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Note

LIQUID—LIQUID EQUILIBRIA FOR TERNARY SYSTEMS CONTAINING ACETONITRILE

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NOTATION

a_{ji}	UNIQUAC binary interaction parameter defined by $\Delta u_{ji}/R$
B_{ij}	second virial coefficient for i—j interaction
C	third parameter of the UNIQUAC equation
l_i	bulk factor of pure component i defined by $l_i = (Z/2)(r_i - q_i) - (r_i - 1)$
P	total pressure
P_i^s	vapor pressure of pure component i
q_i	molecular area parameter of pure component i
r_i	molecular volume parameter of pure component i
R	gas constant
T	absolute temperature
Δu_{ji}	UNIQUAC binary interaction parameter
v_i^L	molar liquid volume of pure component i
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
Z	lattice coordination number, a constant equal to 10
γ_i	activity coefficient of component i
θ_i	area fraction of component i
τ_{ji}	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

INTRODUCTION

Recently, considerable attention has been paid to the calculation of ternary (or multicomponent) liquid—liquid equilibria, which uses local composition models for the activity coefficients obtained from the expressions for the Gibbs energy function by differentiation [1—7]. The NRTL and the UNIQUAC equations have been widely used and the UNIQUAC equation has shown a slightly better general performance in correlating liquid—liquid equilibria [8]. With the two-parameter UNIQUAC equation ternary equilibrium calculations using binary data alone sometimes give only qualitative results. If we use some ternary data to obtain satisfactory ternary representa-

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tion, there is some loss of accuracy in the representation of binary vapor—liquid equilibria [6]. The three-parameter UNIQUAC equation substantially improved fits for vapor—liquid equilibria of some binary systems, but ternary calculations for liquid—liquid equilibria were not shown [9].

The objectives of the present work are: (1) to present isothermal vapor—liquid equilibrium data for two system: methanol—acetonitrile at 328.15 K and chloroform—cyclohexane at 313.15 K, and ternary liquid—liquid equilibrium data for three systems: acetonitrile—methanol—cyclohexane at 313.15 K, acetonitrile—carbon tetrachloride—cyclohexane at 318.15 K and acetonitrile—chloroform—cyclohexane at 313.15 K; (2) to make a comparison between experimental results for the ternary systems and calculated results obtained from the three-parameter UNIQUAC equation.

EXPERIMENTAL SECTION

Materials

Spectrograde methanol, carbon tetrachloride, reagent grade acetonitrile and cyclohexane were used without further purification. C.P. chloroform was fractionated in a glass column packed with McMahon packing. Refractive indices of the compounds used for experimental work were measured with a Shimadzu Pulfrich refractometer at 298.15 K and are compared with the literature values in Table 1.

Methods

Isothermal vapor—liquid equilibrium data were obtained using the Scatchard vapor-recirculating still described in a previous paper [11]. Observed boiling temperatures were controlled to within ±0.05 K. Vapor and liquid samples were analyzed with a Shimadzu model GC-4C gas chromatograph. The uncertainty introduced in compositions was less than ±0.002 mole fraction. The error of pressure measurements was expected within ±13 Pa. Liquid—liquid equilibrium data were determined by titration and analysis methods, using the apparatus described previously [12]. Compositions of conjugate solutions were analyzed by gas chromatography.

TABLE 1

Refractive indices of compounds used at 298.15 K

Compound	Experimental	Lit. [10]
Methanol	1.32658	1.32652
Carbon tetrachloride	1.45715	1.45739
Cyclohexane	1.42352	1.42354
Acetonitrile	1.34170	1.34163
Chloroform	1.44292	1.44393

EXPERIMENTAL RESULTS AND DATA ANALYSIS

Table 2 lists isothermal binary vapor—liquid equilibrium data. The liquid phase activity coefficients were calculated by taking vapor phase nonideality into account.

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

where x_i is the liquid phase mole fraction, y_i is the vapor phase mole fraction, v_i^L is the molar liquid volume, P is the total pressure and P_i^s is the pure component vapor pressure. The Antoine equation is used to calculate P_i^s: methanol [10]; acetonitrile [13]; chloroform [14]; cyclohexane [10].

The vapor phase fugacity coefficients are given by

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

The pure component and cross virial coefficients were estimated by the method of Hayden and O'Connell [15]. The observed vapor—liquid equili-

TABLE 2

Isothermal binary vapor—liquid equilibrium data

x_1	y_1	P (kPa)	γ_1	γ_2	g^E (J mole^{-1})
Methanol(1)—acetonitrile(2) at 328.15 K					
0.068	0.209	49.05	2.271	1.009	174.1
0.167	0.375	57.10	1.914	1.030	362.3
0.178	0.388	57.82	1.880	1.034	381.6
0.276	0.486	63.07	1.647	1.072	512.1
0.366	0.546	66.42	1.464	1.136	601.2
0.466	0.603	68.74	1.310	1.220	633.9
0.590	0.670	70.95	1.183	1.365	618.8
0.597	0.674	71.09	1.179	1.374	617.1
0.659	0.708	72.06	1.135	1.476	590.4
0.661	0.708	71.94	1.130	1.482	584.5
0.778	0.778	72.65	1.064	1.744	467.4
0.816	0.804	72.51	1.045	1.858	410.0
0.949	0.931	70.77	1.016	2.328	157.3
Chloroform(1)—cyclohexane(2) at 313.15 K					
0.017	0.045	25.48	1.420	1.005	27.6
0.091	0.209	28.88	1.394	1.018	120.1
0.162	0.330	32.04	1.370	1.035	208.4
0.202	0.392	33.20	1.351	1.022	212.5
0.392	0.581	38.44	1.192	1.066	281.2
0.457	0.626	39.86	1.142	1.104	298.3
0.546	0.690	42.20	1.114	1.157	325.9
0.642	0.758	44.06	1.086	1.195	303.8
0.760	0.836	46.12	1.058	1.263	256.9
0.887	0.915	47.54	1.022	1.433	155.6
0.924	0.941	47.86	1.016	1.488	115.5

TABLE 3

Solubility data for ternary systems

x_1	x_2	x_1	x_2	x_1	x_2
Acetonitrile(1)—methanol(2)—cycloheaxane at 313.15 K					
0.0000	0.2371	0.0864	0.7237	0.4990	0.3776
0.0000	0.7348	0.1655	0.6704	0.5682	0.3125
0.0251	0.7357	0.2252	0.6260	0.6901	0.1961
0.0548	0.7312	0.3739	0.4912	0.8961	0.0000
0.0787	0.0000	0.4302	0.4411		
Acetonitrile(1)—carbon tetrachloride(2)—cyclohexane(3) at 318.15 K					
0.0935	0.0000	0.1875	0.1957	0.5230	0.1854
0.1092	0.0508	0.2673	0.2228	0.6230	0.1509
0.1224	0.1161	0.2827	0.2269	0.6365	0.1451
0.1436	0.1531	0.3248	0.2261	0.7480	0.0914
0.1680	0.1784	0.4109	0.2164	0.8883	0.0000
Acetonitrile(1)—chloroform(2)—cyclohexane at 313.15 K					
0.8961	0.0000	0.5763	0.1167	0.3438	0.1177
0.8630	0.0206	0.5410	0.1189	0.2833	0.1083
0.7993	0.0548	0.4956	0.1209	0.2550	0.1010
0.7220	0.0858	0.4570	0.1216	0.1613	0.0677
0.6544	0.1054	0.3960	0.1203	0.0787	0.0000
0.6207	0.1119				

brium data are thermodynamically consistent, as the derived activity coefficients passed the requirement of the area test according to a practical guide [16]. Tables 3 and 4 represent solubility and tie-line data for the three ternary systems, respectively.

The three-parameter UNIQUAC equation [9] gives the activity coefficient for any component i.

$$\ln \gamma_i = \ln(\phi_i/x_i) + (Z/2)\, q_i \ln(\theta_i/\phi_i) + l_i - (\phi_i/x_i) \sum_j x_j l_j + \\ + C\left[-q_i \ln\left(\sum_j \theta_j \tau_{ji}\right) + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}}\right] \quad (3)$$

where the coordination number Z is set to 10 and the segment fraction Φ, the area fraction θ and the bulk factor l are given by

$$\phi_i = r_i x_i / \sum_j r_j x_j \quad (4)$$

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

$$l_i = (Z/2)(r_i - q_i) - (r_i - 1) \quad (6)$$

The pure component molecular structure constants r and q depend on mole-

TABLE 4

Tie-line data for ternary systems

Acetonitrile-rich phase		Cyclohexane-rich phase	
x_1^{I}	x_2^{I}	x_1^{II}	x_2^{II}
Acetonitrile(1)—methanol(2)—cyclohexane(3) at 313.15 K			
0.8116	0.0824	0.0712	0.0058
0.6944	0.1940	0.0648	0.0141
0.5841	0.3013	0.0617	0.0258
0.4526	0.4253	0.0555	0.0446
0.3161	0.5458	0.0456	0.0663
0.2395	0.6193	0.0415	0.0877
0.0972	0.7207	0.0252	0.1339
Acetonitrile(1)—carbon tetrachloride(2)—cyclohexane(3) at 318.15 K			
0.8606	0.0208	0.1043	0.0646
0.8258	0.0482	0.1366	0.1324
0.8211	0.0510	0.1313	0.1413
0.7829	0.0731	0.1563	0.1774
0.7472	0.0981	0.2014	0.2124
0.7368	0.1035	0.2110	0.2162
Acetonitrile(1)—chloroform(2)—cyclohexane(3) at 313.15 K			
0.8404	0.0345	0.1054	0.0354
0.7958	0.0559	0.1395	0.0559
0.7607	0.0703	0.1532	0.0668
0.7249	0.0842	0.1844	0.0773
0.6938	0.0975	0.2166	0.0881
0.6854	0.0994	0.2174	0.0899
0.6669	0.1040	0.2396	0.0959
0.6308	0.1131	0.2710	0.1025

cular volume and surface area and can be calculated by the methods described by Abrams and Prausnitz [5].

The binary adjustable parameter τ_{ij} is expressed by

$$\tau_{ij} = \exp(-\Delta u_{ij}/CRT) = \exp(-a_{ij}/CT) \qquad (7)$$

where C is a third binary parameter and must be the same for all three binary systems constituting a ternary system.

The compositions of two liquid phases (I and II) in equilibrium are calculated by solving a set of equations which show one for each component i as follows

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \qquad (8)$$

Table 5 gives the results obtained in binary phase equilibrium data reduction. Binary parameters for partially miscible systems were determined from mutual solubility data. Energy parameters for the methanol—acetonitrile system at 40°C and for the carbon tetrachloride—cyclohexane system at 45°C were estimated by linear interpolation. Figures 1—3 show calculated and experimental liquid—liquid equilibria for the three ternary systems. The original UNIQUAC equation ($C = 1.0$) provides a good agreement between

TABLE 5

Correlation of binary vapor—liquid and liquid—liquid equilibrium data

System, 1—2	Temp. (°C)	No. of data points	Parameters (K)		C	Root-mean square dev.		Ref.
			a_{21}	a_{12}		Relative pressure (×1000)	Vapor mole fraction (×1000)	
Methanol—acetonitrile	55	13	145.9	77.1	0.7	14.9	4.5	This work
			153.6	60.8	1.0	15.2	4.5	
	30	8	229.0	19.7	0.7	27.3	7.2	17
			260.8	−17.4	1.0	28.0	7.1	
Carbon tetrachloride —cyclohexane	70	9	−11.6	19.1	0.6	1.0	0.6	18
			−19.9	27.6	1.0	1.0	0.6	
	40	9	45.2	−33.0	0.6	0.6	0.7	18
			68.3	−54.2	1.0	0.6	0.7	
Carbon tetrachloride —acetonitrile	45	13	40.8	425.0	0.6	5.2	4.0	13
			−44.5	476.1	1.0	14.0	11.4	
Chloroform—cyclohexane	40	11	54.9	−1.1	1.0	18.5	3.7	This work
Chloroform—acetonitrile	40	6	144.9	−76.7	1.0	12.4		19
Acetonitrile—cyclohexane	40	S[a]	551.4	113.3	0.7			This work
			541.0	35.5	1.0			
	45	S	597.4	147.3	0.6			This work
			541.0	36.1	1.0			
Methanol—cyclohexane	40	S	724.7	95.7	0.7			This work
			601.2	−1.2	1.0			

[a] S = Solubility data.

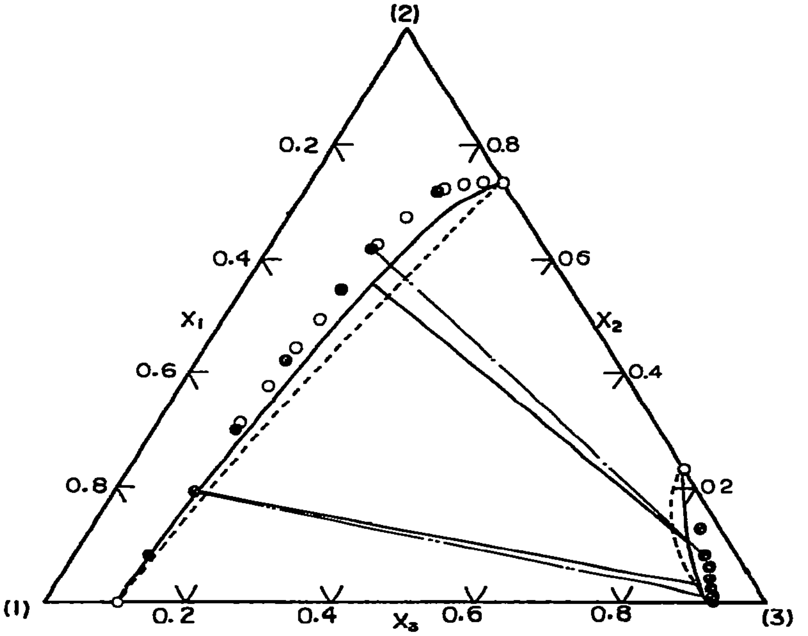

Fig. 1. Liquid—liquid equilibria for the acetonitrile(1)—methanol(2)—cyclohexane(3) system at 313.15 K. Experimental data: ○ (solubility); ●— · · —● (tie-line). Calculated: - - - - - - (C = 1.0); ——— (C = 0.7). Concentrations are in mole fraction.

calculated and experimental results for the acetonitrile—chloroform—cyclohexane system but not for the acetonitrile—methanol—cyclohexane and acetonitrile—carbon tetrachloride—cyclohexane systems. The prediction of

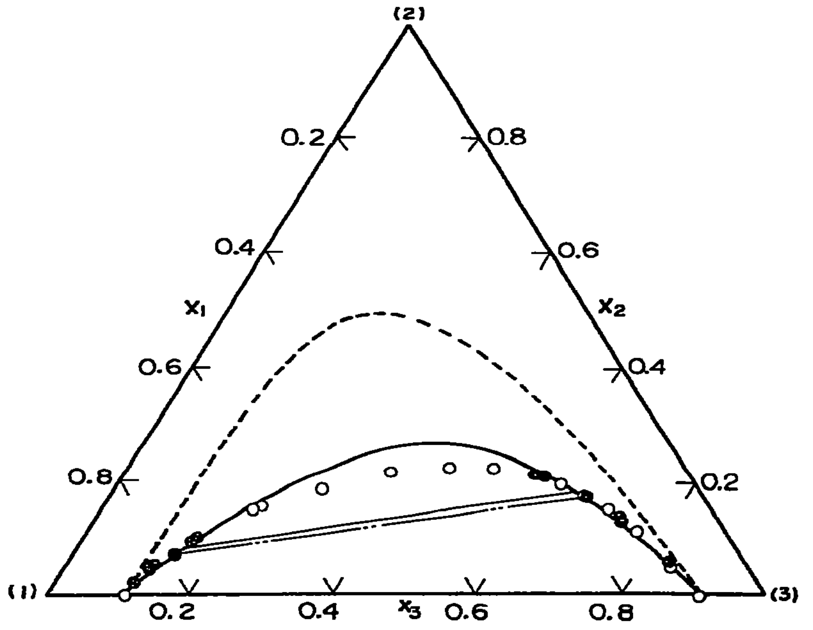

Fig. 2. Liquid—liquid equilibria for the acetonitrile(1)—carbon tetrachloride(2)—cyclohexane(3) system at 318.15 K. Experimental data: ○ (solubility); ●— · · —● (tie-line). Calculated: - - - - - - (C = 1.0); ——— (C = 0.6). Concentrations are in mole fraction.

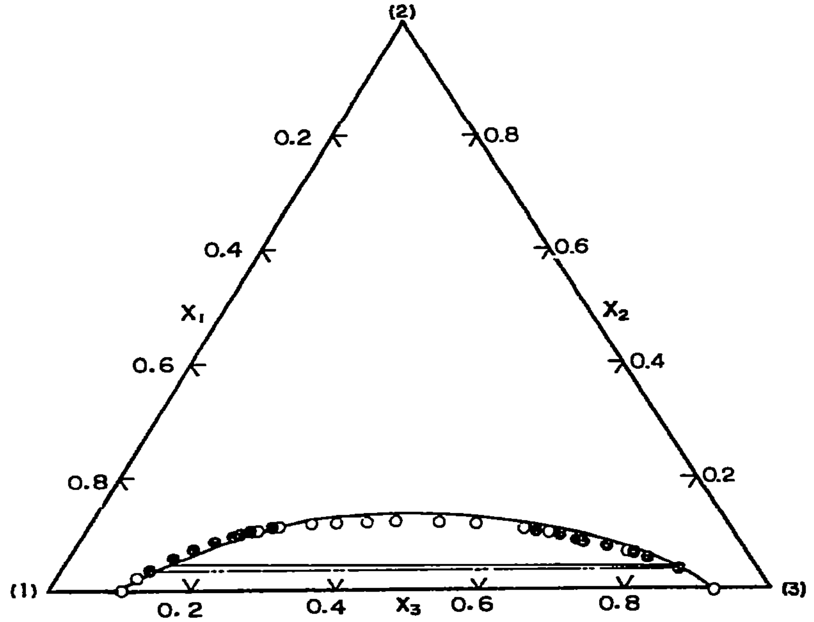

Fig. 3. Liquid–liquid equilibria for the acetonitrile(1)–chloroform(2)–cyclohexane(3) system at 313.15 K. Experimental data: ○ (solubility); ●— · · —● (tie-line). Calculated ——— (C = 1.0). Concentrations are in mole fraction.

ternary liquid–liquid equilibria for systems with two immiscible pairs from binary information is easier than that for systems with only one immiscible pair [1,6]. However, this is not the case for the acetonitrile–methanol–cyclohexane system. The predictions for the two systems were considerably improved with the three-parameter UNIQUAC equation having $C \neq 1.0$, as suggested by Maurer and Prausnitz [9].

We conclude that the three-parameter UNIQUAC equation is better than the original UNIQUAC equation in the correlation of ternary liquid–liquid equilibria without loss of accuracy in the representation of binary vapor–liquid equilibria.

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