over a wide temperaure range. Such data are required for custody transfer of 2-methyl-2-propanol.

The curve fitting for excess volume is important to estimate the density of mixtures. Marsh et al. (*10*) have tried to fit their excess volume data of ethanol + water mixtures to the skewed Redlich-Kister function, equation 1, with standard deviations close to experimental error, but they failed. They found that

$$V_m^E/(\text{cm}^3\ \text{mol}^{-1}) = x_a x_w \left(\frac{\sum_{i=0}^{n} a_i (1 - 2x_a)^i}{(1 + q(1 - 2x_a))} \right) \quad (1)$$

eq 1 does not adequately describe excess volumes of alcohol + water systems due to the steep curvatures in the dilute alcohol region. Davis (*11*) proposed a four-segmented-composition model which has two water-rich regions, a microheterogeneous region, and an alcohol-rich region. The four-segmented-composition model improves the standard deviation in fitting but has discontinuities of its derivatives between segments.

We have measured the excess volumes over the whole composition range at 5 K intervals from 303.15 to 323.15 K and have determined parameters of the switching function whose superiority has been demonstrated in curve fitting excess en-

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