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ISOTHERMAL VAPOUR–LIQUID EQUILIBRIUM FOR THE METHANOL–ETHANOL–ACETONITRILE–BENZENE SYSTEM

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ABSTRACT

Isothermal vapour–liquid equilibrium data at 45 °C were measured for the methanol–ethanol–acetonitrile–benzene system. The measured results agree well with those calculated from the UNIQUAC (universal quasi-chemical) associated-solution model, which assumes the self-association of pure alcohol molecules, the multi-solvation of unlike alcohol *i*-mers and the solvation of alcohol *i*-mers with an active unassociated component (acetonitrile or benzene).

LIST OF SYMBOLS

A, B, C, D	methanol, ethanol, acetonitrile and benzene
a_{IJ}	binary interaction energy parameter for the $I-J$ pair
B_{IJ}	second virial coefficient for the $I-J$ pair
F	objective function as defined by eqn. (21)
h_A, h_B	enthalpies of hydrogen-bond formation of alcohols A and B
h_{AB}, h_{AC}, h_{AD}, h_{BC}, h_{BD}	enthalpies of complex formation between unlike molecules
P	total pressure
P_I^s	saturated vapour pressure of pure component I
q_I	molecular geometric-area parameter of pure component I
R	universal gas constant
r_I	molecular geometric-volume parameter of pure component I
$\bar{S}_A$, $\bar{S}_B$	sums as defined by eqns. (12) and (13)
S_A, S_B	sums as defined by eqns. (14) and (15)
T	absolute temperature
V	true molar volume of alcohol mixture
V_A^0, V_B^0	true molar volumes of pure alcohols A and B
v_I^L	molar liquid volume of pure component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
Z	lattice coordination number, equal to 10

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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-phase mole fraction and vapour-phase mole fraction
τ_{IJ}	$\exp(-a_{IJ}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
$\Phi^o_{A_1}$, $\Phi^o_{B_1}$	monomer segment fractions of pure alcohols A and B
ϕ_I	vapour-phase fugacity coefficient of component I at P and T
ϕ_I^s	vapour-phase fugacity coefficient of pure component I at P_I^s and T

Subscripts

A, B, C, D	alcohols and active non-associating components
A_1, B_1, C_1, D_1	monomers of components A, B, C and D
A_i, B_i	i-mers of alcohols A and B
AB, AC, AD, BC, BD	binary complexes
A_iB_jC, A_iB_jD	complexes containing i molecules of alcohol A, j molecules of alcohol B and one molecule of component C or D
A_iC, A_iD	complexes containing i molecules of alcohol A and one molecule of component C or D
B_iC, B_iD	complexes containing i molecules of alcohol B and one molecule of component C or D
I, J, K	components I, J and K
i, j, k, l	i, j, k and l-mers of alcohols or indices

INTRODUCTION

Isothermal vapour–liquid equilibrium (VLE) and liquid–liquid equilibrium data for ternary mixtures including two alcohols and one non-associating component have been successfully analysed using the UNIQUAC associated-solution model [1–3]. Isothermal VLE have not been reported for any quaternary mixtures containing two alcohols [4]. In the present work isothermal VLE data were obtained for quaternary mixtures of methanol, ethanol, acetonitrile and benzene in order to examine the ability of the UNIQUAC associated-solution model. Binary isothermal VLE data for the six systems constituting the present quaternary system were taken from the literature: for methanol–ethanol at 40 °C [5]; for methanol–acetonitrile at 55 °C [6]; for methanol–benzene at 55 °C [7]; for ethanol–acetonitrile at 40 °C [8]; for ethanol–benzene at 45 °C [7]; and for acetonitrile-benzene at 45 °C [9]. These data were used to obtain the binary parameters of the UNIQUAC associated-solution model.

EXPERIMENTAL

Acetonitrile (Wako Pure Chemical Industries Ltd., analytical reagent grade) was used without further purification. Chemically pure alcohols were refluxed over calcium oxide and then fractionally distilled in a glass column packed with McMahon packing. Chemically pure benzene was subjected to repeated recrystallization. An Anton Paar densiometer (DMA40) was used for density measurements at 25 ° C. A Boublik vapour-recirculation still described previously [10] was utilized to measure the vapour pressures of pure components as well as the VLE data for the mixtures. The experimental densities and vapour pressures of the chemicals used are compared with literature values [11–13] in Table 1. Compositions of the liquid- and vapour-phase samples were determined using a gas chromatograph (Shimadzu GC-7A) and an electronic integrator (Shimadzu Chromatopac E-1B). The measured variables were believed to contain the following errors: pressure, 0.16 Torr; temperature, 0.05 ° C; mole fraction for liquid- and vapour-phase compositions, 0.002.

RESULTS AND DATA ANALYSIS

The VLE at 45 ° C for the methanol–ethanol–acetonitrile–benzene system are given in Table 2. The activity coefficient γ_I and the fugacity coefficient ϕ_I of component I were obtained from eqns. (1) and (2), respectively.

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

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

where the measured variables symbolize: P, total pressure; P^{s}, pure-component vapour pressure; y, vapour-phase mole fraction; x, liquid-phase mole fraction; T, absolute temperature. The term v^{L} is the pure liquid molar volume estimated from the modified Rackett equation [14] and the second

TABLE 1

Densities and vapour pressures of pure components

Component	Density at 25 ° C (g cm^{-3})		Vapour pressure at 45 ° C (Torr)	
	Observed	From ref. 11	Observed	From ref. 11
Methanol	0.78662	0.78664	331.2	331.28
Ethanol	0.78516	0.78504	172.9	173.68
Acetonitrile	0.77661	0.7766	208.3	208.35 (from ref. 12)
Benzene	0.87373	0.87370	223.7	223.51 223.66 (from ref. 13)

TABLE 2

Structural and association parameters for components

Component	r	q	K at 50 °C	$-h$ (kJ mol^{-1})
Methanol	1.15	1.12	173.9	23.2
Ethanol	1.69	1.55	110.4	23.2
Acetonitrile	1.50	1.40		
Benzene	2.56	2.05		

virial coefficients B were calculated using the correlation of Hayden and O'Connell [15].

The VLE data were analysed using the UNIQUAC associated-solution model [1] for mixtures containing two alcohols.

A, B, C and D stand for methanol, ethanol, acetonitrile and benzene, respectively. The model assumes that alcohol molecules linearly associate and solvate to yield alcohol polymers and copolymers, which further form chemical complexes with acetonitrile and benzene. These chemical complexes are A_i, B_i, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, $B_i(A_jB_k)_l$, A_iC, A_iD, B_iC, B_iD, $(A_iB_j)_kC$, $(A_iB_j)_kD$, $(B_iA_j)_kC$, $(B_iA_j)_kD$, $A_i(B_jA_k)_lC$, $A_i(B_jA_k)_lD$, $B_i(A_jB_k)_lC$ and $B_i(A_jB_k)_lD$, which are given by chemical reactions

$$
\begin{array}{ll}
A_1 + A_1 = A_2 & B_1 + B_1 = B_2 \\
A_2 + A_1 = A_3 & B_2 + B_1 = B_3 \\
\vdots & \vdots \\
A_i + A_1 = A_{i+1} & B_i + B_1 = B_{i+1} \\
A_i + B_j = A_iB_j & B_i + A_j = B_iA_j \\
A_iB_j + A_iB_j = (A_iB_j)_2 & B_iA_j + B_iA_j = (B_iA_j)_2 \\
\vdots & \vdots \\
(A_iB_j)_k + A_iB_j = (A_iB_j)_{k+1} & (B_iA_j)_k + B_iA_j = (B_iA_j)_{k+1} \\
A_i + (B_jA_k)_l = A_i(B_jA_k)_l & B_i + (A_jB_k)_l = B_i(A_jB_k)_l \\
A_i + C = A_iC & B_i + C = B_iC \\
A_i + D = A_iD & B_i + D = B_iD \\
(A_iB_j)_k + C = (A_iB_j)_kC & (B_iA_j)_k + C = (B_iA_j)_kC \\
(A_iB_j)_k + D = (A_iB_j)_kD & (B_iA_j)_k + D = (B_iA_j)_kD \\
A_i(B_jA_k)_l + C = A_i(B_jA_k)_lC & B_i(A_jB_k)_l + C = B_i(A_jB_k)_lC \\
A_i(B_jA_k)_l + D = A_i(B_jA_k)_lD & B_i(A_jB_k)_l + D = B_i(A_jB_k)_lD
\end{array}
$$

where the subscripts i, j, k and l go from one to infinity. The equilibrium constants for these reactions are assumed to be independent of the degree of association and solvation.

The activity coefficients of methanol (A) and acetonitrile (C) of the quaternary system are given by

$$\ln \gamma_{\mathrm{A}} = \ln\left(\frac{\Phi_{\mathrm{A}_1}}{\Phi^{\mathrm{o}}_{\mathrm{A}_1} x_{\mathrm{A}}}\right) + \frac{r_{\mathrm{A}}}{V^{\mathrm{o}}_{\mathrm{A}}} - \frac{r_{\mathrm{A}}}{V} - \left(\frac{Z}{2}\right) q_{\mathrm{A}}\left(\ln\frac{\Phi_{\mathrm{A}}}{\theta_{\mathrm{A}}} + 1 - \frac{\Phi_{\mathrm{A}}}{\theta_{\mathrm{A}}}\right)$$

$$+ q_{\mathrm{A}}\left[1 - \ln\left(\sum_J \theta_{\mathrm{A}} \tau_{J\mathrm{A}}\right) - \sum_J \frac{\theta_J \tau_{\mathrm{A}J}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{3}$$

$$\ln \gamma_{\mathrm{C}} = \ln\frac{\Phi_{\mathrm{C}_1}}{x_{\mathrm{C}}} + 1 - \frac{r_{\mathrm{C}}}{V} - \left(\frac{Z}{2}\right) q_{\mathrm{C}}\left(\ln\frac{\Phi_{\mathrm{C}}}{\theta_{\mathrm{C}}} + 1 - \frac{\Phi_{\mathrm{C}}}{\theta_{\mathrm{C}}}\right)$$

$$+ q_{\mathrm{C}}\left[1 - \ln\left(\sum_J \theta_{\mathrm{C}} \tau_{J\mathrm{C}}\right) - \sum_J \frac{\theta_J \tau_{\mathrm{C}J}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{4}$$

where Z is the coordination number equal to 10 and the segment fraction Φ, the area fraction θ and the adjustable parameter τ_{IJ} related to the energy parameter a_{IJ} for the I–J pair are expressed by

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

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

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

r and q are the pure-component molecular constants the values of which can be calculated using the method of Vera et al. [16]. The activity coefficients of ethanol and benzene are derived by changing the subscript A to B in eqn. (3) and C to D in eqn. (4). The monomer segment fractions, Φ_{A_1}, Φ_{B_1}, Φ_{C_1} and Φ_{D_1} are solved simultaneously from the following mass-balance equations.

$$\Phi_{\mathrm{A}} = \left(1 + r_{\mathrm{A}} K_{\mathrm{AC}} \Phi_{\mathrm{C}_1} + r_{\mathrm{A}} K_{\mathrm{AD}} \Phi_{\mathrm{D}_1}\right) \bar{S}_{\mathrm{A}} + \frac{r_{\mathrm{A}} K_{\mathrm{AB}} \bar{S}_{\mathrm{A}} S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)^2}$$

$$\times \Big\{2 + r_{\mathrm{B}} K_{\mathrm{AB}} S_{\mathrm{A}} \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right) + r_{\mathrm{A}} K_{\mathrm{AB}} S_{\mathrm{B}}$$

$$+ \Phi_{\mathrm{C}_1}\left[\left(r_{\mathrm{A}} K_{\mathrm{AC}} + r_{\mathrm{B}} K_{\mathrm{BC}}\right) + r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}} K_{\mathrm{AC}} S_{\mathrm{A}} \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)\right.$$

$$\left. + r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}} K_{\mathrm{BC}} S_{\mathrm{B}}\right]$$

$$+ \Phi_{\mathrm{D}_1}\left[\left(r_{\mathrm{A}} K_{\mathrm{AD}} + r_{\mathrm{B}} K_{\mathrm{BD}}\right) + r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}} K_{\mathrm{AD}} S_{\mathrm{A}} \left(2 - r_{\mathrm{A}} r_{\mathrm{B}} K^2_{\mathrm{AB}} S_{\mathrm{A}} S_{\mathrm{B}}\right)\right.$$

$$\left. + r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}} K_{\mathrm{BD}} S_{\mathrm{B}}\right]\Big\} \tag{8}$$

$$\begin{aligned}\Phi_{\mathrm{B}} = {} & \left(1 + r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1} + r_{\mathrm{B}}K_{\mathrm{BD}}\Phi_{\mathrm{D}_1}\right)\bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\bar{S}_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)^2} \\ & \times\Big\{2 + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}\left(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right) + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}} \\ & \quad \Phi_{\mathrm{C}_1}\left[\left(r_{\mathrm{A}}K_{\mathrm{AC}} + r_{\mathrm{B}}K_{\mathrm{BC}}\right) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}\left(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)\right. \\ & \left. + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}\right] \\ & + \Phi_{\mathrm{D}_1}\left[\left(r_{\mathrm{A}}K_{\mathrm{AD}} + r_{\mathrm{B}}K_{\mathrm{BD}}\right) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BD}}S_{\mathrm{B}}\left(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)\right. \\ & \left. + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AD}}S_{\mathrm{A}}\right]\Big\} \end{aligned} \tag{9}$$

$$\begin{aligned}\Phi_{\mathrm{C}} = {} & \Phi_{\mathrm{C}_1}\Big\{1 + r_{\mathrm{C}}K_{\mathrm{AC}}S_{\mathrm{A}} + r_{\mathrm{C}}K_{\mathrm{BC}}S_{\mathrm{B}} \\ & + \frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{C}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)}\left[\frac{K_{\mathrm{AC}}}{r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{K_{\mathrm{BC}}}{r_{\mathrm{A}}K_{\mathrm{AB}}} + K_{\mathrm{AC}}S_{\mathrm{A}} + K_{\mathrm{BC}}S_{\mathrm{B}}\right]\Big\}\end{aligned} \tag{10}$$

$$\begin{aligned}\Phi_{\mathrm{D}} = {} & \Phi_{\mathrm{D}_1}\Big\{1 + r_{\mathrm{D}}K_{\mathrm{AD}}S_{\mathrm{A}} + r_{\mathrm{D}}K_{\mathrm{BD}}S_{\mathrm{B}} \\ & + \frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{D}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)}\left[\frac{K_{\mathrm{AD}}}{r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{K_{\mathrm{BD}}}{r_{\mathrm{A}}K_{\mathrm{AB}}} + K_{\mathrm{AD}}S_{\mathrm{A}} + K_{\mathrm{BD}}S_{\mathrm{B}}\right]\Big\}\end{aligned} \tag{11}$$

where the sums $\bar{S}_{\mathrm{A}}$, $\bar{S}_{\mathrm{B}}$, S_{A} and S_{B} are defined by

$$\bar{S}_{\mathrm{A}} = \Phi_{\mathrm{A}_1}/\left(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right)^2 \tag{12}$$

$$\bar{S}_{\mathrm{B}} = \Phi_{\mathrm{B}_1}/\left(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}\right)^2 \tag{13}$$

$$S_{\mathrm{A}} = \Phi_{\mathrm{A}_1}/\left(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}\right) \tag{14}$$

$$S_{\mathrm{B}} = \Phi_{\mathrm{B}_1}/\left(1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}\right) \tag{15}$$

The true molar volume of the quaternary mixture V is given by

$$\begin{aligned}\frac{1}{V} = {} & \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}} + \left(\frac{2}{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{S_{\mathrm{A}}}{r_{\mathrm{A}}} + \frac{S_{\mathrm{B}}}{r_{\mathrm{B}}}\right)\frac{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)} \\ & + \frac{\Phi_{\mathrm{C}_1}}{r_{\mathrm{C}}}\Big\{1 + r_{\mathrm{C}}K_{\mathrm{AC}}S_{\mathrm{A}} + r_{\mathrm{C}}K_{\mathrm{BC}}S_{\mathrm{B}} \\ & + \left[\left(\frac{1}{r_{\mathrm{B}}K_{\mathrm{AB}}} + S_{\mathrm{A}}\right)K_{\mathrm{AC}} + \left(\frac{1}{r_{\mathrm{A}}K_{\mathrm{AB}}} + S_{\mathrm{B}}\right)K_{\mathrm{BC}}\right]\frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{C}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}\right)}\Big\}\end{aligned}$$

$$+\frac{\Phi_{\mathrm{D}_1}}{r_{\mathrm{D}}}\left\{1 + r_{\mathrm{D}}K_{\mathrm{AD}}S_{\mathrm{A}} + r_{\mathrm{D}}K_{\mathrm{BD}}S_{\mathrm{B}}\right.$$

$$\left.+\left[\left(\frac{1}{r_{\mathrm{B}}K_{\mathrm{AB}}} + S_{\mathrm{A}}\right)K_{\mathrm{AD}} + \left(\frac{1}{r_{\mathrm{A}}K_{\mathrm{AB}}} + S_{\mathrm{B}}\right)K_{\mathrm{BD}}\right]\frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{D}}K_{\mathrm{AB}}^2 S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2 S_{\mathrm{A}}S_{\mathrm{B}}\right)}\right\} \tag{16}$$

The true molar volumes $V_{\mathrm{A}}^{\mathrm{o}}$ and $V_{\mathrm{B}}^{\mathrm{o}}$ and the monomer-segment fractions for pure alcohols $\Phi_{\mathrm{A}_1}^{\mathrm{o}}$ and $\Phi_{\mathrm{B}_1}^{\mathrm{o}}$ are expressed by

$$\frac{1}{V_{\mathrm{A}}^{\mathrm{o}}} = \lim_{\substack{x_{\mathrm{B}}\to 0\\ x_{\mathrm{C}}\to 0\\ x_{\mathrm{D}}\to 0}} \frac{1}{V} = \frac{1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1}^{\mathrm{o}}}{r_{\mathrm{A}}} \tag{17}$$

$$\frac{1}{V_{\mathrm{B}}^{\mathrm{o}}} = \lim_{\substack{x_{\mathrm{A}}\to 0\\ x_{\mathrm{C}}\to 0\\ x_{\mathrm{D}}\to 0}} \frac{1}{V} = \frac{1 - K_{\mathrm{B}}\Phi_{\mathrm{B}_1}^{\mathrm{o}}}{r_{\mathrm{B}}} \tag{18}$$

$$\Phi_{\mathrm{A}_1}^{\mathrm{o}} = \left[2K_{\mathrm{A}} + 1 - (1 + 4K_{\mathrm{A}})^{0.5}\right]/2K_{\mathrm{A}}^2 \tag{19}$$

$$\Phi_{\mathrm{B}_1}^{\mathrm{o}} = \left[2K_{\mathrm{B}} + 1 - (1 + 4K_{\mathrm{B}})^{0.5}\right]/2K_{\mathrm{B}}^2 \tag{20}$$

The association constants at 50 ° C were taken from the paper by Brandani [17]. The enthalpy of hydrogen-bond formation of -23.2 kJ mol^{-1} was obtained for alcohols from Stokes and Burfitt [18]. The values of the solvation constant at 50 °C and the enthalpy of complex formation are $K_{\mathrm{AB}} = 130$ and $h_{\mathrm{AB}} = -23.2$ kJ mol^{-1} for methanol–ethanol [1], $K_{\mathrm{AC}} = 30$ and $h_{\mathrm{AC}} = -17$ kJ mol^{-1} for methanol–acetonitrile [19], $K_{\mathrm{AD}} = 4$ and $h_{\mathrm{AD}} = -8.3$ kJ mol^{-1} for methanol–benzene [19], $K_{\mathrm{BC}} = 50$ (40 °C) and $h_{\mathrm{BC}} = -17$ kJ mol^{-1} for ethanol–acetonitrile [19] and $K_{\mathrm{BD}} = 3$ and $h_{\mathrm{BD}} = -8.3$ kJ mol^{-1} for ethanol–benzene [19]. All the h values were assumed to be independent of temperature and the van't Hoff relation gives the temperature dependence of the equilibrium constants. The association and structural constants for the pure components are given in Table 3.

Binary-parameter estimation was performed using a computer program similar to that described by Prausnitz et al. [20] and minimizing the objective function given by

$$F = \sum_{i=1}^{N}\left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2}\right] \tag{21}$$

where a circumflex indicates the calculated value and the standard deviations in the measured variables were taken as: pressure, $\sigma_P = 1$ Torr; temperature, $\sigma_T = 0.05$ K; liquid-phase mole fraction, $\sigma_x = 0.001$; vapour-phase mole fraction, $\sigma_y = 0.003$. The estimated energy parameters and the

TABLE 3

Vapour–liquid equilibrium data for the methanol(**1**)–ethanol(**2**)–acetonitrile(**3**)–benzene(**4**) system at 45 °C [a]

No.	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
1	0.136	0.418	0.292	0.154	0.166	0.279	0.293	0.262
2	0.192	0.732	0.039	0.037	0.260	0.509	0.100	0.131
3	0.694	0.224	0.044	0.038	0.693	0.116	0.073	0.118
4	0.118	0.606	0.143	0.133	0.140	0.385	0.198	0.277
5	0.477	0.245	0.148	0.130	0.468	0.125	0.160	0.247
6	0.197	0.319	0.249	0.235	0.241	0.205	0.230	0.324
7	0.197	0.210	0.302	0.291	0.256	0.159	0.256	0.329
8	0.094	0.108	0.414	0.384	0.188	0.114	0.318	0.380
9	0.201	0.719	0.022	0.058	0.259	0.491	0.054	0.196
10	0.295	0.447	0.070	0.188	0.311	0.250	0.094	0.345
11	0.507	0.217	0.073	0.203	0.486	0.111	0.079	0.324
12	0.398	0.115	0.128	0.359	0.446	0.066	0.109	0.379
13	0.400	0.105	0.253	0.242	0.439	0.062	0.199	0.300
14	0.275	0.452	0.201	0.072	0.308	0.275	0.252	0.165
15	0.464	0.445	0.068	0.023	0.517	0.292	0.121	0.070
16	0.680	0.230	0.068	0.022	0.697	0.123	0.112	0.068
17	0.279	0.287	0.118	0.316	0.321	0.169	0.119	0.391
18	0.210	0.544	0.071	0.175	0.233	0.332	0.104	0.331
19	0.203	0.706	0.071	0.020	0.262	0.509	0.160	0.069
20	0.505	0.188	0.202	0.105	0.499	0.102	0.202	0.197
21	0.181	0.251	0.438	0.130	0.238	0.197	0.369	0.196
22	0.266	0.491	0.099	0.144	0.289	0.290	0.136	0.285
23	0.229	0.379	0.309	0.083	0.267	0.259	0.320	0.154
24	0.209	0.307	0.381	0.103	0.250	0.230	0.350	0.170
25	0.118	0.578	0.234	0.070	0.142	0.395	0.295	0.168

[a] $B_{11} = -1764$ cm^{3}mol^{-1}, $B_{22} = -1518$ cm^{3}mol^{-1}, $B_{33} = -4550$ cm^{3}mol^{-1}, $B_{44} = -1259$ cm^{3}mol^{-1}, $B_{12} = -1662$ cm^{3}mol^{-1}, $B_{13} = -2204$ cm^{3}mol^{-1}, $B_{14} = -464$ cm^{3}mol^{-1}, $B_{23} = -2303$ cm^{3}mol^{-1}, $B_{24} = -665$ cm^{3}mol^{-1}, $B_{34} = -1194$ cm^{3}mol^{-1}, $v_1^L = 40.31$ cm^{3}mol^{-1}, $v_2^L = 59.32$ cm^{3}mol^{-1}, $v_3^L = 53.75$ cm^{3}mol^{-1} and $v_4^L = 91.75$ cm^{3}mol^{-1}.

TABLE 4

Binary calculated results obtained from vapour–liquid equilibrium data reduction

System	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters (K)	
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{AB}	a_{BA}
Methanol(A)–ethanol(B)	40	13	0.34	0.00	0.0		−35.53	180.59
Methanol(A)–acetonitrile(B)	55	13	1.59	0.00	1.2	5.3	480.17	−113.15
Methanol(A)–benzene(B)	55	9	0.94	0.06	1.4	4.7	−71.04	220.25
Ethanol(A)–acetonitrile(B)	40	14	0.89	0.02	0.6	4.2	520.85	71.20
Ethanol(A)–benzene(B)	45	12	0.83	0.02	0.6	3.9	10.38	97.26
Acetonitrile(A)–benzene(B)	45	12	0.78	0.02	0.5	3.6	−10.54	258.38

P (torr)	γ_1	γ_2	γ_3	γ_4	ϕ_1	ϕ_2	ϕ_3	ϕ_4
321.7	1.1948	1.2299	1.5329	2.4734	0.979	0.978	0.943	0.997
252.0	1.0393	1.0070	3.1241	4.0466	0.979	0.981	0.960	1.000
333.2	1.0053	0.9840	2.6469	4.7115	0.972	0.974	0.951	1.005
301.7	1.0895	1.0989	1.9984	2.8344	0.979	0.979	0.950	0.995
368.8	1.0934	1.0711	1.8902	3.1667	0.972	0.972	0.942	0.997
350.1	1.3006	1.2855	1.5339	2.1736	0.977	0.975	0.942	0.994
357.8	1.4118	1.5472	1.4352	1.8218	0.977	0.975	0.940	0.994
348.7	2.1248	2.1072	1.2674	1.5526	0.980	0.977	0.940	0.993
256.6	1.0071	1.0069	3.0502	3.9228	0.979	0.981	0.962	0.998
337.5	1.0800	1.0789	2.1694	2.7843	0.976	0.976	0.951	0.992
395.8	1.1450	1.1506	2.0344	2.8414	0.971	0.970	0.944	0.993
408.7	1.3835	1.3329	1.6487	1.9351	0.972	0.970	0.941	0.990
401.1	1.3291	1.3456	1.4858	2.2409	0.971	0.970	0.936	0.995
308.0	1.0479	1.0728	1.8396	3.2034	0.977	0.977	0.946	1.001
289.8	0.9796	1.0890	2.4777	4.0191	0.976	0.978	0.954	1.005
323.8	1.0036	0.9884	2.5518	4.5700	0.972	0.974	0.951	1.008
369.7	1.2899	1.2421	1.7756	2.0515	0.975	0.974	0.946	0.990
316.2	1.0666	1.1050	2.2221	2.6905	0.978	0.978	0.953	0.993
245.9	0.9670	1.0195	2.6754	3.8583	0.980	0.981	0.959	1.003
363.4	1.0850	1.1225	1.7198	3.0914	0.972	0.972	0.940	1.001
328.0	1.3119	1.4741	1.3061	2.2454	0.978	0.978	0.939	1.002
325.1	1.0721	1.0980	2.1350	2.9007	0.976	0.976	0.950	0.995
317.0	1.1233	1.2404	1.5571	2.6732	0.977	0.977	0.942	1.003
324.7	1.1807	1.3927	1.4113	2.4353	0.978	0.977	0.940	1.003
291.5	1.0682	1.1431	1.7525	3.1737	0.979	0.980	0.947	1.001

root-mean-square deviations of the measured values from the most probable calculated ones are listed in Table 4. The deviations between the experimental and predicted values of the vapour compositions and the total pressure

TABLE 5

Quaternary calculated results for the methanol(**1**)–ethanol(**2**)–acetonitrile(**3**)–benzene(**4**) system at 45 ° C

	Vapour mole fractions ($\times 10^3$)				Pressure	
	δy_1	δy_2	δy_3	δy_4	δP (Torr)	$\delta P/P$ (%)
Absolute mean deviation	5.5	7.4	3.6	7.1	2.3	0.7
Root-mean-square deviation	6.5	9.1	4.8	9.5	3.0	0.9

for the present quaternary system are given in Table 5. The magnitude of the deviations is nearly the same as that obtained for many ternary alcohol mixtures [1,2,19].

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