Thermochimica Acta, 114 (1987) 227–238
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

LIQUID–LIQUID EQUILIBRIA FOR THE ACETONITRILE + METHANOL + SATURATED HYDROCARBON AND ACETONITRILE + 1-BUTANOL + SATURATED HYDROCARBON SYSTEMS *

ISAMU NAGATA

Department of Chemical Engineering, Kanazawa University, Kanazawa 920 (Japan)

(Received 19 August 1986)

ABSTRACT

Tie-line results at 25 °C and atmospheric pressure are presented for {(acetonitrile + methanol) + cyclohexane, or + n-hexane, or + n-heptane or + n-octane} and for {(acetonitrile + 1-butanol) + cyclohexane, or + n-hexane or + n-heptane}. Vapor–liquid equilibria for acetonitrile + methanol at 25 °C are reported. The UNIQUAC associated-solution model is used to correlate binary vapor–liquid equilibria and mutual solubilities for the 13 systems constituting the ternary systems and to predict the ternary liquid–liquid equilibria by using binary parameters alone.

INTRODUCTION

Ternary liquid–liquid equilibria (LLE) for {(acetonitrile + paraffin) + methanol or + 1-butanol} have already been measured [1,2]. The UNIQUAC associated-solution model [3] is able to predict ternary LLE for alcohol mixtures with good accuracy. The predicted values for acetonitrile + methanol + cyclohexane at 40 °C are in close agreement with the experimental results. However, some discrepancies were observed between the calculated and measured solubility envelopes for acetonitrile + methanol + n-hexane at 25 °C. So this paper presents new measured tie-line results for four acetonitrile + methanol + saturated hydrocarbon systems and three acetonitrile + 1-butanol + saturated hydrocarbon systems at 25 °C to test the predictive ability of the UNIQUAC associated-solution model. Vapor–liquid equilibrium (VLE) data for the four binary systems constituting the three ternary 1-butanol systems have already been reported: for acetonitrile + 1-butanol at 60 °C [4]; for 1-butanol + cyclohexane at 45 °C [5]; for 1-butanol + n-hexane at 59.38 °C [6]; for 1-butanol + n-heptane at 60 °C [7].

---

* Partly presented at the 9th IUPAC Conference on Chemical Thermodynamics, Lisbon, Portugal, 14–18 July 1986.

0040-6031/87/$03.50 © 1987 Elsevier Science Publishers B.V.

EXPERIMENTAL

Materials

C.P. methanol was fractionally distilled after drying over calcium oxide. Guaranteed reagent acetonitrile, 1-butanol, cyclohexane, n-hexane, n-heptane and n-octane were used without further purification. Gas chromatographic analyses did not detect any appreciable impurities in the chemicals. Densities of the compounds used for experimental work, measured with an Anton Paar densimeter (DMA 40) at 25 °C, agreed well with literature values [8].

Apparatus

The still used to obtain VLE data was an all-glass Boublik vapor-recirculation one [9]. Compositions of the liquid and vapor phase samples of the methanol + acetonitrile system were determined by using a Shimadzu Pulfrich refractometer at 25 °C. The experimental errors involved in the VLE measurements were considered to be: 0.002 mole fraction for liquid and vapor compositions; 0.02 kPa for pressure; 0.05 °C for temperature.

Each two-phase mixture in an equilibrium cell of volume 70 cm^3 was stirred intensely for 2 h and then was allowed to settle for 2 h at 25 ± 0.01 °C within a thermostatted water bath. Two liquid samples in equilibrium were withdrawn with Hamilton syringes and were analyzed by means of a gas chromatograph (Shimadzu GC-8C) and an electronic integrator (Shimadzu C-E1B). The gas chromatograph was calibrated with liquid mixtures of known composition. Four analyses were made to obtain a mean value for each sample solution. Experimental mole fractions were reproducible within ± 0.002.

RESULTS AND DISCUSSION

Table 1 presents the VLE results for the methanol–acetonitrile system at 25 °C. Tables 2 and 3 give the measured tie-line data for the four acetonitrile + methanol + saturated hydrocarbon systems and for the three acetonitrile + 1-butanol + saturated hydrocarbon systems at 25 °C, respectively. The activity coefficient of component I was calculated by use of eqns. (1) and (2).

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

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

where P is the total pressure, y is the vapor-phase mole fraction, γ is the

TABLE 1

Vapor–liquid equilibrium data for the system methanol (1) + acetonitrile (2) at 25 °C

x_1	y_1	P (kPa)	γ_1	γ_2	ϕ_1	ϕ_2
0.055	0.172	13.946	2.656	1.032	0.996	0.962
0.172	0.372	16.345	2.139	1.042	0.990	0.958
0.273	0.458	17.452	1.766	1.092	0.987	0.957
0.351	0.500	18.172	1.559	1.174	0.985	0.956
0.483	0.570	18.838	1.336	1.315	0.983	0.956
0.570	0.619	18.905	1.233	1.407	0.982	0.957
0.689	0.680	19.078	1.129	1.651	0.981	0.959
0.784	0.744	18.812	1.070	1.881	0.981	0.961
0.890	0.842	18.025	1.022	2.195	0.980	0.966
0.942	0.906	17.692	1.020	2.439	0.980	0.969

$B_{11} = -2796$ cm^3 mol^{-1}, $B_{22} = -6905$ cm^3 mol^{-1}, $B_{12} = -3307$ cm^3 mol^{-1}, $v_1^{\mathrm{L}} = 39.05$ cm^3 mol^{-1}, $v_2^{\mathrm{L}} = 52.15$ cm^3 mol^{-1}.

activity coefficient, x is the liquid-phase mole fraction, P^{s} is the pure-component vapor pressure, v^{L} is the pure-liquid molar volume and ϕ is the fugacity coefficient. For the 1-butanol + n-hexane and 1-butanol + n-heptane systems the pure-component vapor pressures were taken from the original papers [6,7]. For the 1-butanol + cyclohexane and methanol + acetonitrile systems the pure-component vapor pressures were obtained from the Antoine equation whose constants are available in the literature [8,12]. The results of VLE data reduction for the acetonitrile + 1-butanol system were taken from a previous paper [4]. The modified Rackett equation [13] was used to calculate v^{L}. The second virial coefficients B_{IJ} were estimated from the Hayden–O'Connell correlation [14].

The UNIQUAC associated-solution model [3] gives the activity coefficients for the alcohol (A), acetonitrile (B) and a saturated hydrocarbon (C) in the ternary mixture studied as follows

$$\ln \gamma_{\mathrm{A}} = \ln\left(\frac{\Phi_{\mathrm{A}_1}}{\Phi^0_{\mathrm{A}_1} x_{\mathrm{A}}}\right) + r_{\mathrm{A}}\left(\frac{1}{V_{\mathrm{A}}^{\mathrm{o}}} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right) q_{\mathrm{A}}\left[\ln\left(\frac{\Phi_{\mathrm{A}}}{\theta_{\mathrm{A}}}\right) + 1 - \frac{\Phi_{\mathrm{A}}}{\theta_{\mathrm{A}}}\right] + q_{\mathrm{A}}\left[1 - \ln\left(\sum_J \theta_J \tau_{J\mathrm{A}}\right) - \sum_J \frac{\theta_J \tau_{\mathrm{A}J}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{3}$$

$$\ln \gamma_{\mathrm{B}} = \ln\left(\frac{\Phi_{\mathrm{B}_1}}{x_{\mathrm{B}}}\right) + 1 - \frac{r_{\mathrm{B}}}{V} - \left(\frac{Z}{2}\right) q_{\mathrm{B}}\left[\ln\left(\frac{\Phi_{\mathrm{B}}}{\theta_{\mathrm{B}}}\right) + 1 - \frac{\Phi_{\mathrm{B}}}{\theta_{\mathrm{B}}}\right] + q_{\mathrm{B}}\left[1 - \ln\left(\sum_J \theta_J \tau_{J\mathrm{B}}\right) - \sum_J \frac{\theta_J \tau_{\mathrm{B}J}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{4}$$

TABLE 2

Tie-line data for acetonitrile + methanol + saturated hydrocarbon at 25 ° C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
Acetonitrile (1) + methanol (2) + cyclohexane (3)					
0.9399	0	0.0601	0.0440	0	0.9560 [a]
0.7637	0.1618	0.0745	0.0443	0.0083	0.9474
0.5725	0.3428	0.0847	0.0377	0.0168	0.9455
0.4545	0.4536	0.0919	0.0338	0.0235	0.9427
0.3656	0.5413	0.0931	0.0312	0.0373	0.9315
0.2577	0.6360	0.1063	0.0249	0.0485	0.9266
0.1425	0.7352	0.1223	0.0187	0.0769	0.9044
0.0688	0.7905	0.1407	0.0092	0.0904	0.9004
0	0.8285	0.1715	0	0.1244	0.8756 [b]
Acetonitrile (1) + methanol (2) + n-hexane (3)					
0.9433	0	0.0567	0.0584	0	0.9416
0.7350	0.2062	0.0588	0.0512	0.0119	0.9369
0.5883	0.3465	0.0652	0.0461	0.0202	0.9337
0.5156	0.4148	0.0696	0.0464	0.0308	0.9228
0.2567	0.6538	0.0895	0.0331	0.0699	0.8970
0.1447	0.7476	0.1077	0.0237	0.1008	0.8755
0.0828	0.7846	0.1326	0.0161	0.1330	0.8509
0	0.7995	0.2005	0	0.2550	0.7450
Acetonitrile (1) + methanol (2) + n-heptane (3)					
0.9622	0	0.0378	0.0621	0	0.9379
0.7428	0.2170	0.0402	0.0560	0.0156	0.9284
0.6011	0.3563	0.0426	0.0551	0.0237	0.9212
0.4763	0.4780	0.0457	0.0477	0.0376	0.9147
0.3611	0.5889	0.0500	0.0390	0.0519	0.9091
0.2082	0.7310	0.0608	0.0281	0.0778	0.8941
0.1274	0.8082	0.0644	0.0197	0.0962	0.8841
0.0701	0.8480	0.0819	0.0120	0.1207	0.8673
0	0.8926	0.1074	0	0.1582	0.8418
Acetonitrile (1) + methanol (2) + n-octane (3)					
0.9801	0	0.0199	0.0568	0	0.9432
0.7874	0.1874	0.0252	0.0490	0.0100	0.9410
0.6503	0.3207	0.0290	0.0441	0.0163	0.9396
0.4860	0.4846	0.0294	0.0410	0.0291	0.9299
0.3701	0.5958	0.0341	0.0349	0.0378	0.9273
0.2225	0.7409	0.0366	0.0248	0.0553	0.9199
0.1021	0.8519	0.0460	0.0137	0.0773	0.9090
0.0705	0.8822	0.0473	0.0106	0.0853	0.9041
0	0.9368	0.0632	0	0.0968	0.9032

[a] Taken from Nagata and Ohta [10].

[b] Taken from Nagata and Katoh [11].

TABLE 3

Tie-line data for acetonitrile + 1-butanol + saturated hydrocarbon at 25 °C

Phase I			Phase II		
x_1	x_2	x_3	x_1	x_2	x_3
Acetonitrile (1) + 1-butanol (2) + cyclohexane (3)					
0.9399	0	0.0601	0.0440	0	0.9560 [a]
0.8644	0.0428	0.0928	0.0610	0.0113	0.9277
0.8057	0.0781	0.1162	0.0747	0.0266	0.8987
0.7588	0.1032	0.1380	0.0905	0.0449	0.8646
0.7068	0.1256	0.1676	0.1166	0.0673	0.8161
0.6117	0.1581	0.2302	0.1696	0.1114	0.7190
0.5682	0.1713	0.2605	0.2022	0.1309	0.6669
0.4747	0.1743	0.3510	0.2961	0.1573	0.5466
Acetonitrile (1) + 1-butanol (2) + n-hexane (3)					
0.9433	0	0.0567	0.0584	0	0.9416
0.8766	0.0484	0.0750	0.0762	0.0145	0.9093
0.8182	0.0889	0.0929	0.0925	0.0353	0.8722
0.7591	0.1210	0.1199	0.1103	0.0612	0.8285
0.7057	0.1473	0.1470	0.1485	0.0921	0.7594
0.6449	0.1634	0.1917	0.1966	0.1216	0.6818
0.5666	0.1851	0.2483	0.2664	0.1570	0.5766
0.4827	0.1854	0.3319	0.3592	0.1777	0.4631
Acetonitrile (1) + 1-butanol (2) + n-heptane (3)					
0.9622	0	0.0378	0.0621	0	0.9379
0.8996	0.0493	0.0511	0.0772	0.0149	0.9079
0.8506	0.0874	0.0620	0.0967	0.0338	0.8695
0.7565	0.1478	0.0957	0.1290	0.0879	0.7831
0.7125	0.1739	0.1136	0.1537	0.1171	0.7292
0.6645	0.1960	0.1395	0.1878	0.1450	0.6672
0.6096	0.2141	0.1763	0.2315	0.1804	0.5881
0.5159	0.2312	0.2529	0.3328	0.2152	0.4520
0.4809	0.2325	0.2866	0.3664	0.2248	0.4088

[a] Taken from Nagata and Ohta [10].

ln γ_C is given by exchanging the suffix B in eqn. (4) with C. Z is the coordination number, set as 10.

The segment fraction Φ_I, the area fraction θ_I and the coefficient τ_{JI}, related to the energy parameter a_{JI}, are defined as

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

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

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

Mass balance equations relate the overall segment fractions for the components to the monomer segment fractions, Φ_{A_1}, Φ_{B_1} and Φ_{C_1}.

$$\Phi_A = \frac{\Phi_{A_1}}{\left(1 - K_A\Phi_{A_1}\right)^2}\left[1 + r_A K_{AB}\Phi_{B_1}\right] \tag{8}$$

$$\Phi_B = \Phi_{B_1}\left[1 + \frac{r_B K_{AB}\Phi_{A_1}}{\left(1 - K_A\Phi_{A_1}\right)}\right] \tag{9}$$

$$\Phi_C = \Phi_{C_1} \tag{10}$$

The true molar volume of the ternary mixture is expressed by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A\left(1 - K_A\Phi_{A_1}\right)} + \frac{\Phi_{B_1}}{r_B}\left[1 + \frac{K_{AB} r_B \Phi_{A_1}}{\left(1 - K_A\Phi_{A_1}\right)}\right] + \frac{\Phi_{C_1}}{r_C} \tag{11}$$

At pure alcohol state V reduces to V_A^0 and Φ_{A_1} to $\Phi_{A_1}^0$

$$\frac{1}{V_A^0} = \frac{\left(1 - K_A\Phi_{A_1}^0\right)}{r_A} \tag{12}$$

$$\Phi_{A_1}^0 = \frac{2K_A + 1 - \left(1 + 4K_A\right)^{1/2}}{2K_A^2} \tag{13}$$

For parameter estimation from the binary VLE data, the computer program used in this work was similar to that described by Prausnitz et al. [15], based on the maximum likelihood principle. The standard deviations in the measured variables were assumed as $\sigma_P = 0.133$ kPa, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$.

A particular set of the energy parameters from mutual solubilities were obtained by solving eqn. (14) for each component.

$$\left(\gamma_I x_I\right)^{\mathrm{I}} = \left(\gamma_I x_I\right)^{\mathrm{II}} \tag{14}$$

where the superscripts I and II denotes two liquid phases in equilibrium. The pure-component structural parameters were calculated by use of the method of Vera et al. [16]: for methanol, $r = 1.15$ and $q = 1.12$; for 1-butanol, $r = 2.77$ and $q = 2.42$; for cyclohexane, $r = 3.18$ and $q = 2.55$; for n-hexane, $r = 3.61$ and $q = 3.09$; for n-heptane, $r = 4.15$ and $q = 3.52$; for n-octane, $r = 4.69$ and $q = 3.95$. The association constant for the alcohol at 50°C was taken from Brandani [17]: for methanol, $K_A = 173.9$; for 1-butanol, $K_A = 69.5$. The enthalpy of hydrogen-bond formation for the alcohol, h_A, was taken as -23.2 kJ mol^{-1} [18]. The values of the solvation constant and the enthalpy of complex formation were as follows: for methanol + acetonitrile, $K_{AB} = 30$ at 50°C and $h_{AB} = -17$ kJ mol^{-1} [3]; for 1-butanol + acetonitrile, $K_{AB} = 40$ at 50°C and $h_{AB} = -17$ kJ mol^{-1} [4]. h_A and h_{AB} were assumed to be independent of temperature and fix the temperature dependence of the

TABLE 4

Results of fitting the UNIQUAC associated-solution model to vapor–liquid and liquid–liquid equilibria for binary systems

System	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters	
			δP (kPa)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB} (K)	a_{BA} (K)
1-Butanol (A) + acetonitrile (B)	60	8	0.495	0.00	1.1	8.1	848.22	82.28
1-Butanol (A) + cyclohexane (B)	45	43	0.097	0.02	0.2		147.26	−85.12
1-Butanol (A) + n-hexane (B)	59.38	24	0.380	0.00	0.9	2.0	186.46	−108.46
1-Butanol (A) + n-heptane (B)	60	19	0.137	0.00	0.3	2.5	161.25	−98.45
Methanol (A) + acetonitrile (B)	25	10	0.107	0.01	1.3	7.8	454.35	−93.34
Acetonitrile (A) + cyclohexane (B)	25	MS [a]					142.38	689.58
Acetonitrile (A) + n-hexane (B)	25	MS					100.74	692.54
Acetonitrile (A) + n-heptane (B)	25	MS					99.25	692.34
Acetonitrile (A) + n-octane (B)	25	MS					113.20	704.95
Methanol (A) + cyclohexane (B)	25	MS					7.86	86.15
Methanol (A) + n-hexane (B)	25	MS					25.89	57.89
Methanol (A) + n-heptane (B)	25	MS					1.96	89.43
Methanol (A) + n-octane (B)	25	MS					−32.89	142.99

[a] MS = mutual solubilities.

equilibrium constants according to the van't Hoff relation. Table 4 presents the results of fitting the UNIQUAC associated-solution model to the VLE and mutual solubility data for the 13 binary systems. Figures 1 and 2 show the experimental results for the four acetonitrile + methanol + saturated hydrocarbon systems and for the three acetonitrile + 1-butanol + saturated hydrocarbon systems, together with calculated values. The largest difference

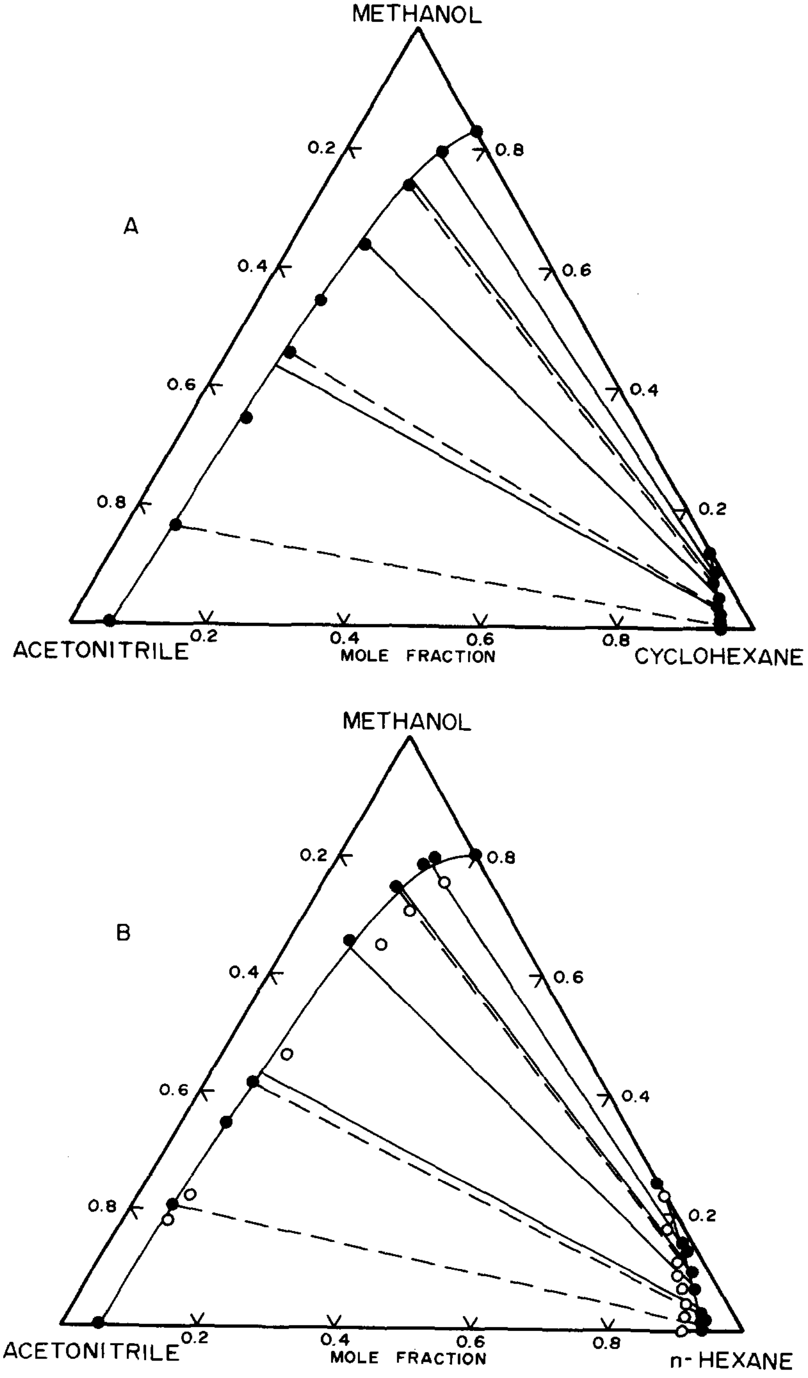
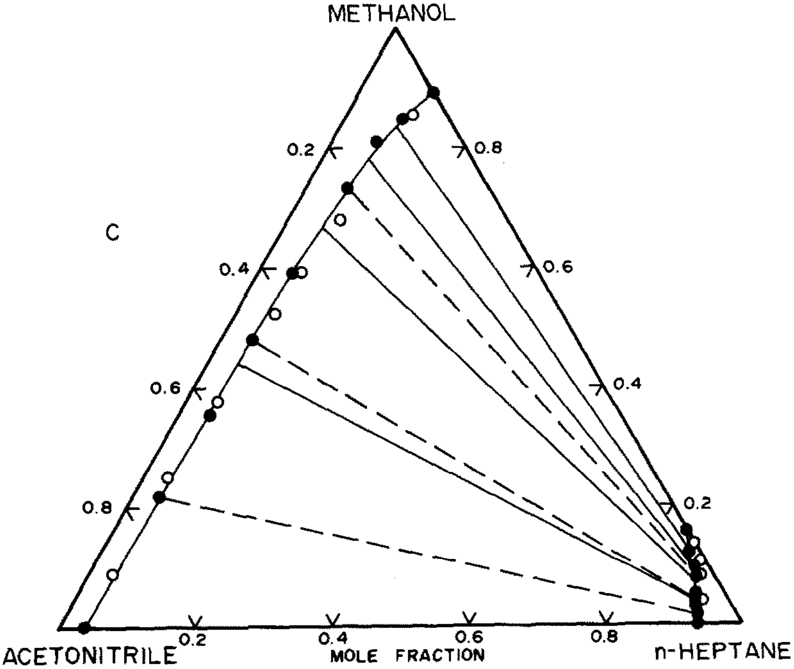


Fig. 1. Experimental tie-lines and binodal curves predicted from the UNIQUAC associated-solution model at 25°C. Experimental: (○) Kikic et al. [2]; (●-----●) this work. Calculated (———): (A) acetonitrile + methanol + cyclohexane; (B) acetonitrile + methanol + n-hexane.



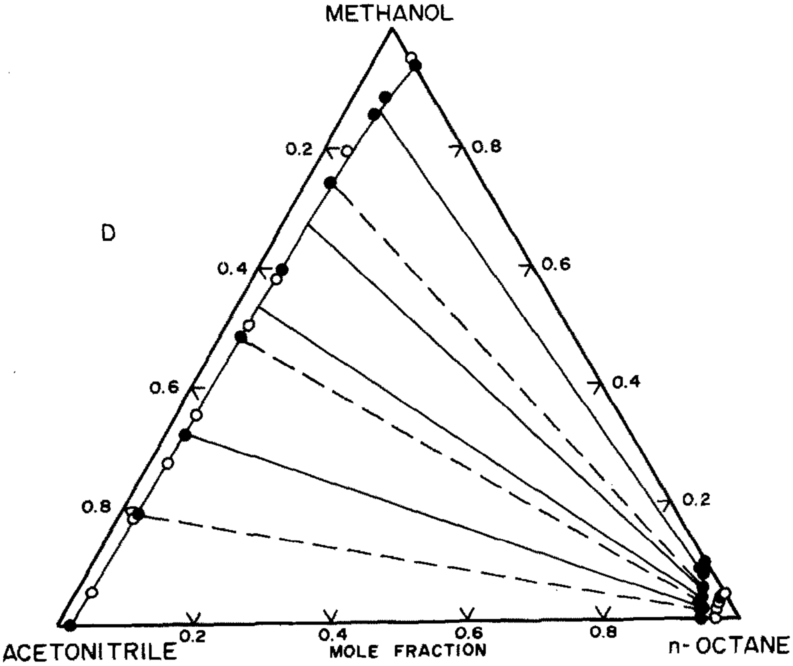


Fig. 1 (continued). (C) Acetonitrile + methanol + n-heptane; (D) acetonitrile + methanol + n-octane.

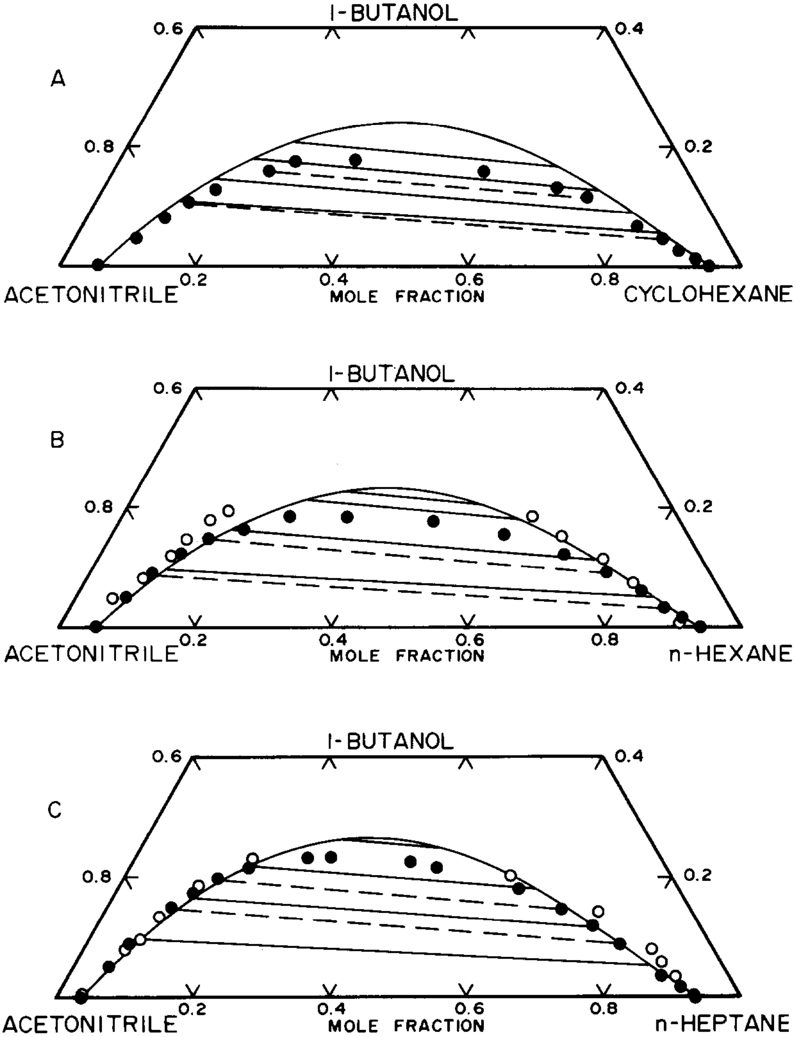


Fig. 2. Experimental tie-lines and binodal curves predicted from the UNIQUAC associated-solution model at 25°C. Experimental: (○) Kikic et al. [1]; (●-----●) this work. Calculated (———): (A) acetonitrile + 1-butanol + cyclohexane; (B) acetonitrile + 1-butanol + n-hexane; (C) acetonitrile + 1-butanol + n-heptane.

between both experimental mole fraction results are observed for the acetonitrile + methanol + n-hexane system. The calculated results agree rather well with the present data. Furthermore, for the five other systems the present results differ somewhat from the data of Kikic et al. [1,2]. It may be concluded that the UNIQUAC associated-solution model is able to predict the ternary LLE for the systems studied with sufficient accuracy using only binary parameters.

LIST OF SYMBOLS

A, B, C	alcohol, acetonitrile and saturated hydrocarbon
a_{IJ}	binary interaction parameter
B_{IJ}	second virial coefficient
h_A	enthalpy of hydrogen-bond formation
h_{AB}	enthalpy of complex formation between alcohol and acetonitrile
K_A	association constant, $(\Phi_{A_{i+1}}/\Phi_{A_i}\Phi_{A_1})[i/(i+1)]$
K_{AB}	solvation constant between alcohol i-mer and acetonitrile to form complex A_iB, $(\Phi_{A_iB}/\Phi_{A_i}\Phi_{B_1})[i/(ir_A+r_B)]$
P	total pressure
P_I^s	vapor pressure of pure component I
q_I	molecular area parameter of pure component I
R	universal gas constant
r_I	molecular size parameter of pure component I
T	absolute temperature
V	true molar volume of alcohol mixture
V_A^0	true molar volume of pure alcohol liquid
v_I^L	pure-liquid molar volume of component I
x_I	liquid-phase mole fraction of component I
y_I	vapor-phase mole fraction of component I
Z	coördination number, equal to 10

Greek letters

γ_I	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-phase mole fractions
τ_{IJ}	coefficient as defined by $\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
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

Superscripts

0	pure-liquid reference state
L	liquid
s	saturation

Subscripts

A, B, C	alcohol, acetonitrile and saturated hydrocarbon
A_1, A_i	monomer and i-mer of alcohol

A_iB	complex formation between alcohol *i*-mer and acetonitrile
AB	complex formed by A and B
B_1	monomer of acetonitrile
I, *J*, *K*	components

REFERENCES

1 I. Kikic, P. Alessi and M. Orlandini Visalberghi, Proc. Int. Solvent Extraction Conf., Liege (Belgium), Vol. 2, 1980.
2 I. Kikic, P. Alessi, I. Colussi and M. Orlandini Visalberghi, Can. J. Chem. Eng., 60 (1982) 168.
3 I. Nagata, Fluid Phase Equilibria, 19 (1985) 153.
4 I. Nagata, Thermochim. Acta, 112 (1987) 187.
5 H.T. French, J. Solution Chem., 12 (1983) 869.
6 C. Berro, M. Rogalski and A. Peneloux, J. Chem. Eng. Data, 27 (1982) 352.
7 C. Berro and A. Peneloux, J. Chem. Eng. Data, 29 (1984) 206.
8 J.A. Riddick and W.B. Bunger, Organic Solvents, 3rd edn., Wiley-Interscience, New York, 1970, pp. 77, 78, 86, 93, 145, 151, 399.
9 I. Nagata, J. Chem. Eng. Data, 30 (1985) 201.
10 I. Nagata and T. Ohta, J. Chem. Eng. Data, 28 (1983) 256.
11 I. Nagata and K. Katoh, Thermochim. Acta, 39 (1980) 45.
12 I. Brown and F. Smith, Aust. J. Chem., 7 (1954) 269.
13 C.F. Spencer and R.P. Danner, J. Chem. Eng. Data, 17 (1972) 236.
14 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem., Process Des. Dev., 14 (1975) 209.
15 J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice-Hall, Engelwood Cliffs, NJ, 1980, Chaps. 3, 4, 6 and Appendices C, D.
16 J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113.
17 V. Brandani, Fluid Phase Equilibria, 12 (1983) 87.
18 R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623.