K_3	association constant for open-chain trimer formation of alcohol
K	association constant for open-chain i-mer formation of alcohol, $i > 3$
K_{cy}	association constant for cyclization of open i-mer as defined by θ/i, $i > 4$
$K_{A,B}$	solvation constant for complex formation between alcohol i-mer and acetonitrile
$K_{A_iB_j}$	solvation constant for complex formation between alcohol i-mer and acetonitrile j-mer ($j > 1$)
$K_{A,C}$	solvation constant for complex formation between alcohol i-mer and benzene
K_B'	association constant for head-to-head dimerization of acetonitrile
K_B	association constant for head-to-tail chain association of acetonitrile
K_{BC}	solvation constant for complex formation between acetonitrile and benzene
R	universal gas constant
T	absolute temperature
x_I	mole fraction of component I

Greek Letters

α_{IJ}	nonrandomness parameter of NRTL equation
Δ_{123}	function defined by eq 4
θ	constant related to K_{cy}
τ_{IJ}	$(g_{IJ} - g_{JJ})/T$

Subscripts

chem	chemical
phys	physical
I, J, i, j	component

Registry No. 1-Propanol, 71-23-8; 2-propanol, 67-63-0; acetonitrile, 75-05-8; benzene, 71-43-2.

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Vapor–Liquid Equilibrium of Mixtures Formed by Methanol, 2-Propanol, and Chlorobenzene

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Isothermal vapor–liquid equilibrium data at 55 °C are presented for the binary system 2-propanol–chlorobenzene and the ternary system methanol–2-propanol–chlorobenzene. The experimental results are well correlated with the UNIQUAC associated-solution theory with binary parameters obtained from the maximum likelihood principle.

Introduction

The number of papers on vapor–liquid equilibrium (VLE) of ternary mixtures containing two alcohols is small. This work reports isothermal VLE at 55 °C for the methanol–2-propanol–chlorobenzene and 2-propanol–chlorobenzene systems. VLE at 55 °C for two of the binary systems of the ternary system have already been published in the literature: methanol–2-propanol (*1*) and methanol–chlorobenzene (*2*).

Experimental Section

All chemicals were purchased from Wako Pure Chemical Industries Ltd. Spectrograde methanol and special grade 2-propanol and chlorobenzene were used as received. Gas chromatographic analysis did not show any appreciable impurities in the compounds used.

A Boublik vapor–liquid recirculation still was used to obtain VLE data for the binary and ternary systems. The apparatus and operational procedure are the same as described previously (*3*). The compositions of liquid samples of the two phases in equilibrium were analyzed by combining the use of a Shimadzu GC-7A gas chromatograph and an electronic integrator (Shimadzu Chromatopac C-E1B). The measured quantities were considered to have the following experimental errors: 0.002 for mole fraction, 21.3 Pa for pressure, and 0.05 K for temperature.

Table I. Properties Used in Data Analysis

1	methanol (1)–2-propanol (2)	methanol (1)–chlorobenzene (3)	2-propanol (2)–chlorobenzene (3)
P_i^s, kPa	68.301	68.301	30.597
P_j^s, kPa	30.597	7.159	7.159
v_i^L, cm^3/mol	41	41	81
v_j^L, cm^3/mol	81	104	104
B_{ii}, cm^3/mol	−1437	−1437	−1510
B_{jj}, cm^3/mol	−1510	−2248	−2248
B_{ij}, cm^3/mol	−1506	−662	−1112
r_i	1.15	1.15	2.23
r_j	2.23	3.06	3.06
q_i	1.12	1.12	1.98
q_j	1.98	2.45	2.45

Experimental Results and Analysis of Results

Table I lists properties used in experimental data analysis. P^s is the vapor pressure of pure components, v^L is the pure-liquid molar volume calculated from the modified Rackett

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Table II. Vapor-Liquid Equilibrium Data for the System 2-Propanol (1)-Chlorobenzene (2) at 55 °C

x_1	y_1	P, kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.071	0.586	16.359	4.457	1.013	0.993	0.990
0.128	0.668	19.572	3.364	1.035	0.990	0.989
0.142	0.678	20.318	3.194	1.059	0.990	0.989
0.236	0.723	23.051	2.321	1.159	0.988	0.988
0.332	0.753	24.798	1.846	1.271	0.987	0.988
0.387	0.767	25.558	1.662	1.347	0.987	0.988
0.461	0.782	26.385	1.467	1.479	0.986	0.987
0.558	0.802	27.344	1.288	1.698	0.986	0.987
0.666	0.828	28.371	1.155	2.026	0.985	0.988
0.722	0.843	28.704	1.097	2.248	0.985	0.988
0.845	0.889	29.544	1.017	2.937	0.984	0.989
0.889	0.912	30.064	1.008	3.310	0.984	0.989
0.920	0.934	30.184	1.002	3.461	0.984	0.990

equation (*4*), B is the second virial coefficient estimated from the method Hayden and O'Connell (*5*), and r and q are the pure-component structural constants calculated by the method of Vera et al. (*6*). Tables II and III give experimental VLE data for binary and ternary mixtures. The thermodynamic consistency of the binary data was checked as described by Fredenslund et al. (*7*). Figure 1 shows the experimental results of the 2-propanol–chlorobenzene system.

The activity coefficient of component I was calculated by

$$\gamma_I = P\phi_I y_I / \{x_I P_I^s \phi_I^s \exp[v_I^L(P - P_I^s)/RT]\} \tag{1}$$

where the fugacity coefficients, ϕ_I at P and ϕ_I^s at P_I^s, were calculated from

$$\ln \phi_I = (P/RT)(2\sum_J y_J B_{IJ} - \sum_I \sum_J y_I y_J B_{IJ}) \tag{2}$$

The UNIQUAC associated-solution theory (*8*) has been modified to obtain improved prediction of VLE for ternary mixtures containing two alcohols and one active nonassociating component (*9*). The modified theory assumes that two alcohols, A and B, self-associate and solvate linearly to produce A_i, B_i, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, and $B_i(A_jB_k)_l$, where the indices i, j, k, and l go from one to infinity, and that resultant pure polymers and multisolvated copolymers react with active nonassociating component C to yield additional complexes A_iC, B_iC, $(A_iB_j)_kC$, $(B_iA_j)_kC$, $A_i(B_jA_k)_lC$, and $B_i(A_jB_k)_lC$. Then derived mass balance equations and the expression of the true molar volume of the ternary mixture are not the same as those described in the previous paper (*8*).

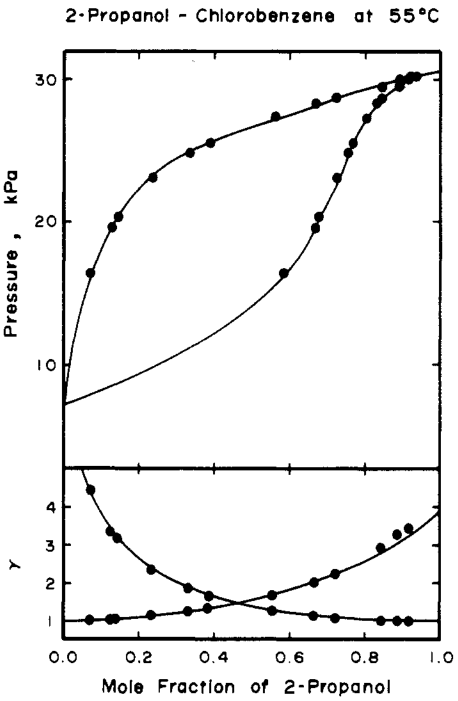

Figure 1. Vapor-liquid equilibrium results for 2-propanol–chlorobenzene at 55 °C: ●, experimental; —, calculated from the UNIQUAC associated-solution theory.

The UNIQUAC associated-solution theory gives the activity coefficient of any component I in the ternary methanol (A)–2-propanol (B)-chlorobenzene (C) system by

$$\ln \gamma_I = \ln\left(\frac{\Phi_{I_1}}{\Phi_{I_1}^0 x_I}\right) + r_I\left(\frac{1}{V^0} - \frac{1}{V}\right) + \left(\frac{Z}{2}\right) q_I\left[\ln\left(\frac{\theta_I}{\Phi_I}\right) - 1 + \frac{\Phi_I}{\theta_I}\right] + q_I\left[1 - \ln\left(\sum_J \theta_J \tau_{JI}\right) - \sum_J \frac{\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{3}$$

where for nonassociating component C, $\Phi_{C_1}^0 = 1$, Φ is the segment fraction, θ is the area fraction, τ_{JI} is an ajustable parameter, V is the true molar volume of the solution, and V_I^0

Table III. Vapor-Liquid Equilibrium Data for the System Methanol (1)-2-Propanol (2)-Chlorobenzene (3) at 55 °C

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	0.050	0.450	0.500	0.189	0.622	0.189	31.011	1.754	1.401	1.625	0.986	0.983	0.988
2	0.067	0.847	0.086	0.136	0.797	0.067	32.424	0.983	0.996	3.512	0.983	0.982	0.991
3	0.084	0.137	0.779	0.544	0.280	0.176	37.064	3.579	2.465	1.162	0.982	0.979	0.989
4	0.087	0.643	0.270	0.214	0.648	0.138	32.931	1.210	1.083	2.336	0.984	0.982	0.989
5	0.221	0.488	0.291	0.468	0.407	0.125	39.903	1.258	1.081	2.380	0.980	0.978	0.990
6	0.280	0.356	0.364	0.588	0.287	0.125	43.836	1.367	1.145	2.091	0.978	0.975	0.990
7	0.298	0.529	0.173	0.519	0.389	0.092	42.690	1.104	1.018	3.157	0.978	0.976	0.991
8	0.455	0.436	0.109	0.662	0.275	0.063	48.836	1.052	0.995	3.933	0.975	0.972	0.993
9	0.566	0.219	0.215	0.803	0.113	0.084	55.795	1.167	0.926	3.036	0.972	0.968	0.993
10	0.586	0.132	0.282	0.844	0.065	0.091	57.435	1.219	0.908	2.581	0.971	0.967	0.993
11	0.588	0.278	0.134	0.786	0.147	0.067	54.969	1.084	0.935	3.832	0.972	0.969	0.994
12	0.652	0.070	0.278	0.881	0.032	0.087	60.528	1.203	0.887	2.638	0.969	0.965	0.993
13	0.662	0.163	0.175	0.852	0.075	0.073	59.422	1.126	0.877	3.455	0.970	0.966	0.994
14	0.740	0.140	0.120	0.873	0.065	0.062	60.502	1.050	0.900	4.362	0.969	0.965	0.995
15	0.834	0.086	0.080	0.920	0.036	0.044	63.608	1.030	0.852	4.892	0.967	0.963	0.997

Table IV. Binary Results of Data Reduction at 55 °C

		root-mean-square dev							
				compn, mol %		parameters, K			
system	no. of data points	ΔP, kPa	ΔT, K	Δx	Δy	a_{AB}	a_{BA}	K_{AB}	h_{AB}, kJ/mol
methanol (A)–2-propanol (B)	20	0.2373	0.07	0.09	0.38	-87.96	208.01	70 (50 °C)	-23.2
methanol (A)–chlorobenzene (B)	13	0.2013	0.06	0.16	0.33	-45.75	139.71	2 (55 °C)	
2-propanol (A)–chlorobenzene (B)	12	0.1627	0.00	0.05	0.34	117.25	-35.22	1 (55 °C)	

is the value of V in pure liquid state. These variables are expressed as follows:

$$\Phi_I = r_I x_I / \sum_J r_J x_J \tag{4}$$

$$\theta_I = q_I x_I / \sum_J q_J x_J \tag{5}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{6}$$

$$\frac{1}{V} = \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right) \times \frac{r_A r_B K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)} + \frac{\Phi_{C_1}}{r_C}\left\{1 + r_C K_{AC} S_A + r_C K_{BC} S_B + \left[\left(\frac{1}{r_B K_{AB}} + S_A\right) K_{AC} + \left(\frac{1}{r_A K_{AB}} + S_B\right) K_{BC}\right] \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\right\} \tag{7}$$

$$\frac{1}{V_I^0} = (1 - K_I \phi_{I_1}^0)/r_I \tag{8}$$

where $\bar{S}_A$, S_A, $\bar{S}_B$, and S_B are defined by

$$\bar{S}_A = \Phi_{A_1}/(1 - K_A \Phi_{A_1})^2 \tag{9}$$

$$S_A = \Phi_{A_1}/(1 - K_A \Phi_{A_1}) \tag{10}$$

$$\bar{S}_B = \Phi_{B_1}/(1 - K_B \Phi_{B_1})^2 \tag{11}$$

$$S_B = \Phi_{B_1}/(1 - K_B \Phi_{B_1}) \tag{12}$$

The monomer segment fractions, Φ_{A_1}, Φ_{B_1}, and Φ_{C_1}, are simultaneously solved from the following mass balance equations by using subroutine NOLBR built in a FACOM M-170 F computer.

$$\Phi_A = (1 + r_A K_{AC} \Phi_{C_1}) \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \{2 + r_B K_{AB} S_A (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A K_{AB} S_B + \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{AC} S_A (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB} K_{BC} S_B]\} \tag{13}$$

$$\Phi_B = (1 + r_A K_{BC} \Phi_{C_1}) \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \{2 + r_A K_{AB} S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_B K_{AB} S_A + \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{BC} S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB} K_{AC} S_A]\} \tag{14}$$

$$\Phi_C = \Phi_{C_1}\left\{1 + r_C K_{AC} \bar{S}_A + r_C K_{BC} \bar{S}_B + \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\left[\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B\right]\right\} \tag{15}$$

At pure alcohol state the segment fraction of monomeric component I, $\Phi_{I_1}^0$, is expressed by

$$\Phi_{I_1}^0 = [2K_I + 1 - (1 + 4K_I)^{1/2}]/2K_I^2 \tag{16}$$

The association constants of pure alcohols at 50 °C were taken from Brandani (*10*): 173.9 for methanol and 49.1 for 2-propanol. The enthalpy of a hydrogen bond was set as −23.2 kJ mol^{-1}, which is the enthalpy of dilution of ethanol in *n*-hexane at 25 °C (*11*). This value was assumed to be independent of temperature and the degree of association and fixes the temperature dependence of the equilibrium constants. The methanol–2-propanol system exhibits slightly positive deviations from an ideal solution and the two other systems exhibit moderate positive deviations. The computer program used for binary parameter estimation, based on the maximum likelihood principle, is similar to that described by Prausnitz et al. (*12*). The standard deviations of the measured variables were the same as those used by Prausnitz et al.: $\sigma_P = 0.133$ kPa for pressure; $\sigma_T = 0.05$ K for temperature; $\sigma_x = 0.001$ for liquid-phase mole fraction; $\sigma_y = 0.003$ for vapor-phase mole fraction. Table IV gives the binary results of the VLE data reduction, and those for the methanol–chlorobenzene system were taken from the previous paper (*8*). Table V lists predicted ternary results. Figure 2 shows the calculated and experimental tie lines, indicating that the agreement is acceptable and the system does not include a ternary azeotrope. The values of the solvation constant and energy parameters for the methanol–2-propanol system were used to predict ternary liquid–liquid equilibria for the methanol–2-propanol–*n*-hexane and methanol–2-propanol–cyclohexane systems with good accuracy (*9*).

Table V. Ternary Calculated Results for the System Methanol (1)–2-Propanol (2)–Chlorobenzene (3) at 55 °C

	vapor compn, mol %			pressure	
	Δy_1	Δy_2	Δy_3	ΔP, kPa	$\Delta P/P$, %
mean dev	0.61	0.52	0.44	0.5881	1.44
root-mean-square dev	0.70	0.62	0.56	0.9193	2.47

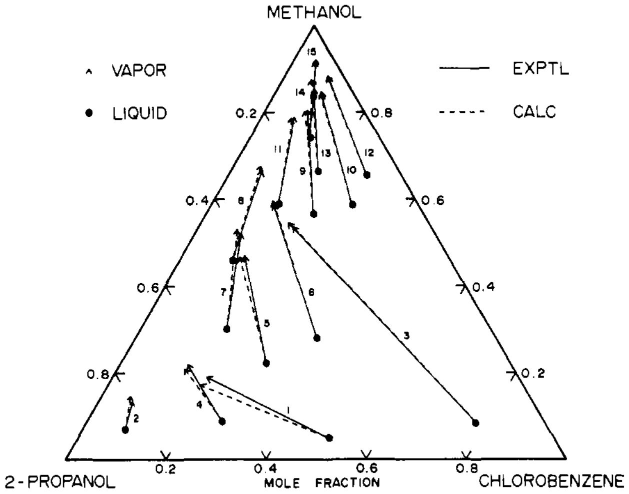

Figure 2. Equilibrium tie lines.

Glossary

A, B, C	methanol, 2-propanol, and chlorobenzene
a_{IJ}, a_{JI}	binary interaction parameters
B_{II}, B_{IJ}	pure and cross second virial coefficients
I, J	components
i, j, k, l	i-, j-, k-, and l-mers of alcohols
K_A, K_B, K_I	association constants of alcohols
K_{AB}, K_{AC}, K_{BC}	solvation constants between unlike molecules
P	total pressure
P_I^s	saturated vapor pressure of pure-component I
q	pure-component area parameter
R	gas constant
r	pure-component volume parameter
T	absolute temperature

V	true molar volume of alcohol solution
V_I^0	true molar volume of pure liquid
v_I^L	molar volume of pure liquid I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	coordination number equal to 10

Greek Letters

γ_I	liquid-phase activity coefficient of component I
θ_I	area fraction of component I
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid and vapor mole fractions
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
$\Phi_{I_1}^0$	monomer segment fraction of component I at pure alcohol reference state
ϕ_I	vapor-phase fugacity coefficient of component I
ϕ_I^s	vapor-phase fugacity coefficient of pure component I at its saturation pressure P_I^s and system temperature T

Registry No. Methanol, 67-56-1; 2-propanol, 67-63-0; chlorobenzene, 108-90-7.

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Osmotic and Activity Coefficients of Tris Sulfate from Isopiestic Vapor Pressure Measurements at 25 °C

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The gravimetric isopiestic technique, with reference standards of NaCl, has been used to determine the osmotic and activity coefficients of Tris sulfate, $(TH)_2SO_4$, where TH represents the protonated form of the base 2-amino-2-(hydroxymethyl)-1,3-propanediol, in the molality range from 0.2 to 6 mol kg^{-1} at 25 °C. The parameters of the Pitzer equation and the Rush-Johnson equation were determined from the results. Tris sulfate was found to be a strong electrolyte, with activity coefficients similar to those of the alkali sulfates.

Introduction

Tris(hydroxymethyl)aminomethane (2-amino-2-(hydroxymethyl)-1,3-propanediol, THAM, or Tris) is useful both as an acidimetric standard (*1*) and as the basis for buffer systems in the physiological pH region (*2*). A solid base, easily purified, it has also been applied extensively, along with its protonated form, to study salt effects and solvent effects on the dissociation of cationic acids (see, for example, ref *3-6*). Despite evidence of anomalous liquid-junction potentials under certain conditions (*7*), Tris buffers may be useful as standards near pH 8 (*8*, *9*).

Because the buffer range (approximately from pH 7 to pH 9 (*10*, *11*)) includes the pH of natural seawater, Tris buffers are also well suited as standards for pH in seawater (*11-13*). Nevertheless, the assignment of reference pH values, based on either an activity or molality scale, may be rendered uncertain by unforeseen interactions between the buffer substances and constituents of the seawater solvent. The synthetic seawater used as a vehicle for the standard buffer contains Na^+, K^+, Mg^{2+}, and Ca^{2+} cations along with Cl^- and SO_4^{2-} anions. A strong interaction between Tris and sulfate, for example, leading possibly to slightly dissociated ion pairs $(TH{\cdot}SO_4)^-$ would alter both the ionic strength and the buffer ratio.

For this reason, we have determined the stoichiometric activity coefficients and osmotic coefficients of Tris sulfate in aqueous solution. The gravimetric isopiestic vapor pressure method was used, with solutions of NaCl as standards. The results demonstrate that $(TH)_2SO_4$ is a strong electrolyte, with activity coefficients comparable with those of Na_2SO_4, K_2SO_4, and $(NH_4)_2SO_4$.

Experimental Section

Tris sulfate was prepared by neutralizing Tris ("Trizma Base" from Sigma Chemical Co., St. Louis, MO 63178) with AnalaR sulfuric acid, diluted to about 1 M and standardized by weight titration. Tris was purified by crystallization and was dried under vacuum, as described earlier (*14*). Stoichiometric amounts of solid Tris and the stock solution of H_2SO_4 were mixed to produce a solution of $(TH)_2SO_4$ of precisely known concentration. The molality of this solution was about 1.2 mol kg^{-1}.

The reference solutions for the isopiestic measurements were prepared from twice recrystallized reagent-grade NaCl. Stock solutions were standardized gravimerically for chloride content.

The gravimetric isopiestic equipment has been described elsewhere (*15*). Solutions were contained in gold-plated silver cups placed on a slab of gold-plated copper 2.5 cm thick inside a vacuum desiccator which was rocked gently in a water bath maintained at 25 ± 0.01 °C. Equilibration times varied from 2 days to 4 weeks, being longest for the most dilute solutions.

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