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Excess molar enthalpies of binary and ternary mixtures containing aniline and 2-butanol

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Abstract

Excess molar enthalpies for (aniline + 2-butanol) and (aniline + 2-butanol + benzene) at 298.15 K, measured using an isothermal dilution calorimeter, are reported. The experimental binary and ternary results have been correlated by use of Redlich–Klister like polynomial equation and compared with those calculated from the UNIQUAC associated-solution model having only binary parameters.

LIST OF SYMBOLS

A, B, C	aniline, 2-butanol and benzene
a_{JI}	binary interaction parameter for J–I pair
A_n	constants of eqn. (1)
A_i, B_i	*i*-mers of aniline and 2-butanol
$\mathrm{A}_i\mathrm{B}_j\mathrm{C}$	complex containing *i* molecules of aniline, *j* molecules of 2-butanol and one molecule of benzene
$\mathrm{A}_i\mathrm{C}$	complex containing *i* molecules of aniline and one molecule of benzene
$\mathrm{B}_i\mathrm{C}$	complex containing *i* molecules of 2-butanol and one molecule of benzene
B_n	constants of eqn. (3)
C_{JI}, D_{JI}	parameters of eqn. (15)
$H_{\mathrm{m}}^{\mathrm{E}}$	excess molar enthalpy
$H_{\mathrm{m},12}^{\mathrm{E}}$, $H_{\mathrm{m},13}^{\mathrm{E}}$, $H_{\mathrm{m},23}^{\mathrm{E}}$	excess molar enthalpies of binary mixtures 1–2, 1–3 and 2–3
h_{A}, h_{B}	enthalpies of hydrogen-bonded formation of aniline and 2-butanol
h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules
K_{A}, K_{B}	association constants of aniline and 2-butanol
K_{AB}, K_{AC}, K_{BC}	solvation constants between unlike molecules

k	constant of eqn. (1)
q_I	molecular geometric area parameter of pure component I
R	universal gas constant
r_I	molecular geometric volume parameter of pure component I
$\bar{S}_I$	sum as defined by eqn. (22)
S_I	sum as defined by eqn. (23)
T	absolute temperature
$\bar{U}_I$	quantity as defined by eqn. (13)
U_I	quantity as defined by eqn. (14)
x_I	liquid mole fraction of component I
x'_I	liquid mole fraction of component I in a binary mixture

Greek letters

γ_I	activity coefficient of component I
δ	experimental value minus calculated value
Δ	function as defined by eqn. (3)
θ_I	area fraction of component I
τ_{JI}	binary parameter as defined by $\exp(-a_{JI}/T)$
Φ_I	segment fraction of component I
Φ_{I1}	monomer segment fraction of component I

Subscripts

A, B, C	aniline, 2-butanol and benzene
A_1, B_1, C_1	monomers of components A, B and C
AB, AC, BC	binary complexes
chem	chemical
I, J, K	components I, J and K
i, j, k	*i, j, k* and *l*-mers of aniline and 2-butanol or indices
phys	physical

Superscripts

0	pure liquid state
*	reference state

INTRODUCTION

As part of investigations to measure excess molar enthalpies of mixtures including aniline and an alcohol [1–5], this paper presents the excess molar enthalpies H_m^E for (aniline + 2-butanol) and (aniline + 2-butanol + benzene). The experimental results have been correlated with Redlich–Kister like polynomials and compared with those predicted from the

UNIQUAC associated-solution model, which is based on the multiauto- and cross-association of aniline and the alcohol and the solvation of the resulting multimers and benzene, allowing for nonpolar interactions between the three components [6]. Excess molar enthalpies H_m^E at 298.15 K for the two component binaries of the ternary system studied here are available from the literature: aniline + benzene [7]; 2-butanol + benzene [8].

EXPERIMENTAL

Aniline (Nacalai Tesque. Inc., special grade) and 2-butanol (Wako Pure Chemical Industries Ltd., special grade) were used as received. Benzene (Kanto Chemical Co., Inc., first grade) was subjected to recrystallization three times. The densities of these chemicals, measured with an Anton-Paar densimeter (DMA40), agreed well with published values [9]. The binary and ternary excess molar enthalpies H_m^E were measured with an isothermal dilution calorimeter at 298.15 K [10]. The experimental error of the measured H_m^E values were less than 0.5% of the measured values.

RESULTS

Table 1 gives the binary experimental H_m^E values of the aniline + 2-butanol. The experimental H_m^E data for the three binary systems were correlated with eqn. (1).

$$H_{m,i,j}^E = x_i x_j \sum_{n=1}^{m} A_n (x_i - x_j)^{n-1} / [1 - k(x_i - x_j)] \qquad (1)$$

TABLE 1

Excess molar enthalpies H_m^E in J mol^{-1} for the aniline(1) + 2-butanol(2) system at 298.15 K

x_1	H_m^E	δ [a]	x_1	H_m^E	δ [a]
0.0249	204.4	−0.8	0.5240	1533.2	−1.4
0.0584	446.3	0.4	0.6052	1442.9	−0.5
0.1180	792.2	0.2	0.6972	1257.9	0.2
0.1929	1111.9	−0.2	0.7930	971.3	−0.8
0.2738	1348.2	0.1	0.8654	692.0	1.4
0.3735	1512.4	−0.2	0.9235	419.7	−1.0
0.4546	1556.0	−0.4	0.9660	196.6	0.2
0.5210	1538.9	2.3			

[a] δ, Experimental value minus calculated value.

TABLE 2

Parameters A_i of eqns. (1) and (2) and standard deviations σ

System (1 + 2)	A_1	A_2	A_3	A_4	A_5	A_6	k	σ/J mol^{-1}
Aniline + 2-butanol	6192.39	−866.68	728.18	−241.68	454.53	−260.40		1.1
Aniline + benzene	3003.51	−721.57	447.94	−333.36				1.3
2-Butanol + benzene	6411.01	3974.37	−194.12	−366.27			−0.8557	

Table 2 shows the parameters of eqn. (1) and the standard deviations σ. Figure 1 presents the experimental H_m^E values and those calculated from eqn. (1).

Table 3 presents the ternary experimental H_m^E values of the aniline(1) + 2-butanol(2) + benzene(3) system. Equation (2) was used to

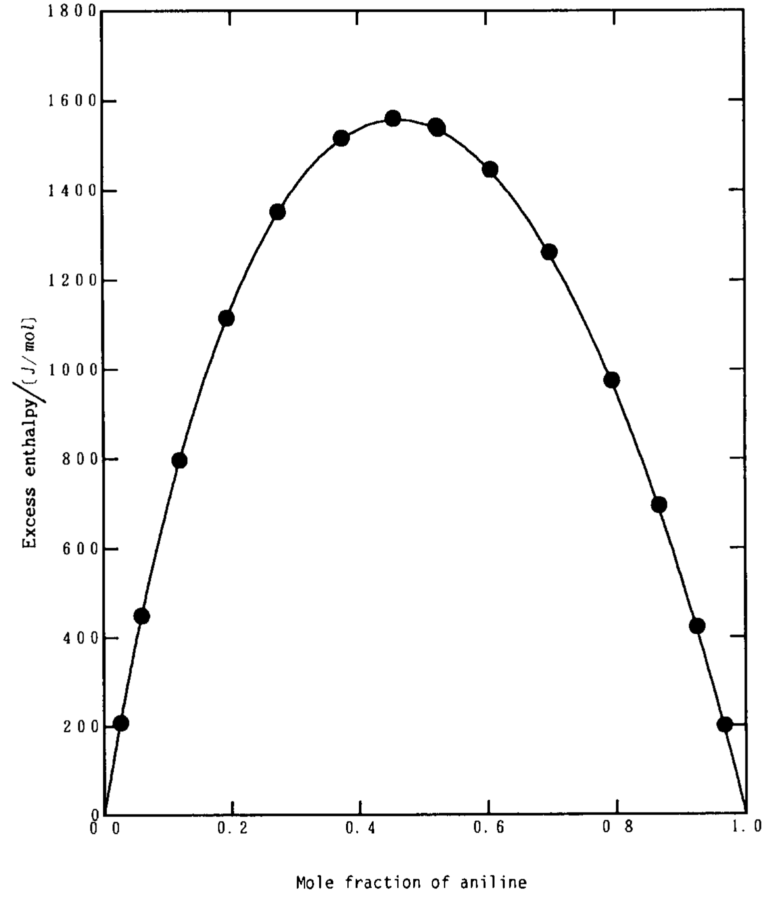

Fig. 1. Experimental excess molar enthalpies for aniline + 2-butanol at 298.15 K: ●, this work; ——, calculated from eqn. (1) or the UNIQUAC associated-solution model.

TABLE 3

Experimental ternary excess molar enthalpies H_m^E in J mol^{-1} at 298.15 K for the aniline(1) + 2-butanol(2) + benzene(3) system obtained by mixing pure benzene with [x_1' aniline + $(1 - x_1')$2-butanol]

x_1	x_2	H_m^E	δ [a]	x_1	x_2	H_m^E	δ [a]	x_1	x_2	H_m^E	δ [a]
$x_1' = 0.2496$				$x_1' = 0.5002$				$x_1' = 0.7510$			
0.2357	0.7083	1412.3	7.1	0.4665	0.4662	1607.6	−19.4	0.7235	0.2399	1156.7	1.7
0.2210	0.6640	1528.3	9.8	0.4355	0.4352	1669.3	−18.7	0.6817	0.2260	1222.9	1.2
0.2018	0.6063	1651.7	12.6	0.3975	0.3972	1722.9	−15.4	0.6338	0.2101	1286.4	2.2
0.1799	0.5406	1746.8	7.4	0.3591	0.3588	1754.1	−11.5	0.5704	0.1891	1350.4	7.6
0.1588	0.4762	1799.1	0.9	0.3179	0.3177	1759.3	−10.7	0.5066	0.1679	1388.0	11.0
0.1376	0.4135	1805.5	−6.5	0.2760	0.2758	1729.2	−13.2	0.4391	0.1456	1395.9	12.2
0.1216	0.3655	1780.5	−8.8	0.2504	0.2502	1695.0	−11.8	0.3837	0.1272	1375.8	13.9
0.1170	0.3515	1767.2	−9.6	0.2365	0.2363	1670.3	−10.4	0.3420	0.1134	1342.3	15.3
0.1059	0.3182	1726.3	−10.3	0.2233	0.2231	1640.1	−11.3	0.3250	0.1077	1323.7	15.8
0.0941	0.2827	1667.4	−9.6	0.2043	0.2042	1592.3	−9.9	0.2900	0.0962	1276.4	16.8
0.0825	0.2480	1592.3	−9.4	0.1800	0.1799	1518.2	−7.5	0.2604	0.0863	1225.9	17.2
0.0712	0.2139	1500.8	−9.5	0.1599	0.1598	1444.4	−6.3	0.2355	0.0781	1174.8	16.2
0.0634	0.1904	1425.8	−10.1	0.1380	0.1379	1349.7	−6.1	0.2064	0.0684	1104.4	14.3
0.0558	0.1676	1342.9	−10.8	0.1229	0.1228	1283.7	2.6	0.1841	0.0610	1041.7	12.1
0.0493	0.1482	1262.4	−12.4	0.0998	0.0997	1149.8	1.7	0.1582	0.0525	958.5	9.8
0.0427	0.1282	1170.0	−12.4	0.0856	0.0855	1053.7	1.2	0.1340	0.0444	868.5	7.6

[a] δ, Experimental value minus calculated value.

correlate the ternary H_m^E results.

$$H^E_{m,123} = H^E_{m,12} + H^E_{m,13} + H^E_{m,23} + x_1x_2x_3\Delta \tag{2}$$

where

$$\Delta/RT = \sum_{n=1}^{m} B_n(1 - 2x_3)^{n-1} \tag{3}$$

The parameters of eqn. (3) were calculated using a unweighted least squares method: $B_1 = 0.7322$, $B_2 = -1.0751$, $B_3 = 0.2275$, $B_4 = -0.8566$, $B_5 = 4.6576$, and $B_6 = -3.7451$; and the absolute arithmetic-mean deviation AAD = 9.9 J mol^{-1}, the standard deviation $\sigma = 11.7$ J mol^{-1}, and the absolute relative-mean deviation is 0.7%. Figure 2 plots contours of the ternary $H^E_{m,123}$, calculated from eqns. (2) and (3).

DATA ANALYSIS

The previous papers [1–5] have shown that the UNIQUAC associated-solution model is useful in analyzing the excess molar enthalpies of binary and ternary mixtures including aniline and an alcohol, so the model will be used in this paper. According to the model assumptions aniline (A) and 2-butanol (B) self-associate to form open homo-chains, A_i and B_i, and these pure open chain molecules cross-associate multifariously to yield open hetero-chains $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$ and $B_i(A_jB_k)_l$, and the resulting open homo- and hetero-chains and benzene (C) solvate to produce additional complexes: A_iC, B_iC, $(A_iB_j)_kC$, $A_i(B_jA_k)_lC$, $(B_iA_j)_kC$ and $B_i(A_jB_k)_lC$, where the subindices i, j, k and l range from one to infinity.

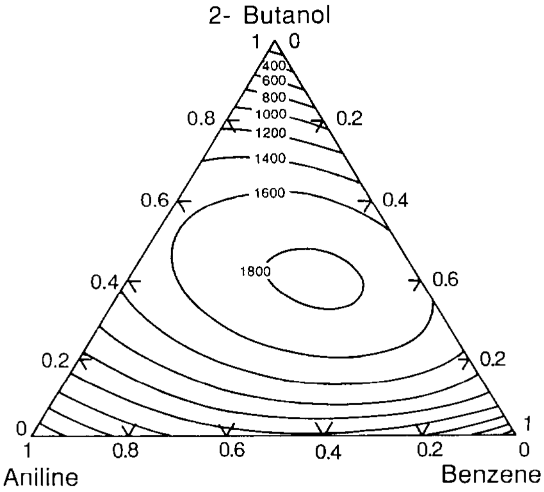

Fig. 2. Curves of constant excess molar enthalpies for aniline(1) + 2-butanol(2) + benzene(3) system at 298.15 K; ——, calculated from eqns. (2) and (3).

The equilibrium constants for the open homo- and hetero-chain formation are assumed to be independent of the degrees of association and solvation and are defined as follows:

$$K_A = \frac{\phi_{A_{i+1}}}{\phi_{A_i}\phi_{A_1}} \frac{i}{i+1} \qquad \text{for } A_i + A_1 = A_{i+1}$$

$$= K_A^* \exp\left[-\frac{h_A}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{4}$$

$$K_B = \frac{\phi_{B_{i+1}}}{\phi_{B_i}\phi_{B_1}} \frac{i}{i+1} \qquad \text{for } B_i + B_1 = B_{i+1}$$

$$= K_B^* \exp\left[-\frac{h_B}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{5}$$

$$K_{AB} = \frac{\phi_{A_iB_jA_kB_l} \quad r_{A_iB_jA_k} r_{B_l}}{\phi_{A_iB_jA_k}\phi_{B_l} r_{A_iB_jA_kB_l} r_A r_B} \qquad \text{for } A_iB_jA_k + B_l = A_iB_jA_kB_l$$

$$= K_{AB}^* \exp\left[-\frac{h_{AB}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{6}$$

$$K_{AC} = \frac{\phi_{A_iC}}{\phi_{A_i}\phi_C} \frac{i}{i r_A + r_c} \qquad \text{for } A_i + C_1 = A_iC$$

$$= K_{AC}^* \exp\left[-\frac{h_{AC}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{7}$$

$$K_{BC} = \frac{\phi_{B_iC}}{\phi_{B_i}\phi_{C1}} \frac{i}{i r_B + r_C} \qquad \text{for } B_i + C_1 = B_iC$$

$$= K_{BC}^* \exp\left[-\frac{h_{BC}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{8}$$

The ternary $H_{\mathrm{m}}^{\mathrm{E}}$ is given by the sum of chemical and physical contributions

$$
\begin{aligned}
H_{\mathrm{m}}^{\mathrm{E}} &= H_{\mathrm{m,chem}}^{\mathrm{E}} + H_{\mathrm{m,phys}}^{\mathrm{E}} \\
&= h_{\mathrm{A}} x_{\mathrm{A}} \left(\frac{\bar{U}_{\mathrm{A}} \phi_{\mathrm{A1}}}{\phi_{\mathrm{A}}} - \bar{U}_{\mathrm{A}}^{0} \phi_{\mathrm{A1}}^{0} \right) + h_{\mathrm{B}} x_{\mathrm{B}} \left(\frac{\bar{U}_{\mathrm{B}} \phi_{\mathrm{B1}}}{\phi_{\mathrm{B}}} - \bar{U}_{\mathrm{B}}^{0} \phi_{\mathrm{B1}}^{0} \right) \\
&\quad + (h_{\mathrm{A}} \bar{U}_{\mathrm{A}} + h_{\mathrm{AC}} U_{\mathrm{A}}) \frac{r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}} x_{\mathrm{A}} \phi_{\mathrm{A1}}}{\phi_{\mathrm{A}}} + (h_{\mathrm{B}} \bar{U}_{\mathrm{B}} + h_{\mathrm{BC}} U_{\mathrm{B}}) \frac{r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}} x_{\mathrm{B}} \phi_{\mathrm{B1}}}{\phi_{\mathrm{B}}} \\
&\quad + \Bigg(h_{\mathrm{A}} \Bigg\{ \frac{\bar{U}_{\mathrm{A}} x_{\mathrm{A}} \phi_{\mathrm{A1}}}{\phi_{\mathrm{A}}} (2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \phi_{\mathrm{A1}} \phi_{\mathrm{B1}} U_{\mathrm{A}} U_{\mathrm{B}})(1 + r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}}) \\
&\quad + \frac{\bar{U}_{\mathrm{A}}}{U_{\mathrm{A}} K_{\mathrm{AB}}} \left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}} \phi_{\mathrm{A}}} (1 + r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}}) + \frac{x_{\mathrm{B}}}{r_{\mathrm{A}} \phi_{\mathrm{B}}} (1 + r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}}) \right] \\
&\quad + \frac{\bar{U}_{\mathrm{A}} U_{\mathrm{B}} x_{\mathrm{B}} \phi_{\mathrm{B1}}}{U_{\mathrm{A}} \phi_{\mathrm{B}}} (1 + r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}}) \Bigg\} \\
&\quad + h_{\mathrm{B}} \Bigg\{ \frac{\bar{U}_{\mathrm{B}} x_{\mathrm{B}} \phi_{\mathrm{B1}}}{\phi_{\mathrm{B}}} (2 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \phi_{\mathrm{A1}} \phi_{\mathrm{B1}} U_{\mathrm{A}} U_{\mathrm{B}})(1 + r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}}) \\
&\quad + \frac{\bar{U}_{\mathrm{B}}}{U_{\mathrm{B}} K_{\mathrm{AB}}} \left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}} \phi_{\mathrm{A}}} (1 + r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}}) + \frac{x_{\mathrm{B}}}{r_{\mathrm{A}} \phi_{\mathrm{B}}} (1 + r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}}) \right] \\
&\quad + \frac{\bar{U}_{\mathrm{B}} U_{\mathrm{A}} x_{\mathrm{A}} \phi_{\mathrm{A1}}}{U_{\mathrm{B}} \phi_{\mathrm{A}}} (1 + r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}}) \Bigg\} \\
&\quad + h_{\mathrm{AB}} \Bigg\{ \left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}} \phi_{\mathrm{A}}} (1 + r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}}) + \frac{x_{\mathrm{B}}}{r_{\mathrm{A}} \phi_{\mathrm{B}}} (1 + r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}}) \right] \\
&\quad \times \frac{(1 + r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \phi_{\mathrm{A1}} \phi_{\mathrm{B1}} U_{\mathrm{A}} U_{\mathrm{B}})}{K_{\mathrm{AB}}} + \frac{2 U_{\mathrm{A}} x_{\mathrm{A}} \phi_{\mathrm{A1}}}{\phi_{\mathrm{A}}} (1 + r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}}) \\
&\quad + \frac{2 U_{\mathrm{B}} x_{\mathrm{B}} \phi_{\mathrm{B1}}}{\phi_{\mathrm{B}}} (1 + r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}}) \Bigg\} \\
&\quad + \Bigg[h_{\mathrm{AC}} r_{\mathrm{A}} K_{\mathrm{AC}} \phi_{\mathrm{C1}} \left(\frac{U_{\mathrm{A}} x_{\mathrm{A}} \phi_{\mathrm{A1}}}{\phi_{\mathrm{A}}} + \frac{x_{\mathrm{A}}}{r_{\mathrm{A}} K_{\mathrm{AB}} \phi_{\mathrm{A}}} \right) \\
&\quad + h_{\mathrm{BC}} r_{\mathrm{B}} K_{\mathrm{BC}} \phi_{\mathrm{C1}} \left(\frac{U_{\mathrm{B}} x_{\mathrm{B}} \phi_{\mathrm{B1}}}{\phi_{\mathrm{B}}} + \frac{x_{\mathrm{B}}}{r_{\mathrm{B}} K_{\mathrm{AB}} \phi_{\mathrm{B}}} \right) \Bigg] \\
&\quad \times (1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \phi_{\mathrm{A1}} \phi_{\mathrm{B1}} U_{\mathrm{A}} U_{\mathrm{B}}) \Bigg) \frac{r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \phi_{\mathrm{A1}} \phi_{\mathrm{B1}} U_{\mathrm{A}} U_{\mathrm{B}}}{(1 - r_{\mathrm{A}} r_{\mathrm{B}} K_{\mathrm{AB}}^{2} \phi_{\mathrm{A1}} \phi_{\mathrm{B1}} U_{\mathrm{A}} U_{\mathrm{B}})^{2}} \\
&\quad - R \sum_{\mathrm{I}} q_{\mathrm{I}} x_{\mathrm{I}} \frac{\sum_{\mathrm{J}} \theta_{\mathrm{J}} \dfrac{\partial \tau_{\mathrm{JI}}}{\partial (1/T)}}{\sum_{\mathrm{J}} \theta_{\mathrm{J}} \tau_{\mathrm{JI}}}
\end{aligned}
\tag{9}
$$

where the segment fraction ϕ_I, the surface fraction θ_I, the symbols $\bar{U}_I$ and U_I and the binary parameter τ_{JI} are expressed by

$$\phi_I = x_I r_I \Big/ \sum_J x_J r_J \tag{10}$$

$$\theta_I = x_I q_I \Big/ \sum_J x_J q_J \tag{11}$$

$$\bar{U}_I = K_I \phi_{I1}/(1 - K_I \phi_{I1})^2 \tag{12}$$

$$U_I = 1/(1 - K_I \phi_{I1}) \tag{13}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{14}$$

The energy parameter a_{JI} is assumed to change with temperature linearly.

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \tag{15}$$

The values of ϕ_{I1}^0 and $\bar{U}_I^0$ at the pure liquid state are expressed by

$$\phi_{I1}^0 = [1 + 2K_I - (1 + 4K_I)^{0.5}]/2K_I^2 \tag{16}$$

$$\bar{U}_I^0 = K_I \phi_{I1}^0/(1 - K_I \phi_{I1}^0)^2 \tag{17}$$

The monomeric segment fractions of components, ϕ_{A1}, ϕ_{B1} and ϕ_{C1}, are solved simultaneously from eqns. (18)–(20).

$$\begin{aligned}\phi_A = {} & (1 + r_A K_{AC} \phi_{C1}) \bar{S}_A + \frac{r_A K_{AB} \bar{S}_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \\ & \times \{2 + r_B K_{AB} S_A (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A K_{AB} S_B \\ & + \phi_{C1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{AC} S_A \\ & \times (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB} K_{BC} S_B]\}\end{aligned} \tag{18}$$

$$\begin{aligned}\phi_B = {} & (1 + r_B K_{BC} \phi_{C1}) \bar{S}_B + \frac{r_B K_{AB} S_A \bar{S}_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)^2} \\ & \times \{2 + r_A K_{AB} S_B (2 - r_A r_B K_{AB}^2 S_A S_B) + r_B K_{AB} S_A \\ & + \phi_{C1}[(r_A K_{AC} + r_B K_{BC}) + r_A r_B K_{AB} K_{BC} S_B \\ & \times (2 - r_A r_B K_{AB}^2 S_A S_B) + r_A r_B K_{AB} K_{AC} S_A]\}\end{aligned} \tag{19}$$

$$\begin{aligned}\phi_C = {} & \phi_{C1}\left\{1 + r_c K_{AC} S_A + r_C K_{BC} S_B + \frac{r_A r_B K_{AB}^2 S_A S_B}{(1 - r_A r_B K_{AB}^2 S_A S_B)}\right. \\ & \left. \times \left[\frac{K_{AC}}{r_B K_{AB}} + \frac{K_{BC}}{r_A K_{AB}} + K_{AC} S_A + K_{BC} S_B\right]\right\}\end{aligned} \tag{20}$$

TABLE 4

Association parameters and molecular structural constants for pure components

Component	K_A at 323.15 K	$-h_A$/kJ mol^{-1}	r	q
Aniline	15.0	15.4	2.98	2.38
2-Butanol	31.1	23.2	2.77	2.42
Benzene			2.56	2.05

where the sums $\bar{S}_I$ and S_I are defined as

$$\bar{S}_I = \phi_{I1}/(1 - K_I\phi_{I1})^2 \qquad (21)$$

$$S_I = \phi_{I1}/(1 - K_I\phi_{I1}) \qquad (22)$$

Table 4 gives the association parameters, K_A and h_A, for aniline [11] and 2-butanol [12, 13] and the pure-component molecular structural constants, r and q, calculated in accordance with the method of Vera et al. [14]. Table 5 gives the solvation parameters, K_{AB} and h_{AB}, for binary mixtures [11, 15]. All h_A and h_{AB} values were assumed to be temperature-independent.

Table 6 shows the results of fitting the UNIQUAC associated-solution model to the binary experimental H_m^E values. The parameters C_{JI} and D_{JI} of eqn. (15) were obtained by minimizing the sum of the squares of deviations between the experimental and calculated H_m^E for all data points by means of the simplex method of Nelder and Mead [16].

The absolute arithmetic mean deviation (AAD), root-mean-square

TABLE 5

Solvation parameters for binary mixtures

System (A + B)	K_{AB} at 323 K	$-h_{AB}$/kJ mol^{-1}
Aniline + 2-butanol	16.0 (298.15 K)	17.5
Aniline + benzene	1.0	10.8
1-Propanol + benzene	2.5	8.3

TABLE 6

The results of fitting the UNIQUAC associated-solution model to binary excess enthalpy data

System (A + B)	Number of data points	Parameters				AAD[a]/ J mol^{-1}
		C_{BA}/K	C_{AB}/K	D_{BA}	D_{AB}	
Aniline + 2-butanol	15	364.1	322.0	0.3196	0.8742	1.0
Aniline + benzene	14	−188.1	519.5	−1.0731	−2.1112	4.5
2-Butanol + benzene	18	1914.8	335.3	−0.6689	0.5887	8.2

[a] AAD, absolute arithmetic mean deviation.

deviation (RMSD) and absolute relative deviation (ARD) between the forty-nine ternary experimental H_m^E and predicted values from the UNIQUAC associated-solution model are AAD = 24.5 J mol^{-1}, RMSD = 32.1 J mol^{-1}, and ARD = 1.8%, showing that agreement is acceptable.

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