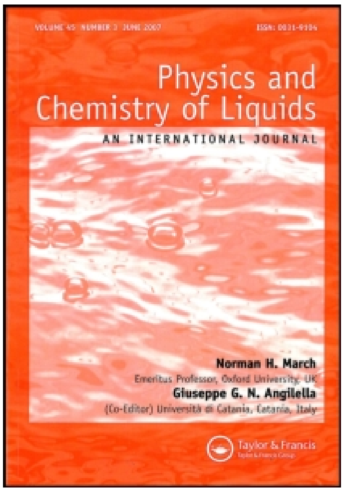

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Ternary Liquid-Liquid Equilibria Of (Acetonitrile *n*-Octane Propanols or Butanols)

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TERNARY LIQUID-LIQUID EQUILIBRIA OF (ACETONITRILE + *n*-OCTANE + PROPANOLS OR BUTANOLS)

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The liquid liquid equilibria of (acetonitrile + *n* – octane + 1-propanol or 2-propanol or 1-butanol or 2-butanol, or iso-butanol or tert-butanol) at 298.15 K have been measured. The ternary experimental results agree well with those predicted from the UNIQUAC associated-solution model with binary parameters alone.

KEY WORDS: Ternary liquid liquid equilibria, associated solution, molecular complexation.

INTRODUCTION

As the continuation of studies on ternary liquid liquid equilibria of (acetonitrile + saturated hydrocarbon + aliphatic alcohol), this paper presents liquid liquid equilibrium results for ternary mixtures of (acetonitrile + *n*-octane + A), where A is 1-propanol or 2-propanol or 1-butanol or 2-butanol or iso-butanol or tert-butanol. The phase equilibria of binary mixtures constituting the present ternary mixtures have been reported: vapour liquid equilibria of acetonitrile + 1-propanol at 318.15 K,[1] acetonitrile + 2-propanol at 323.15 K,[2] acetonitrile + 1-butanol at 333.15 K,[3] acetonitrile + 2-butanol at 333.15 K,[4] acetonitrile + iso-butanol at 333.15 K,[5] acetonitrile + tert-butanol at 333.15 K,[6] *n*-octane + 1-propanol at 363.15 K,[7] *n*-octane + 2-propanol at 353.15 K,[8] *n*-octane + 1-butanol at 333.15 K,[9] *n*-octane + 2-butanol at 333.15 K,[9] *n*-octane + iso-butanol at 333.15 K,[9] and *n*-octane + tert-butanol at 318.15 K;[10] mutual solubilities of acetonitrile + *n*-octane at 298.15 K.[11] The binary phase equilibrium data are used to evaluate the binary parameters of the UNIQUAC associated-solution model.[12] Then, the experimental liquid-liquid equilibria will be compared with those predicted from the UNIQUAC associated-solution model having only binary parameters.

EXPERIMENTAL

The special grade chemicals employed were supplied by Wako Pure Chemical Industries Ltd. and they were used as received. Gas chromatographic analysis did not show any appreciable peaks in the chemicals. Densities of the chemicals were measured with an Anton Paar densimeter (DMA40) at 298.15 K and agreed well with literature values.[13]

Each two-phase mixture was vigorously agitated with a magnetic stirrer in an equilibrium cell of volume 70 cm^3 for 2 h and then was allowed to settle for 2 h at 298.15 ± 0.01 K within a temperature-controlled water bath. Two equilibrium liquid samples were withdrawn with Hamilton syringes and were analysed using a Shimadzu gas chromatograph (GC-8C) and a Shimadzu Chromatopac (C-R3A). Experimental mole fractions were reproduced within ± 0.002.

RESULTS AND DISCUSSION

Table 1 gives the experimental tie-line results for six ternary mixtures at 298.15 K. The binary vapour liquid equilibrium results were reduced with the UNIQUAC associated-solution model using the following thermodynamic relations

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

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

where P, y_I, γ_I, x_I, P_I^s, v_I^L, and R are the total pressure, the vapour mole fraction, the activity coefficient, the liquid mole fraction, the pure-component vapour pressure, the pure-liquid molar volume, and the gas constant, respectively. The values of P_I^s were obtained from original references or the Antoine equation.[13] The values of v_I^L were estimated from a modified Rackett equation.[14] ϕ_I is the fugacity coefficient at P and T and ϕ_I^s is that at P_I^S and T. The second virial coefficients B were estimated from the Hayden O'Connell method.[15]

In a ternary mixture including acetonitrile (A), the alcohol (B) and n-octane (C) the UNIQUAC associated-solution model assumes the linear association of alcohol molecules ($B_{i-1} + B_1 = B_i$) and a solvation equilibrium between the terminal groups of open alcohol chains and one acetonitrile molecule ($B_i + A = B_iA$). The equilibrium constants (K_B and K_{BA}) are considered to be independent of the temperature and the degree of association. The model gives the activity coefficients of acetonitrile and the alcohol by

$$\begin{aligned}\ln \gamma_A = \ln \frac{\Phi_A}{x_A} + 1 - \frac{r_A}{V} - \left(\frac{Z}{2}\right) q_A \left(\ln \frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) \\ + q_A \left[1 - \ln \left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right]\end{aligned} \tag{3}$$

$$\begin{aligned}\ln \gamma_B = \ln \frac{\Phi_{B_1}}{\Phi_{B_1} x_A} + \frac{r_B}{V_B} - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_B \left(\ln \frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right) \\ + q_B \left[1 - \ln \left(\sum_J \theta_J \tau_{JB}\right) - \sum_J \frac{\theta_J \tau_{BJ}}{\sum_K \theta_K \tau_{KJ}}\right]\end{aligned} \tag{4}$$

Table 1 Tie-line results for ternary mixtures at 298.15 K.

Phase I			*Phase II*		
x_1	x_2	x_3	x_1	x_2	x_3
Acetonitrile (1) + 1-propanol (2) + *n*-octane (3)					
0.8382	0.1203	0.0415	0.0671	0.0289	0.9040
0.7627	0.1818	0.0555	0.0766	0.0594	0.8640
0.6763	0.2466	0.0771	0.1062	0.1061	0.7877
0.6216	0.2823	0.0961	0.1236	0.1413	0.7351
0.5865	0.3024	0.1111	0.1419	0.1678	0.6903
0.5329	0.3276	0.1395	0.1669	0.2051	0.6280
0.4612	0.3471	0.1917	0.2120	0.2572	0.5308
Acetonitrile (1) + 2-propanol (2) + *n*-octane (3)					
0.9019	0.0667	0.0314	0.0611	0.0148	0.9241
0.8488	0.1116	0.0396	0.0593	0.0293	0.9114
0.7556	0.1892	0.0552	0.0836	0.0744	0.8420
0.6850	0.2427	0.0723	0.1043	0.1196	0.7761
0.6366	0.2752	0.0882	0.1229	0.1533	0.7238
0.6027	0.2962	0.1011	0.1399	0.1775	0.6826
0.5715	0.3136	0.1149	0.1581	0.2016	0.6403
Acetonitrile (1) + 1-butanol (2) + *n*-octane (3)					
0.9146	0.0507	0.0347	0.0666	0.0151	0.9183
0.8698	0.0869	0.0433	0.0775	0.0318	0.8907
0.7822	0.1524	0.0654	0.1100	0.0850	0.8050
0.7053	0.2011	0.0936	0.1565	0.1450	0.6985
0.6578	0.2256	0.1166	0.1923	0.1796	0.6281
0.6271	0.2395	0.1334	0.2137	0.2014	0.5849
0.5962	0.2520	0.1518	0.2438	0.2195	0.5367
0.5816	0.2547	0.1637	0.2597	0.2251	0.5152
Acetonitrile (1) + 2-butanol (2) + *n*-octane (3)					
0.9332	0.0363	0.0305	0.0662	0.0130	0.9208
0.8781	0.0810	0.0409	0.0805	0.0348	0.8847
0.8465	0.1065	0.0470	0.0881	0.0536	0.8583
0.7144	0.1976	0.0881	0.1568	0.1511	0.6922
0.7854	0.1508	0.0638	0.1212	0.1005	0.7783
0.6783	0.2176	0.1041	0.1785	0.1779	0.6436
0.6332	0.2394	0.1274	0.2163	0.2102	0.5735
0.5931	0.2537	0.1532	0.2570	0.2326	0.5103
Acetonitrile (1) + iso-butanol (2) + *n*-octane (3)					
0.9287	0.0382	0.0331	0.0589	0.0110	0.9301
0.8665	0.0891	0.0444	0.0771	0.0365	0.8884
0.7729	0.1587	0.0684	0.1101	0.0897	0.8002
0.7060	0.2019	0.0922	0.1514	0.1407	0.7079
0.6718	0.2189	0.1093	0.1798	0.1684	0.6518
0.6372	0.2362	0.1266	0.2085	0.1903	0.6012
0.5955	0.2488	0.1557	0.2458	0.2166	0.5376
0.5745	0.2556	0.1699	0.2708	0.2262	0.5030
Acetonitrile (1) + tert-butanol (2) + *n*-octane (3)					
0.9373	0.0327	0.0300	0.0664	0.0116	0.9220
0.9207	0.0471	0.0322	0.0674	0.0181	0.9145
0.8761	0.0840	0.0399	0.0788	0.0392	0.8820
0.7955	0.1460	0.0584	0.1081	0.0925	0.7994
0.7334	0.1900	0.0766	0.1338	0.1426	0.7236
0.6614	0.2316	0.1070	0.1829	0.2002	0.6169
0.6363	0.2450	0.1187	0.2051	0.2177	0.5772
0.5364	0.2777	0.1859	0.2967	0.2673	0.4360

where Z is the coordination number equal to 10 and the segment fraction Φ_I, the area fraction θ_I, and the binary parameter τ_{IJ} are defined by

$$\Phi_I = x_I r_I / \sum_J x_J r_J \tag{5}$$

$$\theta_I = x_I q_I / \sum_J x_J q_J \tag{6}$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \tag{7}$$

ln γ_C for n-octane is expressed by exchanging the subscript A in Eq. (3) with C.

The apparent segment fractions of acetonitrile and the alcohol are related to the monomer segment fractions of these components from Eqs (8) and (9).

$$\Phi_A = \Phi_{A_1}\left[1 + \frac{r_A K_{BA} \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] \tag{8}$$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})^2}(1 + r_B K_{BA} \Phi_{A_1}) \tag{9}$$

$\Phi_C = \Phi_{C_1}$. The values of Φ_{A_1} and Φ_{B_1} are simultaneously solved from Eqs (8) and (9).

The true molar volume of the mixture is given by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A}\left[1 + \frac{K_{BA} r_A \Phi_{B_1}}{(1 - K_B \Phi_{B_1})}\right] + \frac{\Phi_{B_1}}{r_B(1 - K_B \Phi_{B_1})} + \frac{\Phi_{C_1}}{r_C} \tag{10}$$

$\Phi^\circ_{B_1}$ and V°_B for the pure alcohol are expressed as

$$\Phi^\circ_{B_1} = \frac{2K_B + 1 - (1 + 4K_B)^{0.5}}{2K_B^2} \tag{11}$$

$$\frac{1}{V^\circ_B} = \frac{(1 - K_B \Phi^\circ_{B_1})}{r_B} \tag{12}$$

The structural parameters of pure components calculated from the method of Vera *et al.*[16] and $r = 1.50$ and $q = 1.40$ for acetonitrile, $r = 2.23$ and $q = 1.98$ for propanols, $r = 2.77$ and $q = 2.42$ for butanols, and $r = 4.69$ and $q = 3.95$ for n-octane. The association constants at 323.15 K are 87.0 for 1-propanol, 49.1 for 2-propanol, 69.5 for 1-butanol, 31.1 for 2-butanol, 50.6 for iso-butanol, and 23.1 for tert-butanol.[17] The enthalpy of a hydrogen bond is -23.2 kJ mol^{-1} for the alcohol.[18] The solvation constants at 323.15 K are 30 for 1-propanol + acetonitrile,[19] 23 for 2-propanol + acetonitrile,[12] 40 for 1-butanol + acetonitrile,[3] 20 for 2-butanol + acetonitrile,[4] 30 for iso-butanol + acetonitril,[5] and 15 for tert-butanol + acetonitrile.[6] The enthalpy of complex formation is -17 kJ mol^{-1} for all alcohol + acetonitrile.[12] The enthalpies of hydrogen bond and complex formation were assumed to be independent of temperature and fix the temperature dependence of the equilibrium constants by means of the van't Hoff relation.

Optimum binary parameters were obtained using a computer programme based on the maximum likelihood principle.[20] The standard deviations of the measured

Table 2 The results of fitting the UNIQUAC associated-solution model to vapour–liquid and liquid–liquid equilibria and root-mea square deviations δP, δT, δx, and δy for binary mixtures.

	Temp. (K)	*No. of data points*	*Parameters*		*Root-mean-square deviations*			
			a_{AB} *(K)*	a_{BA} *(K)*	δP *(Torr)*	δT *(K)*	δx *(× 10^3)*	δy *(× 10*
Acetonitrile (A) + 1-butanol (B)	333.15	8	82.28	848.22	3.71	0.00	1.1	8.1
Acetonitrile (A) + 2-butanol (B)	333.15	10	122.61	571.75	2.17	0.00	1.1	4.7
Acetonitrile (A) + iso-butanol (B)	333.15	14	104.83	638.85	2.02	0.00	1.5	5.3
Acetonitrile (A) + tert-butanol (B)	333.15	11	82.74	533.91	2.06	0.00	0.9	5.9
Acetonitrile (A) + 1-propanol (B)	318.15	9	50.77	523.91	1.42	0.00	0.9	6.4
Acetonitrile (A) + 2-propanol (B)	323.15	15	84.11	538.50	0.53	0.01	0.5	3.7
n-Octane (A) + 1-butanol (B)	333.15	16	−110.71	186.01	1.89	0.00	3.0	11.9
n-Octane (A) + 2-butanol (B)	333.15	16	−187.15	314.33	2.61	0.00	3.1	12.9
n-Octane (A) + iso-butanol (B)	333.15	16	−196.87	336.47	4.30	0.01	4.6	16.8
n-Octane (A) + tert-butanol (B)	318.15	14	234.68	−153.77	0.20	0.00	0.0	
n-Octane (A) + 1-propanol (B)	363.15	22	−123.16	197.07	1.72	0.00	2.5	5.0
n-Octane (A) + 2-propanol (B)	353.15	25	143.42	−85.57	1.70	0.00	1.0	1.2
Acetonitrile (A) + *n*-Octane (B)	298.15		113.20	704.90				

variables are 1 Torr for pressure, 0.05 K for temperature, 0.001 for liquid mole fraction, and 0.003 for vapour mole fraction.

The binary parameters from the mutual solubilities were sought by solving Eq. (13) for each component.

$$(x_I \gamma_I)^I = (x_I \gamma_I)^{II} \tag{13}$$

where the superscripts *I* and *II* indicate two liquid phases in equilibrium. Table 2 shows the results of binary phase equilibrium data reduction. Ternary solubility envelopes for the six ternary mixtures were predicted from the UNIQUAC associated-solution model with the energy parameters listed in Table 2 by using the iso-activity criterion of Eq. (13). The measured results are compared with the predicted values in Figure 1.

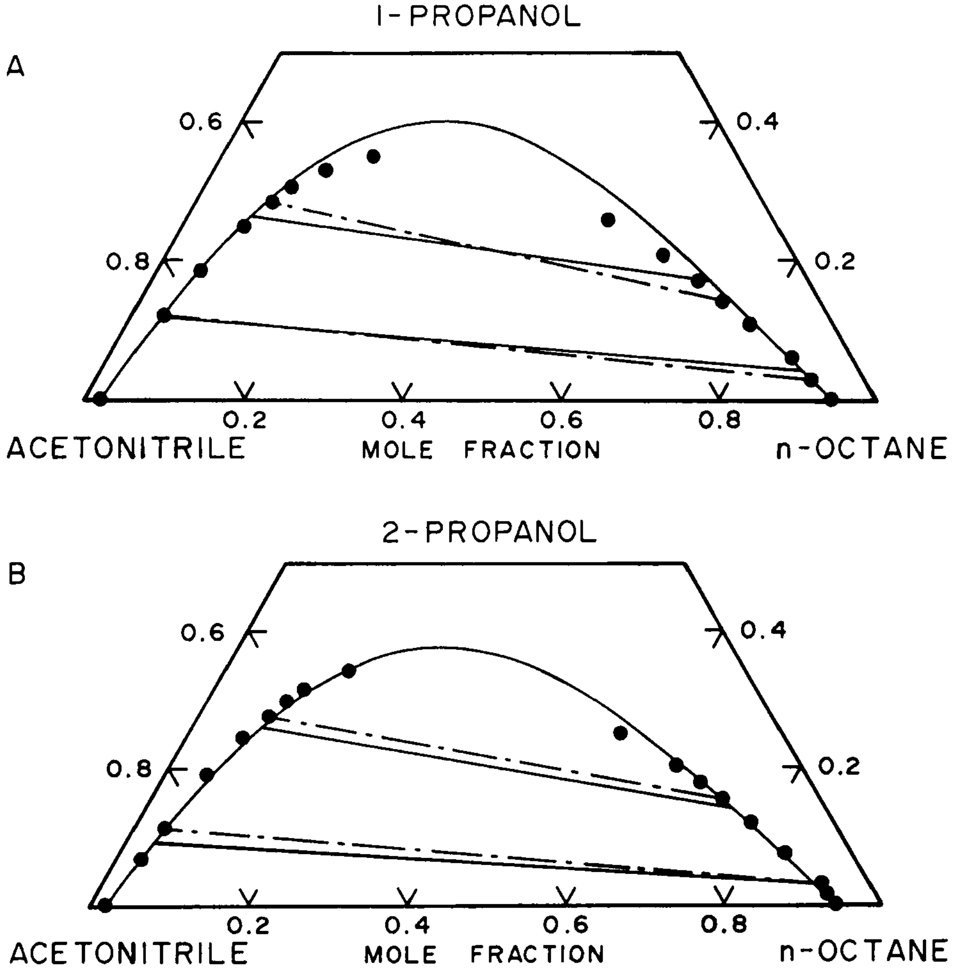

Figure 1

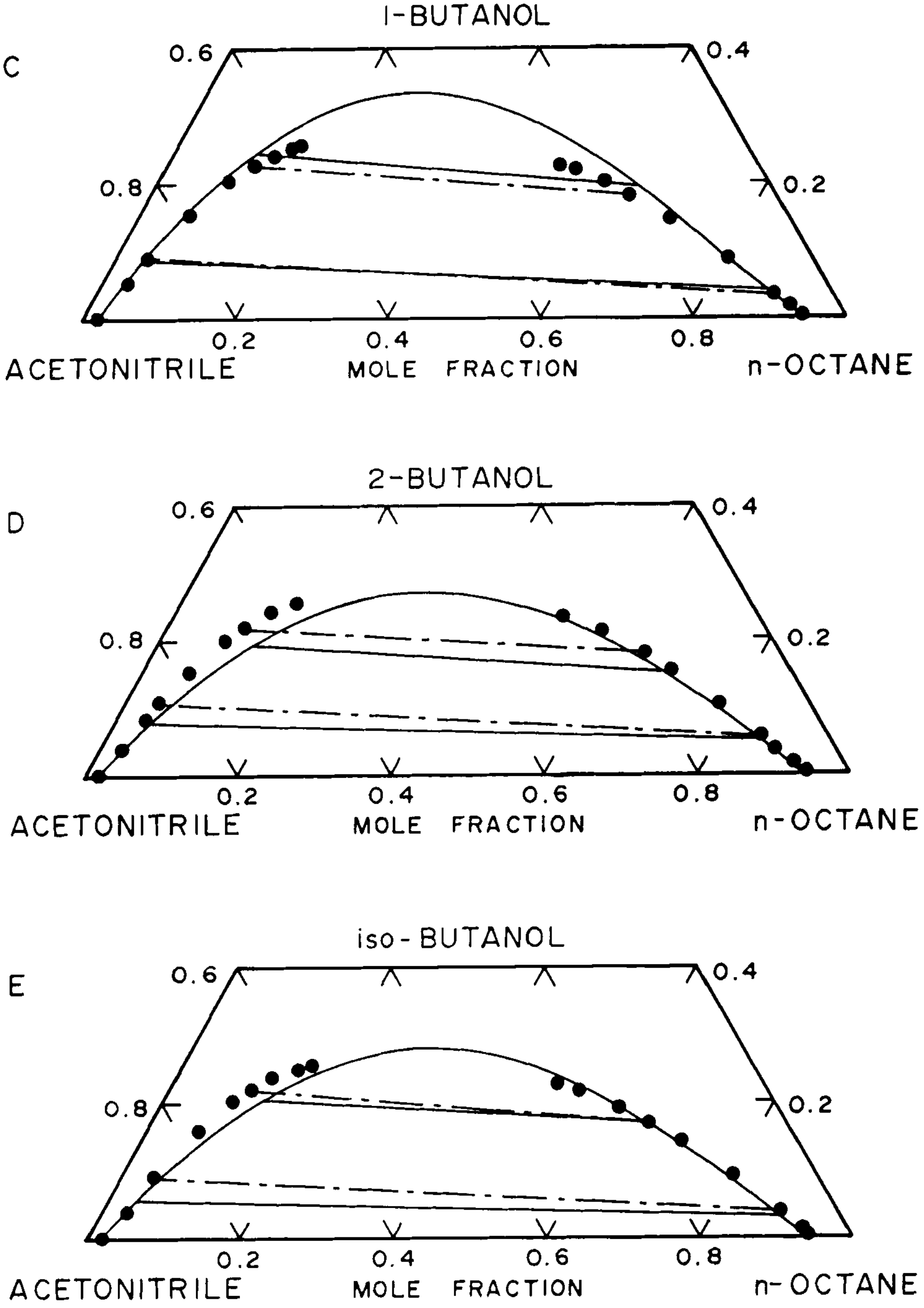

Figure 1 (cont)

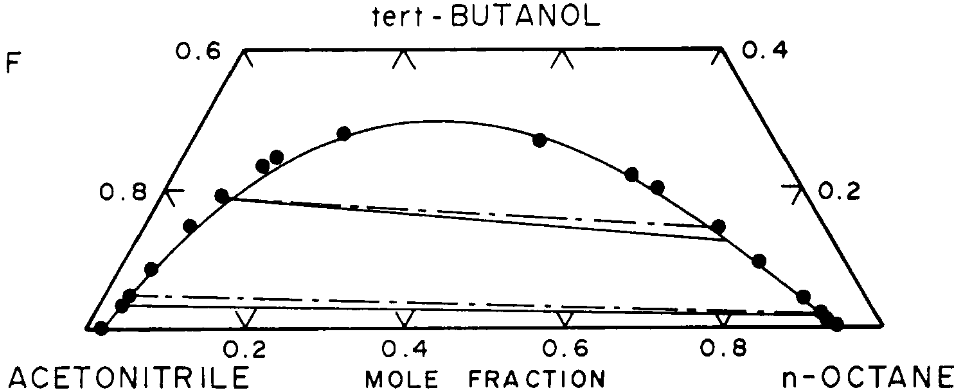

Figure 1 Experimental and calculated liquid-liquid equilibria of ternary mixtures at 298.15 K. ●—·●, Tie-line; - -, calculated from the UNIQUAC associated-solution model (A, acetonitrile + 1-propanal + *n*-octane; B, acetonitrile + 2-propanol + *n*-octane; C, acetonitrile + 1-butanol + *n*-octane; D, acetonitrile + 2-butanol + *n*-octane; E, acetonitrile + iso-butanol + *n*-octane; F, acetonitrile + tert-butanol + *n*-octane).

LIST OF SYMBOLS

A, B, C	acetonitrile, alcohol and saturated hydrocarbon
a_{IJ}	binary interaction parameter
B_{IJ}	second virial coefficient
I, J, K	components
K_B	association constant, $(\Phi_{B_{i+1}}/\Phi_{B_1})[i/(i+1)]$
K_{BA}	solvation constant, $(\Phi_{B_iA}/\Phi_{B_i}\Phi_{A_1})[i/(ir_B+r_A)]$
P	total pressure
P_I^s	saturated vapour pressure of pure component I
q_I	molecular area parameter of pure component I
R	universal gas constant
r_I	molecular volume parameter of pure component I
T	absolute temperature
V	true molar volume of alcohol mixture
V_B°	true molar volume of pure alcohol liquid
v_I^L	molar volume of pure liquid I
x_I	liquid mole fraction of component I
y_I	vapour mole fraction of component I
Z	coordination number equal to 10

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{A_1}	segment fraction of acetonitrile monomer in alcohol mixture

Φ_{B_1}	segment fraction of alcohol monomer in alcohol mixture
$\Phi_{B_1}^{0}$	segment fraction of alcohol monomer in pure alcohol solution
Φ_{C_1}	segment fraction of saturated hydrocarbon monomer in alcohol mixture
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

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