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Isothermal vapour–liquid equilibrium for the ternary system ethanol + acetonitrile + acetone at 45°C

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Abstract

Vapour–liquid equilibrium data for the ternary ethanol + acetonitrile + acetone system at 45°C have been measured using a modified Boublik recirculating still. The experimental results are analysed by use of two activity coefficient models with binary parameters alone: UNIQUAC associated-solution and extended UNIQUAC. The former gives smaller deviations between experimental and calculated vapour composition and pressure values than does the latter.

LIST OF SYMBOLS

a_{IJ}	binary interaction parameter for I–J pair
A, B, C	ethanol, acetonitrile, and acetone
B_{IJ}	second virial coefficient for I–J pair
h_A	enthalpy of hydrogen-bond formation
h_{AB}, h_{AC}	enthalpies of complex formation of chemical complexes A_iB and A_iC
i	number of associated alcohol monomers
I, J, K	components
K_A	association constant
K_{AB}, K_{AC}	solvation constants
P	total pressure
P_I^s	vapour pressure of pure component I
q_I	molecular area parameter of pure component I
q_I'	molecular interaction area parameter of pure component I
r_I	molecular volume parameter of pure component I
R	universal gas constant
T	absolute temperature

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v_I^L	molar liquid volume of pure component I
V	true molar volume of alcohol mixture
$V_A^\ominus$	true molar volume of pure alcohol liquid
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase 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
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase, and vapour-phase mole fractions
τ_{IJ}	binary parameter as defined by $\exp(-a_{IJ}/T)$
ϕ_I	vapour-phase fugacity coefficient of component I at system temperature T and pressure P
ϕ_I^s	vapour-phase fugacity coefficient of pure component I at system temperature T and saturation pressure P_I^s
Φ_{A1}	segment fraction of ethanol monomer in mixture
$\Phi_{A1}^\ominus$	segment fraction of ethanol monomer in pure ethanol
Φ_{B1}, Φ_{C1}	segment fractions of acetonitrile and acetone monomers

Superscript

*	reference state of 50°C

INTRODUCTION

The thermodynamic properties of ternary alcohol mixtures have been studied in this laboratory. As part of the programme of experimental studies of ternary mixtures containing one alcohol and two polar nonassociating components, this work reports vapour–liquid equilibrium (VLE) results for the ethanol + acetonitrile + acetone system at 45°C and the experimental data are compared with those calculated from the UNIQUAC associated-solution and extended UNIQUAC models [1,2]. The VLE of the three binary systems constituting the ternary system are available from the literature: ethanol + acetonitrile at 40°C [3]; ethanol + acetone at 50°C [3]; acetonitrile + acetone at 45°C [4].

EXPERIMENTAL

C.P. Ethanol was distilled in a glass column packed with McMahon packing after drying over calcium oxide. Acetonitrile (Wako Pure Chemical Industries Ltd., guaranteed reagent grade) was used as received. Acetone (Wako Pure Chemical Industries Ltd., special grade) was fractionated after

TABLE 1

Densities and vapour pressures of pure components

Component	Density at 25°C (g mol^{-1})		Vapour pressure at 45°C (mmHg)	
	Obs.	Lit. [5]	Obs.	Lit. [5]
Ethanol	0.78509	0.78504	174.0	173.68
Acetonitrile	0.77661	0.7766	208.3	208.35(6)
Acetone	0.78442	0.78440	509.1	509.08

drying over calcium chloride. Densities of the compounds used were measured with an Anton Paar densimeter (DMA40). The measured densities and vapour pressures of the compounds compare well with the literature values as shown in Table 1 [5,6].

Vapour–liquid equilibrium data were obtained using a modified Boublik recirculating still as described previously [7]. Compositions of the liquid and vapour-phase samples were analysed using a gas chromatograph (Shimadzu GC-7A) and an electronic integrator (Shimadzu Chromatopac E-1B). The experimental errors of the measured variables were 0.16 Torr for pressure; 0.05 K for temperature; 0.002 for liquid and vapour mole fractions.

RESULTS AND DATA ANALYSIS

The ternary experimental VLE results of the ethanol + acetonitrile + acetone system at 45°C are given in Table 2, together with the activity coefficients γ_I and the fugacity coefficients ϕ_I calculated with eqns. (1) and (2).

$$\gamma_\text{I} = \frac{P\phi_\text{I} y_I}{x_\text{I} P_\text{I}^\text{s} \phi_\text{I}^\text{s} \exp\left[v_\text{I}^\text{L}(P - P_\text{I}^\text{s})/RT\right]} \tag{1}$$

$$\ln \phi_\text{I} = \left(2\sum_\text{J} y_\text{J} B_\text{IJ} - \sum_\text{I}\sum_\text{J} y_\text{I} y_\text{J} B_\text{IJ}\right)\frac{P}{RT} \tag{2}$$

where P is the total pressure, y_I the vapour-phase mole fraction, x_I the liquid-phase mole fraction, P_I^s the pure-component vapour pressure and V_I^L the pure-liquid molar volume estimated by the modified Rackett equation [8]. The second virial coefficients B_IJ were calculated from the method of Hayden and O'Connell [9].

The experimental data were correlated by the UNIQUAC associated-solution [1] and extended UNIQUAC models [2]. The models give the activity coefficients of components as follows.

UNIQUAC associated-solution model

According to the model assumptions, ethanol molecules (A) form open chains A_i ($A_{i-1} + A_1 = A_i$) and chemical complexes A_iB and A_iC with

TABLE 2

Experimental results for the ethanol (1) + acetonitrile (2) + acetone (3) system at 45° [a]

No.	x_1	x_2	x_3	y_1	y_2	y_3	P (mmHg)	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
1	0.411	0.398	0.191	0.332	0.343	0.325	312.0	1.440	1.270	1.063	0.981	0.939	0.980 [b]
				0.333	0.345	0.322	309.7	1.433	1.270	1.044	0.981	0.939	0.980 [c]
2	0.383	0.194	0.423	0.251	0.139	0.610	377.3	1.406	1.268	1.081	0.977	0.932	0.973
				0.250	0.141	0.609	375.8	1.393	1.280	1.076	0.977	0.932	0.973
3	0.303	0.421	0.276	0.258	0.313	0.429	335.3	1.629	1.173	1.041	0.980	0.935	0.977
				0.259	0.317	0.424	329.7	1.610	1.168	1.013	0.981	0.936	0.978
4	0.699	0.199	0.102	0.486	0.274	0.240	278.9	1.108	1.830	1.317	0.982	0.947	0.982
				0.489	0.275	0.236	278.6	1.113	1.834	1.296	0.982	0.947	0.982
5	0.617	0.202	0.181	0.411	0.226	0.363	307.2	1.167	1.630	1.233	0.980	0.942	0.979
				0.411	0.227	0.362	306.8	1.166	1.639	1.227	0.980	0.942	0.979
6	0.534	0.379	0.087	0.425	0.403	0.172	280.8	1.279	1.418	1.115	0.983	0.944	0.983
				0.427	0.405	0.168	281.0	1.285	1.426	1.093	0.983	0.944	0.983
7	0.519	0.292	0.189	0.372	0.284	0.344	310.2	1.269	1.428	1.130	0.980	0.940	0.979
				0.373	0.285	0.342	310.1	1.272	1.433	1.122	0.980	0.940	0.979
8	0.108	0.214	0.678	0.083	0.112	0.805	430.4	1.879	1.047	1.011	0.976	0.924	0.968
				0.084	0.115	0.801	428.6	1.905	1.069	1.001	0.976	0.924	0.968
9	0.125	0.128	0.747	0.087	0.065	0.848	455.7	1.799	1.073	1.021	0.975	0.922	0.966
				0.089	0.066	0.845	450.5	1.810	1.084	1.006	0.975	0.922	0.967
10	0.194	0.607	0.199	0.222	0.463	0.315	300.3	1.969	1.082	0.954	0.984	0.938	0.982
				0.220	0.457	0.323	302.4	1.968	1.074	0.985	0.984	0.938	0.981

11	0.205	0.420	0.375	0.186	0.280	0.534	351.2	1.818	1.099	0.997	0.980	0.932	0.976
				0.185	0.281	0.534	351.3	1.804	1.102	0.998	0.980	0.932	0.976
12	0.207	0.130	0.663	0.137	0.072	0.791	436.2	1.637	1.124	1.029	0.975	0.924	0.968
				0.138	0.073	0.789	434.0	1.640	1.134	1.021	0.975	0.925	0.968
13	0.104	0.443	0.453	0.103	0.273	0.624	364.5	2.060	1.051	0.999	0.980	0.930	0.974
				0.105	0.273	0.622	363.8	2.086	1.050	0.995	0.980	0.930	0.974
14	0.089	0.738	0.173	0.133	0.564	0.303	282.2	2.425	1.021	0.994	0.988	0.940	0.984
				0.134	0.563	0.303	283.1	2.447	1.023	0.997	0.988	0.940	0.984
15	0.296	0.601	0.103	0.314	0.511	0.175	280.6	1.708	1.131	0.959	0.985	0.942	0.984
				0.315	0.507	0.178	283.3	1.729	1.132	0.985	0.985	0.941	0.984
16	0.098	0.519	0.383	0.110	0.344	0.546	343.6	2.204	1.068	0.978	0.982	0.932	0.977
				0.108	0.336	0.556	343.3	2.173	1.042	0.994	0.982	0.932	0.977
17	0.097	0.712	0.191	0.137	0.549	0.314	289.0	2.346	1.053	0.955	0.987	0.939	0.984
				0.139	0.534	0.327	289.4	2.383	1.027	0.995	0.987	0.939	0.983
18	0.196	0.714	0.090	0.254	0.593	0.153	281.7	2.098	1.107	0.964	0.987	0.940	0.985
				0.256	0.584	0.160	273.7	2.058	1.061	0.979	0.987	0.942	0.985
19	0.192	0.708	0.100	0.246	0.582	0.172	274.0	2.018	1.068	0.949	0.987	0.942	0.985
				0.250	0.574	0.176	276.0	2.064	1.060	0.979	0.987	0.942	0.985
20	0.147	0.756	0.097	0.209	0.624	0.167	268.6	2.198	1.052	0.932	0.989	0.942	0.986
				0.213	0.612	0.175	270.5	2.254	1.038	0.985	0.988	0.942	0.986

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[a] $B_{11} = -1518$ cm^3 mol^{-1}, $B_{22} = -4550$ cm^3 mol^{-1}, $B_{33} = -1510$ cm^3 mol^{-1}, $B_{12} = -2303$ cm^3 mol^{-1}, $B_{13} = -1277$ cm^3 mol^{-1}, $B_{23} = -2458$ cm^3 mol^{-1}, $v_1^L = 59.43$ cm^3 mol^{-1}, $v_2^L = 53.75$ cm^3 mol^{-1}, $v_3^L = 76.35$ cm^3 mol^{-1}.

[b] Experimental results.

[c] Calculated values from the UNIQUAC associated solution model.

acetonitrile (B) and acetone (C) ($A_i + B_1 = A_iB$ and $A_i + C_1 = A_iC$). The equilibrium constants of the three reactions are assumed to be independent of the degree of association and are given by

$$K_A = \frac{\Phi_{Ai}}{\Phi_{Ai}\Phi_{A1}} \frac{i}{i+1} = K_A^* \exp\left[-\frac{h_A}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{3}$$

$$K_{AB} = \frac{\Phi_{AiB}}{\Phi_{Ai}\Phi_{B1}} \frac{i}{ir_A + r_B} = K_{AB}^* \exp\left[-\frac{h_{AB}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{4}$$

$$K_{AC} = \frac{\Phi_{AiC}}{\Phi_{Ai}\Phi_{C1}} \frac{i}{ir_A + r_C} = K_{AC}^* \exp\left[-\frac{h_{AC}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{5}$$

where Φ_{Ai}, Φ_{Ai+1}, Φ_{A1}, Φ_{AiB}, Φ_{B1}, Φ_{AiC} and Φ_{C1} are the segment fractions of A_i, A_{i+1}, A_1, $A_{i\mathrm{B}}$, B_1, A_iC and C_1, respectively; h_A, h_{AB} and h_{AC} are the enthalpies of hydrogen bonding and complex formation. γ_I is the molecular size parameter of pure component I.

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A1}}{\Phi_{A1}^{\ominus} x_A}\right) + \frac{r_B}{V_A^{\ominus}} - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_A \left[\ln\left(\frac{\Phi_A}{\theta_A}\right) + 1 - \frac{\Phi_A}{\theta_A}\right] + q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{6}$$

$$\ln \gamma_B = \ln\left(\frac{\Phi_{B1}}{x_B}\right) + 1 - \frac{r_B}{V} - \left(\frac{Z}{2}\right) q_B \left[\ln\left(\frac{\Phi_B}{\theta_B}\right) + 1 - \frac{\Phi_B}{\theta_B}\right] + q_B\left[1 - \ln\left(\sum_J \theta_J \tau_{JB}\right) - \sum_J \frac{\theta_J \tau_{BJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{7}$$

where Z is the coordination number set as 10 and the segment fraction Φ_I, the surface fraction θ_I and the binary adjustable parameter τ_{JI} related to the energy parameter a_{JI} are expressed by

$$\Phi_I = r_I x_I / \sum_J r_J x_J \tag{8}$$

$$\theta_I = q_I x_I / \sum_J q_J x_J \tag{9}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{10}$$

ln γ_C of acetone (C) is given by changing the subscript B to C in eqn. (7).

The monomer segment fractions Φ_{A1}, Φ_{B1} and Φ_{C1} are obtained by simultaneous solution of eqns. (11–13).

$$\Phi_A = \frac{\Phi_{A1}}{(1 - K_A\Phi_{A1})^2}[1 + r_A(K_{AB}\Phi_{B1} + K_{AC}\Phi_{C1})] \tag{11}$$

$$\Phi_B = \Phi_{B1}\left[1 + \frac{r_B K_{AB}\Phi_{A1}}{(1 - K_A\Phi_{A1})}\right] \tag{12}$$

$$\Phi_C = \Phi_{C1}\left[1 + \frac{r_C K_{AC}\Phi_{A1}}{(1 - K_A\Phi_{A1})}\right] \tag{13}$$

The true molar volume of the ternary mixture V is

$$\frac{1}{V} = \frac{\Phi_{A1}}{r_A(1 - K_A\Phi_{A1})} + \frac{\Phi_{B1}}{r_B}\left[1 + \frac{K_{AB}r_B\Phi_{A1}}{(1 - K_A\Phi_{A1})}\right] + \frac{\Phi_{C1}}{r_C}\left[1 + \frac{K_{AC}r_C\Phi_{A1}}{(1 - K_A\Phi_{A1})}\right] \tag{14}$$

If $\Phi_A = 1$, Φ_{A1} and V reduce $\Phi_{A1}^{\ominus}$ and $V_A^{\ominus}$.

$$\Phi_{A1}^{\ominus} = \left[2K_A + 1 - (1 + 4K_A)^{0.5}\right]/2K_A^2 \tag{15}$$

$$\frac{1}{V_A^{\ominus}} = \frac{(1 - K_A\Phi_{A1})}{r_A} \tag{16}$$

The values of r and q were estimated from the method of Vera et al. [10].

Extended UNIQUAC *model*

The activity coefficient of component I is expressed by

$$\ln \gamma_I = \ln\left(\frac{\Phi_I}{x_I}\right) + 1 - \frac{\Phi_I}{x_I} - \left(\frac{Z}{2}\right)q_I\left[\ln\left(\frac{\Phi_I}{\theta_I}\right) + 1 - \frac{\Phi_I}{\theta_I}\right] - q_I' \ln\left(\sum_J \theta_I \tau_{JI}\right) + q_I \sum_J \left(\frac{q_J'}{q_J}\right)\theta_J - q_I \sum_J \frac{(q_J'/q_J)\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}} \tag{17}$$

The values of r, q and q' were taken from Prausnitz et al. [11] and Nagata [2]. These values are given in Table 3.

TABLE 3

Pure-component molecular structural parameters

Component	UNIQUAC associated-solution		Extended UNIQUAC		
	r	q	r	q	q'
Ethanol	1.69	1.55	2.11	1.97	0.92
Acetonitrile	1.50	1.40	1.87	1.97	$q^{0.2}$
Acetone	2.06	1.85	2.57	2.34	$q^{0.2}$

The binary VLE data were reduced by minimizing the objective function

$$F=\sum_{i=1}^{N}\left[\frac{(P_i-\hat{P}_i)^2}{\sigma_P^2}+\frac{(T_i-\hat{T}_i)^2}{\sigma_T^2}+\frac{(x_{1i}-\hat{x}_{1i})^2}{\sigma_x^2}+\frac{(y_{1i}-\hat{y}_{1i})^2}{\sigma_y^2}\right] \tag{18}$$

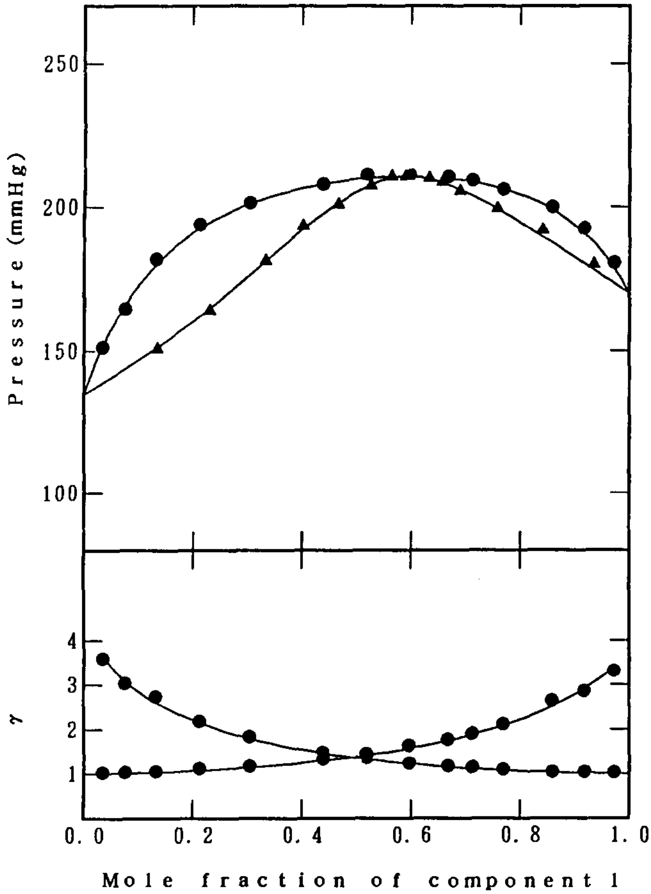

Fig. 1. Vapour–liquid equilibria for ethanol (1) + acetonitrile (2) at 40°C. (———) Calculated from the UNIQUAC associated-solution model. Experimental: (•) liquid-phase mole fraction; (▲) vapour-phase mole fraction.

TABLE 4

Binary results of vapour–liquid equilibrium data reduction

System (A + B)	Temp. (°C)	Number of data points	Model [a]	Root-mean-square deviations				Variance [b] of fit	Energy parameters	
				δP (mmHg)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)		a_{AB} (K)	a_{BA} (K)
Ethanol + acetonitrile	40	14	I	0.89	0.02	0.6	4.2	3.82	520.85	71.20
			II	0.95	0.02	0.5	4.3	3.82	286.07	171.03
Ethanol + acetone	50	13	I	0.26	0.00	0.1		0.09	314.20	−9.78
			II	0.37	0.00	0.2		0.20	153.38	90.10
Acetonitrile + acetone	45	10	I	0.80	0.03	0.3	1.5	1.75	37.09	−17.86
			II	0.42	0.01	0.2	1.5	0.67	120.93	−61.63

[a] **I**, UNIQUAC associated-solution model; **II**, extended UNIQUAC model.

[b] Variance of fit = (sum of squared, weighted residuals)/(number of degrees of freedom) = F/(number of data points minus number of parameters).

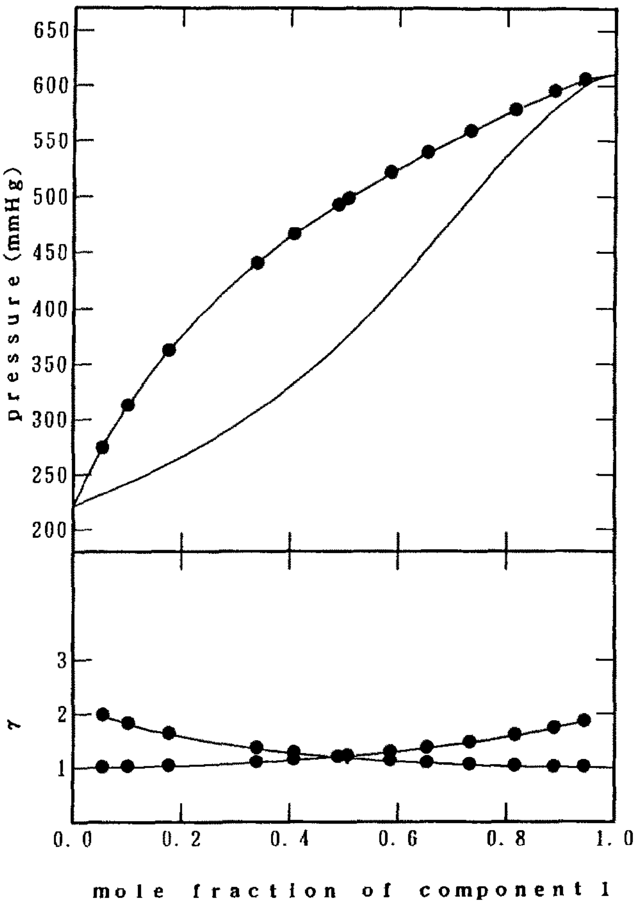

Fig. 2. Vapour–liquid equilibria for ethanol (1) + acetone (2) at 50°C. (———) Calculated from the UNIQUAC associated-solution model. Experimental: (•) liquid-phase mole fraction.

where a circumflex denotes the calculated value, and the standard deviations of the measured variables are $\sigma_P = 1$ Torr for pressure; $\sigma_T = 0.05$ K for temperature; $\sigma_x = 0.001$ for liquid mole fraction; $\sigma_y = 0.003$ for vapour mole fraction. The computer program used is similar to that described by Prausnitz et al. [11]. In the binary and ternary data reduction the pure component vapour pressures were taken from the literature [5,6].

The association parameters for ethanol are $K_A = 110.4$ at 50°C [12] and $h_A = -23.2$ kJ mol^{-1} [13]. The solvation constant and the enthalpy of complex formation are as follows: $K_{AB} = 50$ at 40°C and $h_{AB} = -17$ kJ mol^{-1} [1] for ethanol + acetonitrile; $K_{AC} = 35$ at 50°C and $h_{AC} = -21$ kJ mol^{-1} for ethanol + acetone.

Table 4 gives the binary calculated results. Figures 1 and 2 compare the calculated values derived from the UNIQUAC associated-solution model with the experimental results for the ethanol + acetonitrile and ethanol +

TABLE 5

Ternary calculated results for the ethanol (1) + acetonitrile (2) + acetone (3) system at 45°C

Deviation	Model [a]	Vapour mole fractions			Pressure	
		δy_1 ($\times 10^3$)	δy_2 ($\times 10^3$)	δy_3 ($\times 10^3$)	δP (mmHg)	$\delta P/P$ (%)
Absolute mean	I	1.6	4.2	4.2	1.94	0.59
	II	2.5	4.7	4.9	3.02	0.89
Root mean square	I	1.9	5.8	5.3	2.82	0.89
	II	3.1	5.6	6.0	3.79	1.12

[a] I, UNIQUAC associated-solution model; II, extended UNIQUAC model.

acetone systems. All the three systems show positive deviations from Raoult's law.

Table 5 shows the ternary predicted results based on the binary parameters. The UNIQUAC associated-solution model gives the smaller deviations in

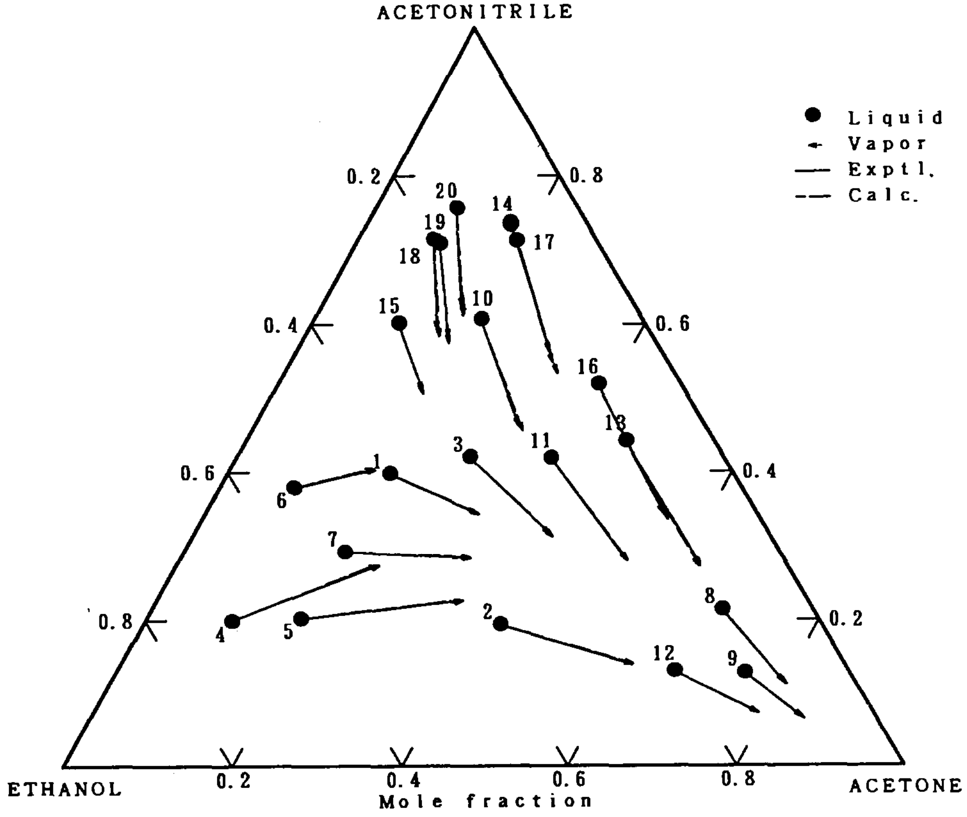

Fig. 3. Equilibrium tie-lines: calculated values are obtained from the UNIQUAC associated-solution model.

the vapour compositions and pressure than the extended UNIQUAC model, showing that agreement is good. In Table 2 the predicted values based on the UNIQUAC associated-solution model are given and nos. 10, 11, 13–20 data points show that the experimental activity coefficients of acetone are less than unity and the UNIQUAC associated-solution model (the extended UNIQUAC model also) is able to predict these values quite well. The calculated tie-lines are illustrated with the experimental results in Fig. 3.

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