Thermochimica Acta, 208 (1992) 73–82
Elsevier Science Publishers B.V., Amsterdam

Excess molar enthalpies of binary and ternary mixtures containing aniline and 1-propanol

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(Received 30 December 1991)

Abstract

Excess molar enthalpies for aniline + 1-propanol and aniline + 1-propanol + benzene at 298.15 K have been measured using an isothermal dilution calorimeter. The experimental values have been correlated with smoothing polynomials and compared with those calculated from the UNIQUAC associated-solution model with binary parameters.

LIST OF SYMBOLS

A, B, C	aniline, 1-propanol and benzene
a_{JI}	binary interaction parameter for J–I pair
A_n	constants of eqns (1) and (2)
A_i, B_i	i-mers of aniline and 1-propanol
A_iB_jC	complex containing i molecules of aniline, j molecules of 1-propanol and one molecule of benzene
A_iC	complex containing i molecules of aniline and one molecule of benzene
B_iC	complex containing i molecules of 1-propanol and one molecule of benzene
B_n	constant of eqn. (4)
C_{JI}, D_{JI}	coefficients of eqn. (16)
H_m^E	excess molar enthalpy
$H_{m,12}^E$, $H_{m,13}^E$, $H_{m,23}^E$	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 1-propanol
h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules

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K_A, K_B	association constants of aniline and 1-propanol
K_{AB}, K_{AC}, K_{BC}	solvation constants between unlike molecules
k	constant of eqn. (1)
l	constant of eqn. (4)
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
Z	lattice coordination number, here set as 10

Greek letters

γ_I	activity coefficient of component I
δ	experimental value minus calculated value
Δ	function as defined by eqn. (4)
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_{I_1}	monomer segment fraction of component I

Subscripts

A, B, C	aniline, 1-propanol 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, l	*i, j, k* and *l*-mers of aniline and 1-propanol or indices
phys	physical

Superscripts

$^\circ$	pure liquid state
$*$	reference state

INTRODUCTION

The ternary liquid–liquid equilibrium and excess molar enthalpy data of aniline + methanol or ethanol + hydrocarbon mixtures have been successfully predicted by using the UNIQUAC associated-solution model with only binary parameters [1, 2]. This paper reports the excess molar enthalpies for aniline + 1-propanol and aniline + 1-propanol + benzene measured with an isothermal dilution calorimeter at 298.15 K [3]. The UNIQUAC associated-solution model based on the multisolvation of two associating components [4] will be applied for the prediction of the ternary excess molar enthalpy by using binary parameters. Excess molar enthalpies H_m^E at 298.15 K for the two binary systems constituting the ternary system have been reported: aniline + benzene [5]; 1-propanol + benzene [6].

EXPERIMENTAL

Aniline (Nacalai Tesque Inc., special grade) and 1-propanol (Wako Pure Chemical Industries Ltd., special grade) were used as received. Benzene (Kanto Chemical Co., Inc., first grade) was purified by repeated fractional recrystallization. The densities of the chemicals used, measured with an Anton-Paar densimeter (DMA40), agreed well with literature values [7]. The binary and ternary excess molar enthalpies H_m^E were measured with an isothermal dilution calorimeter at 298.15 K. The errors in the observed H_m^E values were less than 0.5% of the measured values.

RESULTS

Tables 1 and 2 give the H_m^E values for the aniline + 1-propanol and aline + 1-propanol + benzene systems at 298.15 K. The binary experimental H_m^E data for the aniline + 1-propanol and aniline + benzene systems

TABLE 1

Excess molar enthalpies for the aniline(1) + 1-propanol(2) system at 298.15 K

x_1	H_m^E (J mol^{-1})	δ [a] (J mol^{-1})	x_1	H_m^E (J mol^{-1})	δ [a] (J mol^{-1})
0.0157	31.1	−0.1	0.4787	775.4	−0.1
0.0488	102.7	0.1	0.5381	789.9	−0.0
0.1029	225.5	−0.1	0.6024	780.4	0.1
0.1684	369.2	−0.0	0.6768	734.1	−0.1
0.2343	497.7	−0.3	0.7557	640.4	−0.4
0.3062	614.2	0.0	0.8274	512.7	0.5
0.3547	677.8	0.9	0.8968	343.6	0.3
0.3836	707.6	−0.3	0.9409	210.7	−0.1
0.4255	744.1	−0.1	0.9773	84.4	−1.2

[a] δ = experimental value minus calculated value.

TABLE 2

Experimental ternary excess molar enthalpies at 298.15 K for the aniline(1) + 1-propanol(2) benzene(3) system obtained by mixing pure benzene with [x_1' aniline + (1 − x_1')1-propanol]

x_1	x_3	H_m^E (J mol^{-1})	δ[a] (J mol^{-1})	x_1	x_3	H_m^E (J mol^{-1})	δ[a] (J mol^{-1})	x_1	x_3	H_m^E (J mol^{-1})	δ[a] (J mol^{-}
$x_1' = 0.2512$				$x_1' = 0.5004$				$x_1' = 0.7480$			
0.2418	0.0374	611.8	5.3	0.4875	0.0258	832.5	−0.5	0.7271	0.0279	702.4	−2.6
0.2288	0.0888	719.5	10.1	0.4679	0.0650	901.7	−2.2	0.6934	0.0730	780.1	−5.1
0.2146	0.1455	825.9	10.8	0.4443	0.1121	978.2	−3.8	0.6503	0.1306	867.6	−9.3
0.2005	0.2017	922.0	11.5	0.4171	0.1665	1054.3	−7.7	0.5952	0.2043	964.5	−10.1
0.1874	0.2540	1001.8	11.8	0.3874	0.2258	1125.1	−9.8	0.5305	0.2907	1053.0	−7.5
0.1763	0.2982	1060.1	10.8	0.3572	0.2862	1184.1	−10.6	0.4620	0.3824	1115.6	−1.5
0.1641	0.3466	1114.0	8.5	0.3266	0.3473	1229.2	−10.3	0.4118	0.4495	1138.6	3.2
0.1520	0.3947	1157.8	6.2	0.2986	0.4032	1256.7	−9.7	0.3703	0.5050	1141.7	6.6
0.1407	0.4397	1189.1	4.4	0.2719	0.4567	1270.2	−8.5	0.3545	0.5261	1138.8	7.7
0.1304	0.4809	1208.2	2.0	0.2520	0.4963	1271.3	−7.8	0.3179	0.5750	1122.6	9.3
0.1187	0.5274	1218.0	−1.4	0.2287	0.5430	1260.4	−8.9	0.2787	0.6275	1090.4	11.3
0.1068	0.5748	1216.5	−3.6	0.2012	0.5978	1233.6	−8.8	0.2416	0.6770	1044.0	12.4
0.0951	0.6211	1201.1	−6.0	0.1790	0.6422	1199.4	−8.1	0.2117	0.7170	993.4	13.0
0.0844	0.6639	1175.7	−6.4	0.1598	0.6807	1161.3	−5.2	0.1933	0.7416	955.6	12.9
0.0763	0.6961	1147.2	−7.4	0.1417	0.7168	1113.2	−4.9	0.1698	0.7730	898.6	11.9
0.0697	0.7225	1118.5	−7.2	0.1268	0.7467	1065.9	−4.1	0.1495	0.8001	841.3	10.7
0.0622	0.7525	1077.0	−8.4	0.1168	0.7665	1029.8	−3.8	0.1320	0.8235	785.4	9.7
0.0532	0.7882	1017.2	−9.4	0.1068	0.7865	989.5	−3.4				
0.0463	0.8158	961.0	−10.3	0.0913	0.8175	918.3	−3.0				
				0.0788	0.8426	851.9	−2.7				

[a] δ = experimental value minus calculated value.

were correlated with eqn. (1).

$$H_{\mathrm{m},ij}^{\mathrm{E}} = x_i x_j \sum_{n=1}^{m} A_n (x_i - x_j)^{n-1} / [1 - k(x_i - x_j)] \tag{1}$$

Mrazek and Van Ness [6] fitted eqn. (2) to the H_m^E values for the 1-propanol + benzene system

$$H_{\mathrm{m},ij}^{\mathrm{E}} = 10^4 x_2 x_3 \Big/ \sum_{n=1}^{m} A_n (x_2 - x_3)^{n-1} \tag{2}$$

Table 3 shows the parameters of eqns. (1) and (2) and the standard deviations σ. The experimental H_m^E values for the three binary systems are presented in Fig. 1.

TABLE 3

Parameters A_n 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 + 1-propanol	3132.82	2640.31	430.13	263.97			−0.6536	0.5
Aniline + benzene	3003.51	−721.57	447.94	−333.36				1.3
1-Propanol + benzene	2.6287	1.5119	0.2274	0.5056	−0.1927	0.0603		

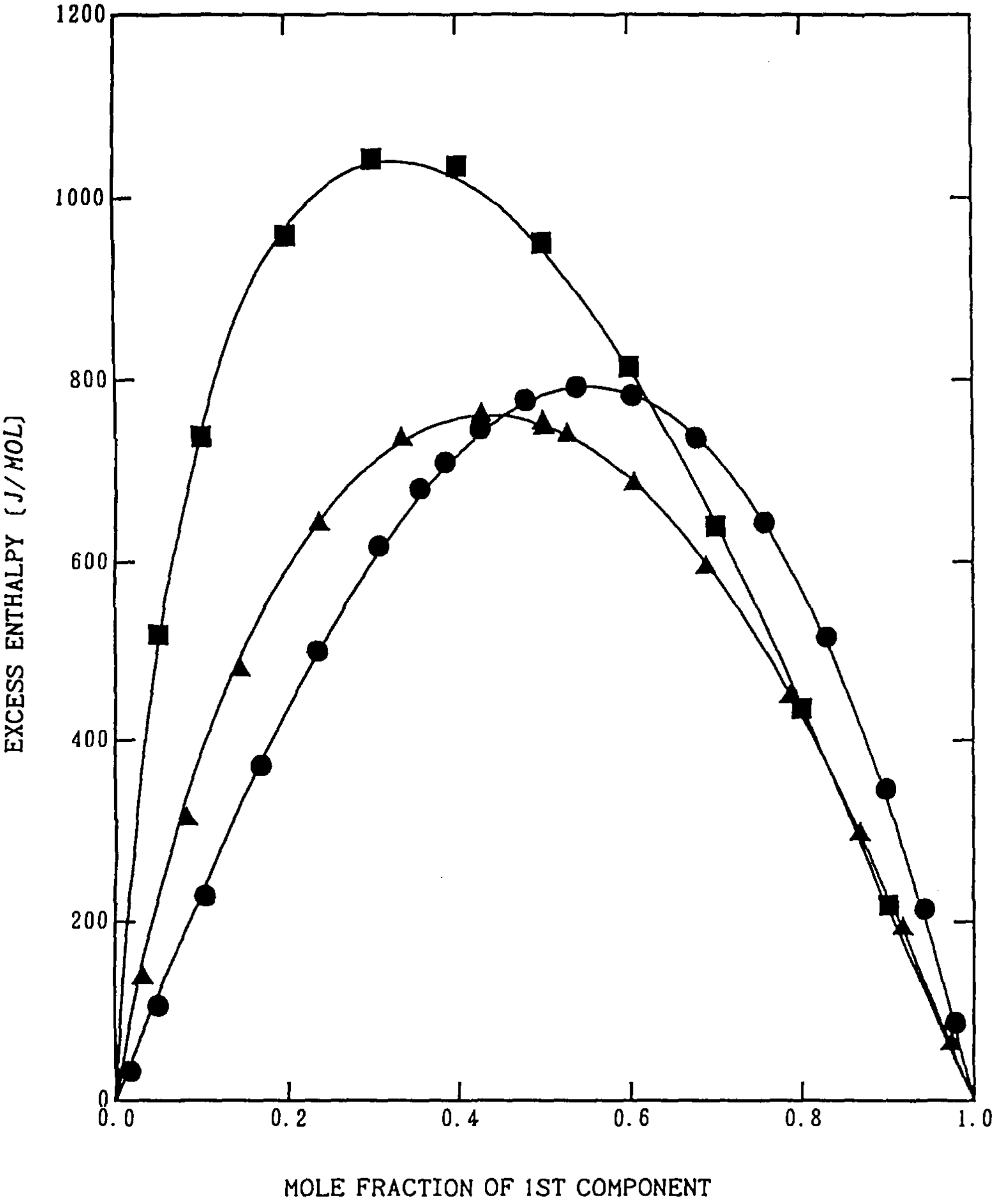

Fig. 1. Experimental excess molar enthalpies for three binary systems at 298.15 K; ●, aniline(1) + 1-propanol(2), this work, ▲; aniline(1) + benzene(2) [5]; ■, 1-propanol(1) + benzene (2) [6]; ——, calculated from smoothing equations or the UNIQUAC associated-solution model.

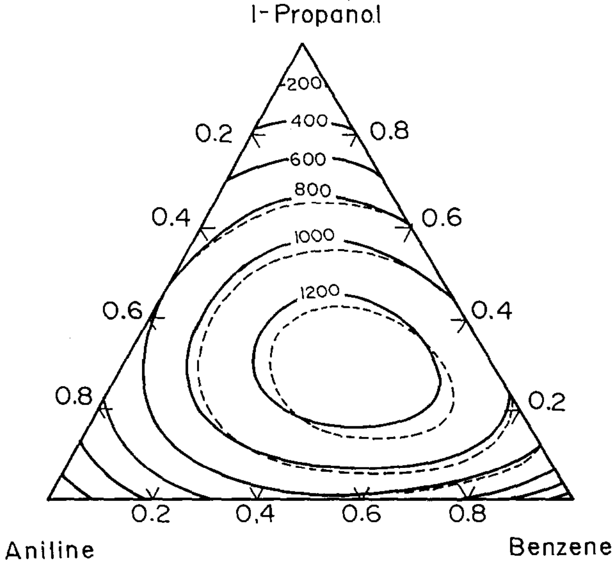

Fig. 2. Curves of constant excess molar enthalpies for the aniline(1) + 1-propanol(2) + benzene(3) system at 298.15 K; ——, calculated from eqns. (3) and (4); ------, calculated from the UNIQUAC associated-solution model.

The ternary experimental H_m^E values of the aniline(1) + 1-propanol(2) + benzene(3) system were fitted to eqn. (3)

$$H_{m,123}^E = H_{m,12}^E = H_{m,13}^E + H_{m,23}^E + x_1x_2x_3\Delta \quad (3)$$

where

$$\Delta/RT = \sum_{n=1}^{m} B_n(1-2x_3)^{n-1}/[1-l(1-2x_3)] \quad (4)$$

The parameters of eqn. (4) were obtained using a unweighted least squares method: $B_1 = 1.6375$; $B_2 = 0.6402$, $B_3 = 0.2537$, $B_4 = 0.3745$, $B_5 = -0.3670$, and $l = -1.1202$; and the arithmetic mean deviation AAD = 7.3 J mol^{-1}, the standard deviation $\sigma = 8.5$ J mol^{-1}, and the relative mean deviation is 0.7%. Contours of the ternary $H_{m,123}^E$, calculated from eqns (3) and (4), are plotted in Fig. 2.

DATA ANALYSIS

We assume that aniline(A) and 1-propanol(B) self-associate to form homopolymers A_i and B_i and these homopolymers solvate multiply to produce copolymers $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$ and $B_i(A_jB_k)_l$, and that the resulting polymers and benzene (C) make further 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 take values from one to infinity. The equilibrium constants are assumed to be independent of the degrees of association and solvation and are defined in terms of the segment fractions and molecular volume parameters of chemical species.

$$K_{\mathrm{A}} = \frac{\Phi_{\mathrm{A}_{i+1}}}{\Phi_{\mathrm{A}_i}\Phi_{A_1}}\frac{i}{i+1} \qquad \text{for } \mathrm{A}_i + \mathrm{A}_1 = \mathrm{A}_{i+1}$$

$$= K_{\mathrm{A}}^* \exp\left[-\frac{h_{\mathrm{A}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{5}$$

$$K_{\mathrm{B}} = \frac{\Phi_{\mathrm{B}_{i+1}}}{\Phi_{\mathrm{B}_i}\Phi_{\mathrm{B}_1}}\frac{i}{i+1} \qquad \text{for } \mathrm{B}_i + \mathrm{B}_1 = \mathrm{B}_{i+1}$$

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

$$K_{\mathrm{AB}} = \frac{\Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}}{\Phi_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}\Phi_{\mathrm{B}_1}}\frac{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k}r_{\mathrm{B}_l}}{r_{\mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l}r_{\mathrm{A}}r_{\mathrm{B}}} \qquad \text{for } \mathrm{A}_i\mathrm{B}_j\mathrm{A}_k + \mathrm{B}_l = \mathrm{A}_i\mathrm{B}_j\mathrm{A}_k\mathrm{B}_l$$

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

$$K_{\mathrm{AC}} = \frac{\Phi_{\mathrm{A}_i\mathrm{C}}}{\Phi_{\mathrm{A}_i}\Phi_{\mathrm{C}_1}}\frac{i}{ir_{\mathrm{A}} + r_{\mathrm{C}}} \qquad \text{for } \mathrm{A}_i + \mathrm{C}_1 = \mathrm{A}_i\mathrm{C}$$

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

$$K_{\mathrm{BC}} = \frac{\Phi_{\mathrm{B}_i\mathrm{C}}}{\Phi_{\mathrm{B}_i}\Phi_{\mathrm{C}_1}}\frac{i}{ir_{\mathrm{B}} + r_{\mathrm{C}}} \qquad \text{for } \mathrm{B}_i + \mathrm{C}_1 = \mathrm{B}_i\mathrm{C}$$

$$= K_{\mathrm{BC}}^* \exp\left[-\frac{h_{\mathrm{BC}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{9}$$

The ternary $H_{\mathrm{m}}^{\mathrm{E}}$ is expressed as the sum of two contributions: chemical and physical

$$\begin{aligned}
H_{\mathrm{m}}^{\mathrm{E}} &= H_{\mathrm{m,chem}}^{\mathrm{E}} + H_{\mathrm{m,phys}}^{\mathrm{E}} \\
&= h_{\mathrm{A}}x_{\mathrm{A}}\left(\frac{\bar{U}_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} - \bar{U}_{\mathrm{A}}^0\Phi_{\mathrm{A}_1}^0\right) + h_{\mathrm{B}}x_{\mathrm{B}}\left(\frac{\bar{U}_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} - U_{\mathrm{A}}^0\Phi_{\mathrm{B}_1}^0\right) \\
&\quad + (h_{\mathrm{A}}\bar{U}_{\mathrm{A}} + h_{\mathrm{AC}}U_{\mathrm{A}})\frac{r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{A}} \\
&\quad + (h_{\mathrm{B}}\bar{U}_{\mathrm{B}} + h_{\mathrm{BC}}U_{\mathrm{B}})\frac{r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} \\
&\quad + \Bigg(h_{\mathrm{A}}\Bigg\{\frac{\bar{U}_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})(1 + r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1}) \\
&\quad + \frac{\bar{U}_{\mathrm{A}}}{U_{\mathrm{A}}K_{\mathrm{AB}}}\left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}(1 + r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1}) + \frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}(1 + r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\right]
\end{aligned}$$

$$
\begin{aligned}
&+\frac{\bar{U}_A U_B x_B \Phi_{B_1}}{U_A U_B}(1+r_B K_{BC}\Phi_{C_1})\Bigr\}\\
&+h_B\Bigl\{\frac{\bar{U}_B x_B \Phi_{B_1}}{\Phi_B}(2-r_A r_B K_{AB}^2 \Phi_{A_1}\Phi_{B_1}U_A U_B)(1+r_B K_{BC}\Phi_{C_1})\\
&+\frac{\bar{U}_B}{U_A K_{AB}}\biggl[\frac{x_A}{r_B \Phi_A}(1+r_A K_{AC}\Phi_{C_1})+\frac{x_B}{r_A \Phi_B}(1+r_B K_{BC}\Phi_{C_1})\biggr]\\
&+\frac{\bar{U}_B U_A x_A \Phi_{A_1}}{U_B \Phi_A}(1+r_A K_{AC}\Phi_{C_1})\Bigr\}\\
&+h_{AB}\Bigl\{\biggl[\frac{x_A}{r_B \Phi_A}(1+r_A K_{AC}\Phi_{C_1})\\
&+\frac{x_B}{r_A \Phi_B}(1+r_B K_{BC}\Phi_{C_1})\biggr]\frac{(1+r_A r_B K_{AB}^2 \Phi_{A_1}\Phi_{B_1}U_A U_B)}{K_{AB}}\\
&+\frac{2U_A x_A \Phi_{A_1}}{\Phi_A}(1+r_A K_{AC}\Phi_{C_1})+\frac{2U_B x_B \Phi_{B_1}}{\Phi_B}(1+r_B K_{BC}\Phi_{C_1})\Bigr\}\\
&+\Bigl\{h_{AC} r_A K_{AC}\Phi_{C_1}\biggl(\frac{U_A X_A \Phi_{A_1}}{\Phi_A}+\frac{x_A}{r_A K_{AB}\Phi_A}\biggr)\\
&+h_{BC} r_B K_{BC}\Phi_{C_1}\biggl(\frac{U_B x_B \Phi_{B_2}}{\Phi_B}+\frac{x_B}{r_B K_{AB}\Phi_B}\biggr)\Bigr\}(1-r_A r_B K_{AB}^2 \Phi_{A_1}\Phi_{B_1}U_A U_B)\Bigr)\\
&\times\frac{r_A r_B K_{AB}^2 \Phi_{A_1}\Phi_{B_1}U_A U_B}{(1-r_A r_B K_{AB}^2 \Phi_{A_1}\Phi_{B_1}U_A U_B)^2}-R\sum_I q_I x_I \frac{\sum_J \theta_J \dfrac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J \tau_{JI}} \qquad (10)
\end{aligned}
$$

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 given by

$$\Phi_I = x_I r_I \Big/ \sum_J x_J r_J \qquad (11)$$

$$\theta_I = x_I q_I \Big/ \sum_J x_J q_J \qquad (12)$$

$$\bar{U}_I = K_I \Phi_{I_1}/(1-K_I \Phi_{I_1})^2 \qquad (13)$$

$$U_I = 1/(1-K_I \Phi_{I_1}) \qquad (14)$$

$$\tau_{JI} = \exp(-a_{JI}/T) \qquad (15)$$

The energy parameter a_{JI} is assumed to be a linear function of temperature

$$a_{JI} = C_{JI} + D_{JI}(T-273.15) \qquad (16)$$

For the pure liquid state $\Phi^{\circ}_{\mathrm{I}_1}$ and $\bar{U}^{\circ}_{\mathrm{I}}$ are expressed by

$$\Phi^{\circ}_{\mathrm{I}_1} = [1 + 2K_{\mathrm{I}} + (1 + 4K_{\mathrm{I}})^{0.5}]/2K_{\mathrm{I}}^2 \qquad (17)$$

$$\bar{U}^{\circ}_{\mathrm{I}} = K_{\mathrm{I}}\Phi^{\circ}_{\mathrm{I}_1}/(1 - K_{\mathrm{I}}\Phi^{\circ}_{\mathrm{I}_1})^2 \qquad (18)$$

The monomeric segment fractions of components Φ_{A_1}, Φ_{B_1} and Φ_{C_1} are obtained from a simultaneous solution of eqns. (18)–(20)

$$\begin{aligned}\Phi_{\mathrm{A}} = {} & (1 + r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1})\bar{S}_{\mathrm{A}} + \frac{r_{\mathrm{A}}K_{\mathrm{AB}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2}\\ & \times \{2 + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}\\ & + \Phi_{\mathrm{C}_1}[(r_{\mathrm{A}}K_{\mathrm{AC}} + r_{\mathrm{B}}K_{\mathrm{BC}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}\\ & \times (2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}]\}\end{aligned} \qquad (19)$$

$$\begin{aligned}\Phi_{\mathrm{B}} = {} & (1 + r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\bar{S}_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2}\\ & \times \{2 + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\\ & + \Phi_{\mathrm{C}_1}[(r_{\mathrm{A}}K_{\mathrm{AC}} + r_{\mathrm{B}}K_{\mathrm{BC}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}\\ & \times (2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}]\}\end{aligned} \qquad (20)$$

$$\begin{aligned}\Phi_{\mathrm{C}} = {} & \Phi_{\mathrm{C}_1}\left\{1 + r_{\mathrm{C}}K_{\mathrm{AC}}S_{\mathrm{A}} + r_{\mathrm{C}}K_{\mathrm{BC}}S_{\mathrm{B}} + \frac{r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})}\right.\\ & \left. \times \left[\frac{K_{\mathrm{AC}}}{r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{K_{\mathrm{BC}}}{r_{\mathrm{A}}K_{\mathrm{AB}}} + K_{\mathrm{AC}}S_{\mathrm{A}} + K_{\mathrm{BC}}S_{\mathrm{B}}\right]\right\}\end{aligned} \qquad (21)$$

where the sums $\bar{S}_{\mathrm{I}}$ and S_{I} are defined by eqns. (21) and (22)

$$\bar{S}_{\mathrm{I}} = \Phi_{\mathrm{I}_1}/(1 - K_{\mathrm{I}}\Phi_{\mathrm{I}_1})^2 \qquad (22)$$

$$S_{\mathrm{I}} = \Phi_{\mathrm{I}_1}/(1 - K_{\mathrm{I}}\Phi_{\mathrm{I}_1}) \qquad (23)$$

The association parameters for aniline [8] and 1-propanol [9, 10] are shown in Table 4, together with the pure-component molecular structural constants, estimated from the method of Vera et al. [11]. Table 5 gives the solvation parameters for binary mixtures [8, 12]. All standard enthalpies were assumed to be independent of temperature.

TABLE 4

Association parameters and molecular structural constants for pure components

Component	K_{A} at 323.15 K	$-h_{\mathrm{A}}$ (kJ mol^{-1})	r	q
Aniline	15.0	15.4	2.98	2.38
1-Propanol	87.0	23.2	2.23	1.98
Benzene			2.56	2.05

TABLE 5

Solvation parameters for binary mixtures

System (A + B)	K_{AB} at 323.15 K	$-h_{AB}$ (kJ mol^{-1})
Aniline + 1-propanol	23.0 (298.15 K)	20.7
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 (1 + 2)	Number of data points	Parameters				Deviations [a] (J mol^{-1})	
		C_{21}(K)	C_{12}(K)	D_{21}	D_{12}	AAD	σ
Aniline + 1-propanol	18	−1.861	158.8	0.0394	−0.08525	4.6	6.6
Aniline + benzene	14	−188.1	519.5	−1.073	−2.111	4.5	9.0
1-Propanol + benzene	10	807.5	355.0	2.055	1.3727	5.7	8.4

[a] AAD = absolute arithmetic mean deviation; σ = standard deviation.

Table 6 shows the results of fitting the UNIQUAC associated-solution model to the binary experimental H_m^E values. The parameters are eqn. (16), C_{JI} and D_{JI}, were obtained by minimizing the sum of the squares of deviations between the experimental and caluclated H_m^E for all data points by means of the simplex method of Nelder and Mead [13].

The absolute arithmetic mean deviation (AAD), root-mean-square deviation (RMSD) and average relative deviation (ARD) between the fifty-five ternary experimental H_m^E values and predicted values from the UNIQUAC associated-solution model are AAD = 14.8 J mol^{-1}, RMSD = 17.8 J mol^{-1}, and ARD = 1.4%. The values are comparable with those of previous papers [1, 2].

REFERENCES

1 I. Nagata and M. Sano, Fluid Phase Equilibria, 72 (1992) 147.
2 I. Nagata and M. Sano, Thermochim. Acta, 200 (1992) 475.
3 I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79.
4 I. Naguta, K. Tamura and K. Gotoh, Thermochim. Acta, 104 (1986) 179.
5 I. Nagata and K. Tamura, J. Chem. Thermodyn., 24 (1992) 613.
6 R.V. Mrazek and H.C. Van Ness, AIChE J., 7 (196) 190.
7 J.A. Riddick, W.B. Bunger and T.K. Sakano, Organic Solvents, 4th edn., Wiley-Interscience, New York, 1986, pp. 135, 194, 611.
8 I. Nagata and K. Ohtsubo, Thermochim. Acta, 97 (1986) 37.
9 V. Brandani, Fluid Phase Equilibria, 12 (1983) 87.
10 R.H. Stokes and C. Burfitt, J. Chem. Thermodyn., 5 (1973) 623.
11 J.H. Vera, S.G. Sayegh and G.A. Ratcliff, Fluid Phase Equilibria, 1 (1977) 113.
12 I. Nagata, Fluid Phase Equilibria, 19 (1985) 153.
13 J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308.