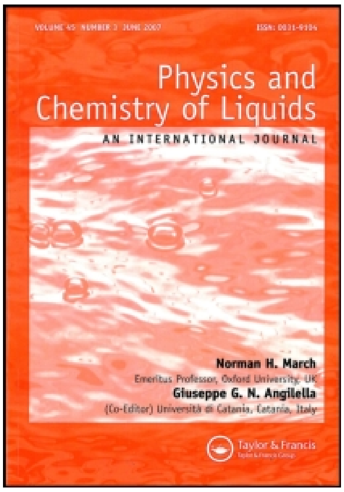

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# Isothermal Vapour-Liquid Equilibria for the Ethanol 1-Propanol Acetonitrile Benzene System

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# ISOTHERMAL VAPOUR-LIQUID EQUILIBRIA FOR THE ETHANOL + 1-PROPANOL + ACETONITRILE + BENZENE SYSTEM

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Isothermal quaternary vapour-liquid equilibria for mixtures containing ethanol, 1-propanol, acetonitrile and benzene have been measured using a vapour-recirculating Boublik still at 318.15 K. The experimental results compare well with those calculated from the UNIQUAC associated-solution model, which assumes the association of alsochols and the solvation of unlike molecules and includes binary parameters alone.

KEY WORDS: Associated solution, molecular complexation, quaternary vapour liquid equilibria.

## LIST OF SYMBOLS

| | |
|---|---|
| $A, B, C, D$ | ethanol, 1-propanol, acetonitrile and benzene |
| $a_{IJ}$ | binary interaction energy parameter for I-J pair |
| $B_{IJ}$ | second virial coefficient for I-J pair |
| $F$ | objective function as defined by Eq. (18) |
| $h_A$, $h_B$ | 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 |
| $S_A$, $S_B$ | sums as defined by Eqs (14) and (15) |
| $\bar{S}_A$, $\bar{S}_B$ | sums as defined by Eqs (16) and (17) |
| $T$ | absolute temperature |
| $V$ | true molar volume of alcohol mixture |
| $V_A^\circ$, $V_A^\circ$ | 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 |

Greek letters

| | |
|---|---|
| $\gamma_I$ | activity coefficient of component I |
| $\theta_I$ | area fraction of component I |
| $\sigma_P$, $\sigma_T$ | standard deviations in pressure and temperature |
| $\sigma_x$, $\sigma_y$ | standard deviations in liquid and vapour-phase mole fractions |
| $\tau_{IJ}$ | $\exp(-a_{IJ}/T)$ |
| $\Phi_I$ | segment fraction of component I |
| $\Phi_{I_1}$ | monomer segment fraction of component I |
| $\Phi^{\circ}_{A_1}$, $\Phi^{\circ}_{B_1}$ | monomer segment fractions of pure alcohols $A$ and $B$ |
| $\phi_I$ | vapour-phase fugacity coefficient of component I at $P$ and $T$ |
| $\phi^s_I$ | vapour-phase fugacity coefficient of pure component I at $P^s_I$ and $T$ |

Subscripts

| | |
|---|---|
| $A$, $B$, $C$, $D$ | alcohols and active nonassociating 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

As part of studies on the thermodynamic properties of quaternary non-electrolyte solutions including two alcohols, this work has two objectives: (1) to report experimental vapour-liquid equilibrium results for the ethanol + 1-propanol + acetonitrile + benzene system at 318.15; (2) to investigate the ability of the UNIQUAC associated-solution model[1,2] in data analysis. Six experimental vapour-liquid equilibrium data sets for binary systems constituting the quaternary system have been reported in the literature: ethanol + 1-propanol[3] at 313.15 K; ethanol + acetonitrile[4] at 313.15 K; ethanol + benzene[5] at 318.15 K; 1-propanol + acetonitrile[6] at 328.15 K; 1-propanol + benzene[5] at 318.15 K; acetonitrile + benzene[7] at 318.15 K.

# EXPERIMENTAL

Acetonitrile and 1-propanol (special grade; Wako Pure Chemical Industries Ltd.) were used without further purification. C.P. benzene was subjected to repeated recrystallization. C.P. ethanol was fractionally distilled after storage over calcium oxide. The densities of these compounds were measured with an Anton Paar (DMA40) densimeter controlled at 298.15 ± 0.01 K. The observed densities and vapour pressures compare well with literature values[8-10] in Table 1.

**Table 1** Densities and vapour pressures of pure components.

| *Component* | *Density at 298.15 K ($g\ cm^{-3}$)* | | *Vapour pressure at 318.15 K (Torr)* | |
|---|---|---|---|---|
| | *Expt.* | *Lit.*[8] | *Expt.* | *Lit.* |
| Acetonitrile | 0.7766 | 0.7766 | 208.3 | 208.35[9] |
| Benzene | 0.8737 | 0.87370 | 223.7 | 223.51[8] |
| Ethanol | 0.7852 | 0.78504 | 172.9 | 173.00[10] |
| 1-Propanol | 0.7997 | 0.79975 | 69.5 | 69.53[8] |

The vapour-liquid equilibrium results were obtained using a Boublik recirculating still as described previously.[11] Vapour and liquid compositions were determined using a Shimadzu gas chromatograph (GC-8A) and a Shimadzu Chromatopac (C-R3A). The experimental errors involved in the measured variables were estimated as 0.16 Torr for pressure, 0.05 K for temperature, 0.002 for vapour and liquid phase mole fractions.

The experimental vapour liquid equilibrium results are shown in Table 2, where the activity coefficients $\gamma_I$ and the fugacity coefficients $\phi_I$ of component I were calculated from Eqs (1) and (2).

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

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

where $P$ is the total pressure, $y$ the vapour-phase mole fraction, $x$ the liquid phase mole fraction, $P^s$ the pure component vapour pressure, $R$ the gas constant and $T$ the absolute temperature. $v^L$ is the pure liquid molar volume calculated from a modified Rackett equation[12] and the second virial coefficients $B$ were estimated using the Hayden-O'Connell correlation.[13]

**Table 2** Experimental results for the ethanol (1) + 1-propanol (2) + acetonitrile (3) + benzene (4) system at 318.15 K[a].

| No. | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $y_1$ | $y_2$ | $y_3$ | $y_4$ | P(Torr) | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ | $\gamma_4$ | $\phi_1$ | $\phi_2$ | $\phi_3$ | $\phi_4$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.108 | 0.109 | 0.197 | 0.586 | 0.144 | 0.065 | 0.217 | 0.574 | 291.2 | 2.240 | 2.459 | 1.547 | 1.276 | 0.985 | 0.979 | 0.958 | 0.987 |
| 2 | 0.206 | 0.223 | 0.142 | 0.429 | 0.196 | 0.087 | 0.182 | 0.535 | 280.0 | 1.536 | 1.546 | 1.734 | 1.564 | 0.984 | 0.978 | 0.960 | 0.988 |
| 3 | 0.321 | 0.237 | 0.110 | 0.332 | 0.258 | 0.074 | 0.163 | 0.505 | 273.8 | 1.269 | 1.210 | 1.962 | 1.867 | 0.984 | 0.978 | 0.960 | 0.989 |
| 4 | 0.182 | 0.550 | 0.065 | 0.203 | 0.162 | 0.201 | 0.153 | 0.484 | 216.9 | 1.116 | 1.127 | 2.490 | 2.325 | 0.986 | 0.983 | 0.969 | 0.991 |
| 5 | 0.400 | 0.349 | 0.063 | 0.188 | 0.316 | 0.109 | 0.136 | 0.439 | 241.5 | 1.101 | 1.069 | 2.532 | 2.534 | 0.985 | 0.979 | 0.965 | 0.991 |
| 6 | 0.197 | 0.759 | 0.011 | 0.033 | 0.285 | 0.442 | 0.069 | 0.204 | 120.6 | 1.013 | 1.005 | 3.740 | 3.376 | 0.990 | 0.989 | 0.982 | 0.998 |
| 7 | 0.621 | 0.136 | 0.064 | 0.179 | 0.437 | 0.039 | 0.123 | 0.401 | 265.6 | 1.076 | 1.075 | 2.469 | 2.673 | 0.983 | 0.976 | 0.961 | 0.991 |
| 8 | 0.400 | 0.533 | 0.016 | 0.051 | 0.443 | 0.240 | 0.075 | 0.242 | 158.5 | 1.017 | 1.017 | 3.652 | 3.401 | 0.988 | 0.985 | 0.976 | 0.997 |
| 9 | 0.697 | 0.235 | 0.018 | 0.050 | 0.633 | 0.089 | 0.064 | 0.214 | 192.8 | 1.012 | 1.036 | 3.351 | 3.371 | 0.986 | 0.980 | 0.971 | 0.997 |
| 10 | 0.420 | 0.513 | 0.034 | 0.033 | 0.463 | 0.231 | 0.146 | 0.160 | 157.7 | 1.007 | 1.012 | 3.322 | 3.465 | 0.988 | 0.984 | 0.974 | 0.999 |
| 11 | 0.391 | 0.348 | 0.134 | 0.127 | 0.314 | 0.114 | 0.260 | 0.312 | 234.4 | 1.086 | 1.088 | 2.198 | 2.599 | 0.984 | 0.979 | 0.960 | 0.996 |
| 12 | 0.610 | 0.123 | 0.139 | 0.128 | 0.436 | 0.036 | 0.234 | 0.294 | 265.5 | 1.092 | 1.096 | 2.149 | 2.751 | 0.982 | 0.975 | 0.955 | 0.995 |
| 13 | 0.321 | 0.220 | 0.238 | 0.221 | 0.261 | 0.072 | 0.301 | 0.366 | 272.9 | 1.278 | 1.262 | 1.656 | 2.036 | 0.983 | 0.977 | 0.953 | 0.994 |
| 14 | 0.208 | 0.215 | 0.294 | 0.283 | 0.188 | 0.081 | 0.331 | 0.400 | 274.6 | 1.430 | 1.464 | 1.483 | 1.748 | 0.983 | 0.978 | 0.953 | 0.994 |
| 15 | 0.105 | 0.108 | 0.402 | 0.385 | 0.129 | 0.058 | 0.377 | 0.436 | 284.5 | 2.015 | 2.163 | 1.276 | 1.450 | 0.984 | 0.978 | 0.950 | 0.993 |
| 16 | 0.210 | 0.545 | 0.127 | 0.118 | 0.191 | 0.198 | 0.291 | 0.320 | 207.5 | 1.090 | 1.072 | 2.308 | 2.542 | 0.986 | 0.982 | 0.964 | 0.996 |
| 17 | 0.699 | 0.228 | 0.055 | 0.018 | 0.646 | 0.090 | 0.189 | 0.075 | 187.6 | 1.002 | 1.051 | 3.140 | 3.550 | 0.986 | 0.981 | 0.967 | 1.001 |
| 18 | 0.404 | 0.528 | 0.052 | 0.016 | 0.451 | 0.246 | 0.223 | 0.080 | 153.4 | 0.992 | 1.019 | 3.223 | 3.484 | 0.988 | 0.985 | 0.973 | 1.001 |
| 19 | 0.206 | 0.727 | 0.051 | 0.016 | 0.267 | 0.386 | 0.258 | 0.089 | 133.2 | 1.001 | 1.011 | 3.312 | 3.365 | 0.990 | 0.988 | 0.976 | 1.001 |
| 20 | 0.609 | 0.131 | 0.201 | 0.059 | 0.463 | 0.042 | 0.339 | 0.156 | 246.1 | 1.078 | 1.115 | 1.993 | 2.953 | 0.983 | 0.977 | 0.954 | 1.001 |
| 21 | 0.424 | 0.330 | 0.190 | 0.056 | 0.356 | 0.115 | 0.370 | 0.159 | 222.8 | 1.080 | 1.101 | 2.092 | 2.873 | 0.985 | 0.980 | 0.958 | 1.002 |
| 22 | 0.220 | 0.541 | 0.184 | 0.055 | 0.206 | 0.209 | 0.417 | 0.168 | 196.9 | 1.066 | 1.083 | 2.161 | 2.732 | 0.987 | 0.984 | 0.962 | 1.002 |
| 23 | 0.099 | 0.110 | 0.601 | 0.190 | 0.126 | 0.060 | 0.525 | 0.289 | 269.2 | 1.978 | 2.083 | 1.121 | 1.858 | 0.985 | 0.980 | 0.947 | 1.001 |
| 24 | 0.205 | 0.224 | 0.436 | 0.135 | 0.196 | 0.096 | 0.469 | 0.239 | 255.8 | 1.411 | 1.554 | 1.316 | 2.055 | 0.985 | 0.980 | 0.950 | 1.001 |

[a] $B_{11}$ = 1518 cm³ mol⁻¹, $B_{22}$ = 1858 cm³ mol⁻¹, $B_{33}$ = −4550 cm³ mol⁻¹, $B_{44}$ = 1259 cm³ mol⁻¹, $B_{12}$ = 1920 cm³ mol⁻¹, $B_{13}$ = 2303 cm³ mol⁻¹, $B_{14}$ = 665 cm³ mol⁻¹, $B_{23}$ = 2462 cm³ mol⁻¹, $B_{24}$ = 879 cm³ mol⁻¹, $B_{34}$ = 1194 cm³ mol⁻¹, $v_1^L$ = 59.43 cm³ mol⁻¹, $v_2^L$ = 73.05 cm³ mol⁻¹, $v_3^L$ = 53.75 cm³ mol⁻¹ and $v_4^L$ = 91.75 cm³ mol⁻¹.

## DATA ANALYSIS

The experimental results were analyzed with the UNIQUAC associated-solution model.[1,2] A, B, C and D indicate ethanol, 1-propanol, acetonitrile and benzene, respectively. The model postulates that in a quaternary mixture containing two alcohols and two nonassociating components the association and multisolvation reactions of alcohol molecules give open hydrogen-bonded chains of any length, $A_i$, $B_i$, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$ and $B_i(A_jB_k)_l$. The terminal hydroxyl groups of alcohol chains and active nonassociating molecules form additional complexes, $A_iC$, $A_iD$, $B_iC$, $B_iD$, $(A_iB_j)_kC$, $(A_iB_j)_kD$, $(B_iA_j)_kC$, $(B_iA_j)_kD$, $A_i(B_jA_k)_lC$, $A_i(B_jA_k)_lD$, $B_i(A_jB_k)_lC$ and $B_i(A_jB_k)_lD$. All successive chemical reactions are summarized as

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

where the subscripts $i$, $j$, $k$ and $l$ take an integer ranging from one to infinity. The equilibrium constants for the above reactions are independent of the degree of association and solvation.

The activity coefficient of component I is given by

$$\ln \gamma_I = \ln\left(\frac{\Phi_{I_1}}{\Phi^{\circ}_{I_1} x_I}\right) + \frac{r_I}{V^{\circ}_I} - \frac{r_I}{V} - \left(\frac{Z}{2}\right) q_I \left(\ln \frac{\Phi_I}{\theta_I} + 1 - \frac{\Phi_I}{\theta_I}\right) + q_I\left[1 - \ln\left(\sum_J \theta_J \tau_{JI}\right) - \sum_J \frac{\theta_J \tau_{IJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{3}$$

where $Z$ is the coordination number, here equal to 10, and the segment fraction $\Phi_I$, the area fraction $\theta_I$, the binary parameter $\tau_{IJ}$ related to the interaction parameter $a_{IJ}$, the true molar volume of the quaternary mixture $V$, the true molar volume of pure component I $V_I$ and the monomer segment fraction of pure alcohol I $\Phi^{\circ}_{I_1}$ are given by

$$\Phi_I = x_I r_I / \sum_J x_J r_J \tag{4}$$

$$\theta_I = x_I q_I / \sum_J x_J q_J \tag{5}$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \tag{6}$$

$$\begin{aligned}\frac{1}{V} &= \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right)\frac{r_A r_B K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\\ &+ \frac{\Phi_{C_1}}{r_C}\Bigg\{1 + r_C K_{AC} S_A + r_C K_{BC} S_B\\ &+ \left[\left(\frac{1}{r_B K_{AB}} + S_A\right)K_{AC} + \left(\frac{1}{r_A K_{AB}} + S_B\right)K_{BC}\right]\frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\Bigg\}\\ &+ \frac{\Phi_{D_1}}{r_D}\Bigg\{1 + r_D K_{AD} S_A + r_D K_{BD} S_B\\ &+ \left[\left(\frac{1}{r_B K_{AB}} + S_A\right)K_{AD} + \left(\frac{1}{r_A K_{AD}} + S_B\right)K_{BD}\right]\frac{r_A r_B r_D K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\Bigg\} \qquad (7)\end{aligned}$$

$$\frac{1}{V_I^\circ} = \frac{1 - K_I \Phi_{I_1}^\circ}{r_I} \qquad (8)$$

$$\Phi_{I_1}^\circ = \frac{2K_I + 1 - (1 + 4K_I)^{0.5}}{2K_I^2} \qquad (9)$$

For acetonitrile $\Phi_{C_1}^\circ = 1$ and for benzene $\Phi_{D_1}^\circ = 1$. The monomer segment fractions in the mixture, $\Phi_{A_1}$, $\Phi_{B_1}$, $\Phi_{C_1}$ and $\Phi_{D_1}$, are obtained by solving simultaneously the following mass balance equations

$$\begin{aligned}\Phi_A &= (1 + r_A K_{AC}\Phi_{C_1} + r_A K_{AD}\Phi_{D_1})\bar{S}_A + \frac{r_A K_{AB}\bar{S}_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2}\\ &\times \{2 + r_B K_{AB} S_A(2 - r_A r_B K_{AB}^2 S_A S_B) + r_A K_{AB} S_B\\ &+ \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{AC} S_A(2 - r_A r_B K_{AB}^2 S_A S_B)\\ &+ r_A r_B K_{AB} K_{BC} S_B]\\ &+ \Phi_{D_1}[(r_A K_{AD} + r_B K_{BD}) + r_A r_B K_{AB} K_{AD} S_A(2 - r_A r_B K_{AB}^2 S_A S_B)\\ &+ r_A r_B K_{AB} K_{BD} S_B]\} \qquad (10)\end{aligned}$$

$$\begin{aligned}\Phi_B &= (1 + r_B K_{BC}\Phi_{C_1} + r_B K_{BD}\Phi_{D_1})\bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2}\\ &\times \{2 + r_A K_{AB} S_B(2 - r_A r_B K_{AB}^2 S_A S_B) + r_B K_{AB} S_A\\ &+ \Phi_{C_1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{BC} S_B(2 - r_A r_B K_{AB}^2 S_A S_B)\\ &+ r_A r_B K_{AB} K_{AC} S_A]\\ &+ \Phi_{D_1}[(r_A K_{AD} + r_B K_{BD}) + r_A r_B K_{AB} K_{BD} S_B(2 - r_A r_B K_{AB}^2 S_A S_B)\\ &+ r_A r_B K_{AB} K_{AD} S_A]\} \qquad (11)\end{aligned}$$

$$\Phi_C = \Phi_{C_1}\left\{1 + r_C K_{AC} S_A + r_C K_{BC} S_B + \frac{r_A r_B r_C K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\left[\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B\right]\right\} \tag{12}$$

$$\Phi_D = \Phi_{D_1}\left\{1 + r_D K_{AD} S_A + r_D K_{BD} S_B + \frac{r_A r_B r_D K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\left[\frac{K_{AD}}{r_B K_{AB}} + \frac{K_{BD}}{r_A K_{AB}} + K_{AD} S_A + K_{BD} S_B\right]\right\} \tag{13}$$

where the sums, $S_A$, $S_B$, $\bar{S}_A$ and $\bar{S}_B$, are given by

$$S_A = \frac{\Phi_{A_1}}{(1 - K_A \Phi_{A_1})} \tag{14}$$

$$S_B = \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})} \tag{15}$$

$$\bar{S}_A = \frac{\Phi_{A_1}}{(1 - K_A \Phi_{A_1})^2} \tag{16}$$

$$\bar{S}_B = \frac{\Phi_{B_1}}{(1 - K_B \Phi_{B_1})^2} \tag{17}$$

The pure component structural parameters, $r$ and $q$, were calculated from the method of Vera *et al.*[14] The association constants for ethanol and 1-propanol at 323.15 K were taken from Brandani.[15] The enthalpy of formation of a hydrogen bond is $-23.2$ kJ mol$^{-1}$, which was obtained from Stokes and Burfitt.[16] The values of the solvation constant at 323.15 K and the enthalpy of complex formation are $K_{AB} = 49.0$ and $h_{AB} = -23.2$ kJ mol$^{-1}$ for ethanol + 1-propanol,[17] $K_{AC} = 50(313.15\text{ K})$ and $h_{AC} = -17$ kJ mol$^{-1}$ for ethanol + acetonitrile,[1] $K_{AD} = 3$ and $h_{AD} = -8.3$ kJ mol$^{-1}$ for ethanol + benzene,[1] $K_{BC} = 30.0$ and $h_{BC} = -17$ kJ mol$^{-1}$ for 1-propanol + acetonitrile,[18] and $K_{BD} = 2.5$ and $h_{BD} = -8.3$ kJ mol$^{-1}$ for 1-propanol + benzene.[1] All $h$'s were assumed to be independent of the temperature and the degree of association and fix the temperature dependence of the equilibrium constants via the van't Hoff relation. Table 3 gives the structural and association parameters for pure components.

**Table 3** Structural and association parameters for pure components.

| *Component* | *r* | *q* | *K* *(323.15 K)* | $-h$ *(kJ mol$^{-1}$)* |
|---|---|---|---|---|
| Acetonitrile | 1.50 | 1.40 | | |
| Benzene | 2.56 | 2.05 | | |
| Ethanol | 1.69 | 1.55 | 110.4 | 23.2 |
| 1-Propanol | 2.32 | 1.98 | 87.0 | 23.2 |

Optimum binary parameters were sought using a computer programme, as described by Prausnitz *et al.*,[19] and minimizing the objective function defined by

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

where a circumflex denotes the calculated value and the standard deviations in the measured variables were used as: $\sigma_P = 1$ Torr; $\sigma_T = 0.05$ K; $\sigma_x = 0.001$; $\sigma_y = 0.003$. Table 4 shows the energy parameters and the root-mean-square deviations of the measured values from the calculated results. Table 5 summarizes the results of quaternary prediction based on the binary parameters alone. The magnitude of the deviations between the experimental and predicted results of the vapour compositions and the total pressure is comparable with that obtained for ternary alcohol mixtures,[1,2,11,18] and confirms the good ability of the UNIQUAC associated-solution model.

**Table 4** The results of fitting the UNIQUAC associated-solution model to vapour-liquid equilibria and r.m.s. deviations $\delta P$, $\delta T$, $\delta x$ and $\delta y$ for binary systems.

| *System* | *Temp. (K)* | *No. of data points* | *Root-mean-square deviations* | | | | *Parameters* | |
|---|---|---|---|---|---|---|---|---|
| | | | *$\delta P$ (Torr)* | *$\delta T$ (K)* | *$\delta x$ ($\times 10^3$)* | *$\delta y$ ($\times 10^3$)* | *$a_{AB}$ (K)* | *$a_{BA}$ (K)* |
| Ethanol (A) + 1-propanol (B) | 313.15 | 10 | 0.20 | 0.00 | 0.0 | | 66.50 | −66.10 |
| Ethanol (A) + acetonitrile (B) | 313.15 | 14 | 0.89 | 0.02 | 0.6 | 4.2 | 520.85 | 71.20 |
| Ethanol (A) + benzene (B) | 318.15 | 12 | 0.83 | 0.02 | 0.6 | 3.9 | 10.38 | 97.26 |
| 1-Propanol (A) + acetonitrile (B) | 328.15 | 10 | 1.51 | 0.00 | 0.8 | 4.1 | 580.27 | 49.41 |
| 1-Propanol (A) + benzene (B) | 318.15 | 11 | 0.14 | 0.00 | 0.1 | 1.4 | 114.53 | −8.23 |
| Acetonitrile (A) + benzene (B) | 318.15 | 12 | 0.78 | 0.02 | 0.5 | 3.6 | −10.54 | 258.38 |

**Table 5** Quaternary calculated results for the ethanol (1) + 1-propanol (2) + acetonitrile (3) + benzene (4) system at 318.15 K.

| | *Vapour mole fractions* | | | | *Pressure* | |
|---|---|---|---|---|---|---|
| | *$\delta y_1$ ($\times 10^3$)* | *$\delta y_2$ ($\times 10^3$)* | *$\delta y_3$ ($\times 10^3$)* | *$\delta y_4$ ($\times 10^3$)* | *$\delta P$ (Torr)* | *$\delta P/P$ (%)* |
| Absolute mean deviation | 2.1 | 3.4 | 6.0 | 3.8 | 2.3 | 1.0 |
| Root-mean-square deviation | 2.7 | 4.4 | 6.7 | 4.8 | 2.9 | 1.2 |

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