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Liquid–Liquid Equilibria for the Systems Acetonitrile–Benzene–Cyclohexane, Acetonitrile–Toluene–Cyclohexane, and Methanol–Ethanol–Cyclohexane

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Ternary liquid–liquid equilibrium data have been measured for the systems acetonitrile–benzene–cyclohexane and acetonitrile–toluene–cyclohexane at 298.15 and 318.15 K and for the system methanol–ethanol–cyclohexane at 298.15 K. The results have been analyzed by using the extended UNIQUAC and UNIQUAC equations with only binary parameters. The ability of the extended UNIQUAC equation in predicting ternary vapor–liquid equilibria from binary data is compared with that of the UNIQUAC equation.

Introduction

The existing equations for the excess Gibbs energy function are generally used to solve phase equilibrium problems and a considerable effort has been given to obtain suitable equations which correlate liquid compositions and activity coefficients. The prediction of ternary liquid–liquid equilibria from binary data is rather more difficult than that of ternary vapor–liquid equilibria. The present work aims to compare the ability of two activity coefficient equations, the extended UNIQUAC equation and the UNIQUAC equation modified by Anderson and Prausnitz (*1*), to predict the ternary liquid–liquid equilibrium data of the three investigated systems and the ternary vapor–liquid equilibrium data of four typical systems taken from the literature by using binary data alone.

Experimental Section

Materials. Pure ethanol was obtained from the Japan Monopoly Corp. and other chemicals were purchased from Wakoh Chemical Co. Acetonitrile (guaranteed reagent grade), toluene, and methanol (spectrograde) were used directly. Benzene (guaranteed reagent grade) was subjected to recrystallization 3 times. Cyclohexane (guaranteed reagent grade) was purified by fractional distillation from a 1-m column packed with McMahon packing. Ethanol was refluxed with calcium oxide and then fractionally distilled. Densities of substances were measured with an Anton Paar (DMA-40) densimeter at 298.15 K and are in excellent agreement with literature values (*2*).

Methods. Two separate methods were used to study liquid–liquid equilibria. The first one is to titrate binary mixtures of known composition with a third component to obtain the binodal curves. The onset of turbidity in the solution determined the end point. During titration, the sample solutions were maintained at a desired temperature within ±0.01 °C by using a water thermostat. The second one is to determine the liquid–liquid tie lines by ensuring equilibrium between two ternary liquid phases and then withdrawing portions of each sample liquid layer with a preheated hypodermic syringe. The sample liquids were analyzed with a Shimadzu (GC-4C) gas chromatograph connected to a Shimadzu (ITG-2A) digital integrator.

Results and Data Reduction

Tables I and II present solubility and tie-line data for the three systems. Two forms of the UNIQUAC equation are used to analyze the experimental data. We use the following modified form of the UNIQUAC equation for the excess Gibbs energy g^E called the extended UNIQAC:

Table I. Solubility Data

x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
Acetonitrile (1)–Benzene (2)–Cyclohexane (3) at 298.15 K							
0.0440	0.0000	0.1897	0.1926	0.5756	0.1841	0.7699	0.1018
0.0494	0.0307	0.2803	0.2091	0.6123	0.1725	0.8197	0.0724
0.0658	0.0640	0.3734	0.2070	0.6659	0.1544	0.8611	0.0453
0.0762	0.0758	0.4975	0.1993	0.7200	0.1288	0.9399	0.0000
0.1136	0.1409						
Acetonitrile (1)–Benzene (2)–Cyclohexane (3) at 318.15 K							
0.0935	0.0000	0.2965	0.1269	0.5163	0.1256	0.7531	0.0688
0.1051	0.0248	0.3360	0.1287	0.5453	0.1232	0.8065	0.0424
0.1365	0.0558	0.3773	0.1297	0.5919	0.1179	0.8644	0.0119
0.1855	0.0966	0.4334	0.1305	0.6425	0.1088	0.8883	0.0000
0.2268	0.1107	0.4737	0.1281	0.6927	0.0902		
Acetonitrile (1)–Toluene (2)–Cyclohexane (3) at 298.15 K							
0.0440	0.0000	0.1444	0.1488	0.5987	0.1676	0.8331	0.0588
0.0547	0.0158	0.1970	0.1825	0.6417	0.1519	0.8662	0.0395
0.0622	0.0514	0.2525	0.1969	0.6997	0.1301	0.9049	0.0125
0.0728	0.0739	0.3737	0.1993	0.7372	0.1129	0.9399	0.0000
0.1111	0.1186	0.4942	0.1838	0.7836	0.0911		
Acetonitrile (1)–Toluene (2)–Cyclohexane (3) at 318.15 K							
0.0935	0.0000	0.2265	0.1126	0.4721	0.1301	0.8176	0.0382
0.1148	0.0315	0.2667	0.1226	0.5536	0.1206	0.8408	0.0250
0.1242	0.0474	0.3278	0.1287	0.6315	0.1043	0.8586	0.0167
0.1393	0.0533	0.3973	0.1311	0.7071	0.0819	0.8741	0.0064
0.1960	0.0980	0.4321	0.1306	0.7761	0.0541	0.8883	0.0000
Methanol (1)–Ethanol (2)–Cyclohexane (3) at 298.15 K							
0.1250	0.0000	0.2592	0.0589	0.4646	0.1091	0.7046	0.0650
0.1345	0.0044	0.2862	0.0682	0.5303	0.1082	0.7475	0.0446
0.1515	0.0104	0.3127	0.0767	0.5687	0.1046	0.7798	0.0256
0.1706	0.0213	0.3544	0.0873	0.6296	0.0916	0.8181	0.0051
0.1939	0.0321	0.3953	0.0978	0.6586	0.0844	0.8287	0.0000
0.2259	0.0462						

$$g^E = g^E(\text{combinatorial}) + g^E(\text{residual}) \quad (1)$$

g^E(combinatorial) is given by the expression of Kikic et al. (*3*). g^E(residual) is different from the original UNIQUAC expression.

$$g^E(\text{combinatorial})/RT = \sum_i x_i \ln (\Phi'/x_i) + (Z/2)\sum_i x_i q_i \ln (\theta_i/\Phi_i) \quad (2)$$

$$g^E(\text{residual})/RT = -\sum q_i^* x_i \ln (\sum \theta_j \tau_{ji}) \quad (3)$$

where

$$\Phi_i' = r_i^{2/3} x_i / \sum_j r_j^{2/3} x_j$$

$$\Phi_i = r_i x_i / \sum_j r_j x_j$$

$$\theta_i = q_i x_i / \sum_j q_j x_j$$

$$\tau_{ij} = \exp(-\Delta u_{ij}/RT) = \exp(-a_{ij}/T)$$

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Table II. Tie-Line Data

phase I		phase II		phase I		phase II	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
Acetonitrile (1)–Benzene (2)–Cyclohexane (3) at 298.15 K							
0.8918	0.0226	0.0602	0.0362	0.7572	0.1082	0.1364	0.1478
0.8309	0.0646	0.0891	0.0973	0.6331	0.1623	0.2370	0.2007
0.8083	0.0774	0.1053	0.1126	0.5466	0.1862	0.3165	0.2080
Acetonitrile (1)–Benzene (2)–Cyclohexane (3) at 318.15 K							
0.8426	0.0263	0.1177	0.0384	0.7355	0.0766	0.2016	0.1030
0.8044	0.0453	0.1506	0.0661	0.6817	0.0943	0.2555	0.1176
0.7693	0.0616	0.1787	0.0845	0.6517	0.1032	0.2844	0.1242
Acetonitrile (1)–Toluene (2)–Cyclohexane (3) at 298.15 K							
0.9030	0.0125	0.0592	0.0278	0.7701	0.0959	0.1547	0.1570
0.8846	0.0264	0.0702	0.0550	0.7187	0.1247	0.2128	0.1928
0.8666	0.0399	0.0863	0.0783	0.6257	0.1567	0.3059	0.2076
0.8183	0.0723	0.1213	0.1277				
Acetonitrile (1)–Toluene (2)–Cyclohexane (3) at 318.15 K							
0.8843	0.0028	0.0984	0.0058	0.7406	0.0682	0.2197	0.1041
0.8514	0.0244	0.1216	0.0416	0.6735	0.0926	0.2966	0.1219
0.8036	0.0411	0.1635	0.0706	0.6191	0.1072	0.3731	0.1294
0.7532	0.0666	0.2084	0.1023				
Methanol (1)–Ethanol (2)–Cyclohexane (3) at 298.15 K							
0.7700	0.0343	0.1462	0.0072	0.5530	0.1092	0.2458	0.0522
0.7226	0.0557	0.1631	0.0147	0.5126	0.1115	0.2732	0.0635
0.6759	0.0782	0.1820	0.0236	0.4896	0.1117	0.2960	0.0700
0.6130	0.0976	0.2080	0.0370				

r, q, and q^* are pure-component molecular structure constants. Values of q^* have been empirically obtained to give a good fit to systems containing different components: water, 0.96; methanol, 0.95; ethanol, 0.92; propanols, 0.89; butanols, 0.88; furfural, 1.17; the other components we studied, $q^* = q^{0.1}$.

The activity coefficient of the extended UNIQUAC equation for any component i is given by

$$\ln \gamma_i = \ln (\Phi_i'/x_i) + 1 - \Phi_i'/x_i - (Z/2)q_i \times \{\ln (\Phi_i/\theta_i) + 1 - \Phi_i/\theta_i\} - q_i^* \ln (\sum_j \theta_j \tau_{ji}) + q_i \sum_j (q_j^*/q_j)\theta_j - q_i \sum_j \frac{(q_j^*/q_j)\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \tag{4}$$

The multicomponent expression for the activity coefficient of the UNIQUAC equation suggested by Anderson and Prausnitz (*1*) is

$$\ln \gamma_i = \ln (\Phi_i/x_i) + 1 - \Phi_i/x_i - (Z/2)q_i\{\ln (\Phi_i/\theta_i) + 1 - \Phi_i/\theta_i\} - q_i' \ln (\sum_j \theta_j'\tau_{ji}) + q_i' - q_i' \sum_j \frac{\theta_j'\tau_{ij}}{\sum_k \theta_k'\tau_{kj}} \tag{5}$$

where

$$\theta_i' = q_i'x_i/\sum_j q_j'x_j$$

Anderson and Prausnitz (*1*) empirically recommended the values of q' for alcohols: methanol, 0.96; ethanol, 0.92; propanols, 0.89; butanols, 0.88.

The parameters a_{ij} and a_{ji} are found from binary experimental vapor–liquid equilibrium and mutual solubility data by solving the following equations for any component i:

$$\phi_i y_i P = \gamma_i x_i \phi_i^s P_i^s \exp[v_i^L(P - P_i^s)/RT] \tag{6}$$

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \tag{7}$$

Computer programs used in this work are similar to those described in detail by Prausnitz et al. (*4*) based on a general application of the maximum-likelihood principle. The method of Hayden and O'Connell (5) is used to estimate the pure-component and cross-virial coefficients. Pure-component vapor pressures are calculated by using the Antoine equation whose constants are available in the literature (*2*, *6*). Table III lists binary interaction parameters. Both equations can reproduce binary equilibrium data well. Figure 1 shows a comparison between experimental and calculated results. The extended UNIQUAC equation is found to give better results than the UNIQUAC equation. Similar results are obtained in the systems acetonitrile–benzene–*n*-heptane (*7*) and acetonitrile–tetrachloromethane–cyclohexane (*8*). Table IV presents the results

Table III. Binary Parameters

system (1–2)	no. of data points	temp, K	energy parameters, K: extended UNIQUAC a_{12}	extended UNIQUAC a_{21}	UNIQUAC a_{12}	UNIQUAC a_{21}	variance of fit: extended UNIQUAC	UNIQUAC	ref
acetonitrile–benzene	11	318.15	−31.82	322.86	−47.50	241.78	8.70	10.27	*7*
acetonitrile–toluene	18	318.15	−28.93	372.53	−162.58	414.41	1.05	2.04	*13*
benzene–cyclohexane	7	313.14	−14.62	131.62	−37.06	95.67	0.75	0.78	*17*
benzene–*n*-heptane	15	318.15	81.72	52.11	20.19	30.09	1.90	1.89	*7*
2-butanone–benzene	10	298.15	−178.27	342.33	−175.82	258.87	1.95	2.01	*12*
cyclohexane–toluene	5	323.15	207.67	−94.69	252.90	−184.70	2.52	2.64	*22*
cyclohexane–toluene	10	298.15	98.70	27.36	115.70	−23.76	0.02	0.02	*14*
ethanol–benzene	11	298.15	66.46	915.87	−123.50	1126.79	3.11	3.06	*12*
ethanol–2-butanone	12	208.15	17.89	295.45	−144.53	505.15	2.19	2.50	*12*
ethanol–cyclohexane	7	308.15	176.34	1235.99	−89.26	1458.38	6.19	5.97	*21*
ethanol–*n*-octane	17	318.15	139.93	1162.52	−98.48	1433.01	2.57	2.22	*15*
methanol–benzene	9	328.15	29.36	862.45	−62.35	980.24	5.00	5.20	*19*
methanol–ethanol	11	298.15	−201.48	187.45	344.90	−193.12	13.31	5.62	*16*
methanol–tetrachloromethane	6	328.15	86.25	1107.86	−41.24	1231.19	13.03	13.13	*20*
methyl acetate–benzene	17	323.15	253.74	−171.31	182.12	−132.01	5.00	5.03	*11*
methyl acetate–trichloromethane	16	323.15	−192.91	3.15	−178.14	105.28	6.71	3.26	*11*
tetrachloromethane–benzene	8	313.15	−8.25	17.83	−9.20	12.61	0.08	0.08	*18*
trichloromethane–benzene	19	323.15	−97.07	6.77	0.11	−45.88	5.03	2.78	*11*
acetonitrile–cyclohexane	MS[a]	318.15	370.60	965.65	36.06	541.00			*10*
acetonitrile–cyclohexane	MS	298.15	459.30	1055.1	62.61	580.67			this work
acetonitrile–*n*-heptane	MS	318.15	330.98	974.93	17.40	571.40			*7*
methanol–cyclohexane	MS	298.15	208.05	1552.7	15.91	1518.2			*9*

[a] MS = mutual solubility.

Table IV. Predicted Results for Ternary Vapor-Liquid Equilibria

			absolute arith mean dev				
			vapor compn, mol %		press., %		
system	temp, K	no. of data points	extended UNIQUAC	UNIQUAC	extended UNIQUAC	UNIQUAC	ref
acetonitrile benzene *n*-heptane	318.15	51	0.49 0.36 0.42	1.24 0.40 0.99	1.04	1.72	*7*
ethanol 2-butanone benzene	298.15	33	0.31 0.23 0.35	0.35 0.27 0.46	0.89	1.39	*12*
methanol tetrachloromethane benzene	328.15	8	0.16 0.11 0.08	0.18 0.13 0.10	0.10	0.13	*20*
methyl acetate trichloromethane benzene	323.15	66	0.31 0.27 0.30	0.41 0.33 0.40	0.85	1.15	*11*

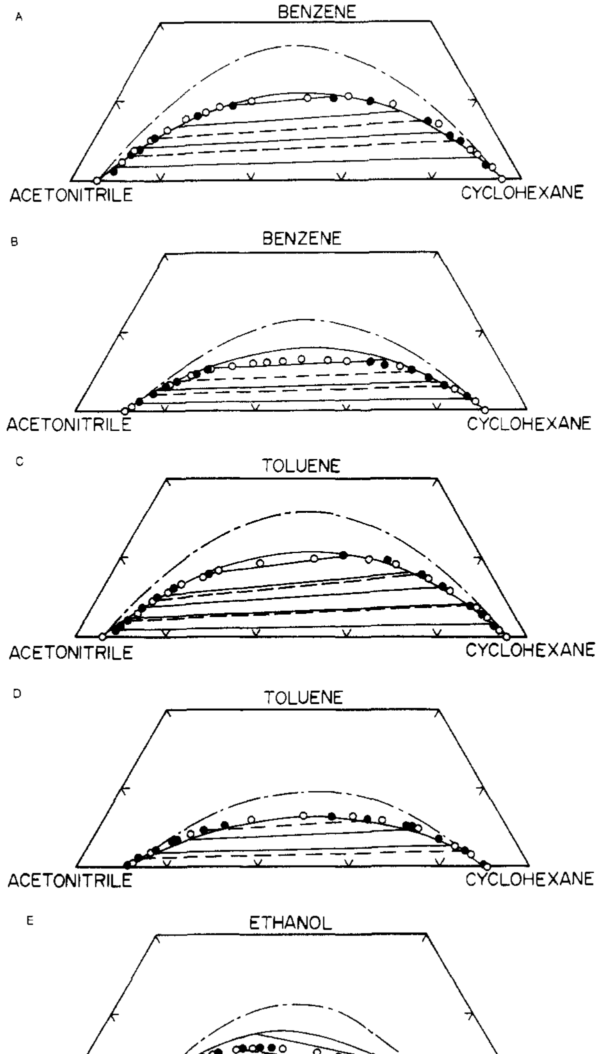

Figure 1. Experimental and predicted liquid-liquid equilibria. Experimental: (○) solubility; (●) tie-line. Calculated: (—) extended UNIQUAC equation; (- - -) UNIQUAC equation. A: acetonitrile-benzene-cyclohexane at 298.15 K. B: acetonitrile-benzene-cyclohexane at 318.15 K. C: acetonitrile-toluene-cyclohexane at 298.15 K. D: acetonitrile-toluene-cyclohexane at 318.15 K. E: methanol-ethanol-cyclohexane at 298.15 K.

of ternary prediction of the vapor-liquid equilibrium in four systems from binary data. Improved results are obtained with the extended UNIQUAC equation in the partially miscible system acetonitrile-benzene-*n*-heptane.

Glossary

a_{ij}	UNIQUAC or extended UNIQUAC binary interaction parameter related to Δu_{ij} and τ_{ij}
g^E	excess molar Gibbs energy
P	total pressure
P_i^s	vapor pressure of pure component *i*
q_i	molecular geometric area parameter for pure component *i*
q_i'	molecular interaction area parameter for pure component *i*
q_i^*	correction factor of interaction for pure component *i*
r_i	molecular volume parameter for pure component *i*
R	gas constant
T	absolute temperature
Δu_{ij}	UNIQUAC or extended UNIQUAC binary interaction parameter
v_i^L	molar liquid volume of component *i*
x_i	liquid-phase mole fraction of component *i*
y_i	vapor-phase 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*
θ_i'	area fraction of component *i* in residual contribution to the UNIQUAC activity coefficient
τ_{ij}	UNIQUAC or extended UNIQUAC binary parameter
ϕ_i	fugacity coefficient of component *i*
ϕ_i^s	fugacity coefficient of pure component *i* at its saturation pressure
Φ_i	segment fraction of component *i*
Φ_i'	modified segment fraction of component *i* in combinatorial contribution to the activity coefficient

Registry No. Acetonitrile, 75-05-8; benzene, 71-43-2; toluene, 108-88-3; methanol, 67-56-1; ethanol, 64-17-5; cyclohexane, 110-82-7.

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Viscosities and Densities of Very Concentrated Aqueous Solutions of $AgNO_3$, $TlNO_3$, and $Cd(NO_3)_2$

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Densities and viscosities of aqueous solutions of the mixed melt (Ag,Tl,Cd)NO_3 have been obtained at 98.5 °C over the entire water mole fraction (x_w) range. The Ag/Tl ratio was fixed at 1.06, and the Cd mole fraction in the melt was varied between 0 and 0.125. The techniques of measurement are those commonly used at room temperature, and thus the precision of measurement was greater than is usually the case with molten salts. The excess volume V^E of the two-component system (melt + water) is negative under all conditions studied and the V^E-x_w relation is slightly skewed. Since few, if any, electrolyte solution viscosities have been measured in the water-poor region, it is somewhat noteworthy to find that the viscosity-concentration behavior can be represented by a simple semilog relation over most of the x_w range.

Introduction

In the study of electrolyte solutions, water has been regarded as the solvent since solubility usually limits the practical concentration range considered. Conceptually, however, the solubility limit is an accidental phenomenon. It is evident that the search for adequate models of electrolyte solutions may be approached profitably from both the molten-salt and the pure-water ends of the concentration scale. Until recently, the domains of molten salts and electrolyte solutions did not overlap; this, fortunately, is now changing (*1*).

The system (Ag,Tl)NO_3 near its eutectic compositions is one of the few which are liquid over the entire concentration range in aqueous solution. Thus, at a constant Ag/Tl ratio of 1.06, the melt enables vapor pressure measurements (for example) to be made below 100 °C (*2*). A third cation (e.g., Cd^{2+}) may be added to the melt, and information on its relative hydration in the system has been obtained (*3*, *4*). The low operating temperatures accessible to these systems mean that physicochemical measurements may be done more precisely than is normally possible. We report here measurements on the densities and viscosities of (Ag,Tl,Cd)NO_3 in aqueous solution at 98.5 °C, over the whole water concentration range, and for various cadmium contents in the melt.

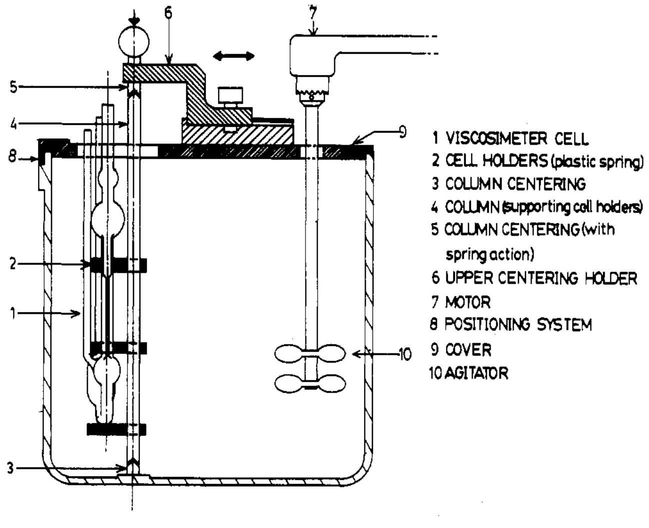

Figure 1. Mounting and alignment of viscometer in bath.

[†] Dépt. de Chimie.

[‡] Dépt. de Design Industriel.

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