Thermochimica Acta, 200 (1992) 475–488
Elsevier Science Publishers B.V., Amsterdam

Thermodynamics of associated solutions involving aniline and ethanol

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(Received 6 August 1991; in revised form 19 November 1991)

Abstract

Excess molar enthalpy data have been measured for the aniline + ethanol and aniline + ethanol + benzene systems at 25°C using an isothermal dilution calorimeter. Experimental results were correlated with polynomial equations and analysed using the UNIQUAC associated-solution model, which assumes self-association for aniline and ethanol, and solvation between unlike molecules. The model can also predict satisfactorily the ternary liquid–liquid equilibria for the systems aniline + ethanol + n-hexane or n-heptane, using binary parameters alone

LIST OF SYMBOLS

A, B, C	aniline, alcohol and hydrocarbon
a_{JI}	binary interaction parameter
A_n	constants of eqns. (1) and (2)
A_i, B_i	i-mers of aniline and alcohol
$\mathrm{A}_i\mathrm{B}_j\mathrm{C}$	complex containing i molecules of aniline, j molecules of alcohol and one molecule of hydrocarbon
$\mathrm{A}_i\mathrm{C}$	complex containing i molecules of aniline and one molecule of hydrocarbon
$\mathrm{B}_i\mathrm{C}$	complex containing i molecules of alcohol and one molecule of hydrocarbon
B_n	constants of eqn. (4)
C_{JI}, D_{JI}	coefficients of eqn. (13)
$H_{\mathrm{m}}^{\mathrm{E}}$	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-bond formation of aniline and alcohol

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h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules
K_A,K_B	association constants of aniline and alcohol
K_{AB}, K_{AC}, K_{BC}	solvation constants between unlike molecules
k	constant of eqn. (1)
l	constant of eqn. (4)
P	total pressure
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. (21) and (22)
S_A, S_B	sums as defined by eqns. (23) and (24)
T	absolute temperature
$\bar{U}_A$, $\bar{U}_B$	quantities as defined by eqns. (8) and (9)
U_A, U_B	quantities as defined by eqns. (10) and (11)
V	true molar volume of aniline mixture given by eqn. (27)
V_A°, V_B°	true molar volumes of pure aniline and alcohol given by eqn. (28)
x_I	liquid mole fraction of component I
x_I'	liquid mole fraction of component I in a binary mixture
Z	lattice coordination number equal to 10

Greek letters

γ_I	activity coefficient of component I
δ	experimental value minus calculated value
Δ_{123}	function as defined by eqn. (4)
θ_I	surface fraction of component I
σ	standard deviation
τ_{JI}	coefficient 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, alcohol and hydrocarbon
A1 B1, C1	monomers of components A, B and C
AB, AC, BC	binary complexes
I, J, K	components I, J and K
i, j, k, l	i-, j-, k- and l-mers of aniline and alcohols or indices

Superscript

pure liquid reference state

INTRODUCTION

This work continues our study of the thermodynamic properties of ternary aniline-containing mixtures. Experimental ternary liquid–liquid equilibrium (LLE) results have been reported for the aniline + methanol or ethanol + saturated hydrocarbon systems at 25°C [1]. This paper presents experimental excess molar enthalpies H_m^E for the binary aniline + ethanol and ternary aniline + ethanol + benzene systems at 25°C. The H_m^E and LLE results were analysed using the UNIQUAC associated-solution model with binary parameters [2,3]. The H_m^E values at 25°C have been reported for two binary mixtures that contain components of the ternary system under investigation: aniline + benzene [4]; and ethanol + benzene [5].

EXPERIMENTAL

Aniline (Nacalai Tesque. Inc., special grade) was used without further purification. C.P. Ethanol was distilled fractionally after shaking with calcium oxide. C.P. Benzene was subjected to repeated fractional crystallization. The densities of all the chemicals, measured with an Anton-Paar densimeter (DMA40), agreed well with the literature values [6]. Excess molar enthalpies were measured using an isothermal dilution calorimeter at 25°C [7]. The experimental error of the excess molar enthalpies is at least 0.5% of the observed values.

RESULTS

Tables 1 and 2 give the experimental results of the aniline + ethanol and aniline + ethanol + benzene systems at 25°C. The excess molar enthalpies of the aniline + ethanol and aniline + benzene systems have been fitted to eqn. (1)

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

The deviations $\delta H_m^E = (H_m^E - H_{m,ij}^E)$ of the experimental results from the calculated values are also given in Table 1. The excess molar enthalpies of the ethanol + benzene system have been fitted by Mrazek and Van Ness [5] using

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

Table 3 lists the coefficient of eqns. (1) and (2) and the standard deviations σ. Figure 1 compares the experimental results with the calculated values. The ternary H_m^E results have been fitted using eqn. (3)

$$H^E_{m,123} = H^E_{m,12} + H^E_{m,13} + H^E_{m,23} + x_1 x_2 x_3 \Delta_{123} \qquad (3)$$

where

$$\Delta_{123}/RT = \sum_{n=1}^{m} B_n (1 - 2x_3)^{n-1} / [1 - l(1 - 2x_3)] \qquad (4)$$

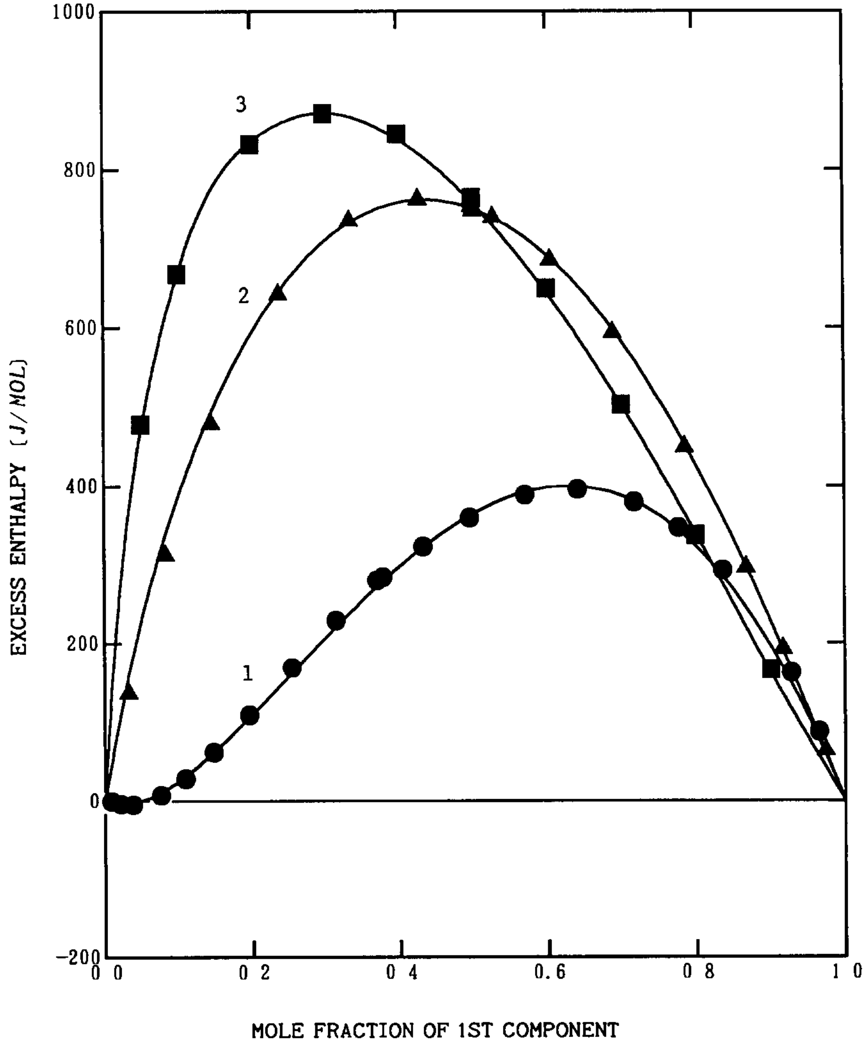

Fig. 1. Experimental excess molar enthalpies for three binary systems at 25°C. (1) aniline(1) + ethanol(2) (●), this work; (2) aniline(1) + benzene(2) (▲), Nagata and Tamura [4], (3) ethanol(1) + benzene(2) (■), Mrazek and Van Ness [5]: (———), calculated from smoothing equations or the UNIQUAC associated-solution model.

TABLE 1

Experimental excess molar enthalpies H_m^E (J mol^{-1}) for the aniline(1)+ethanol(2) system at 25°C

x_1	H_m^E	δH_m^E [a]	x_1	H_m^E	δH_m^E	x_1	H_m^E	δH_m^E
0.0076	−3.4	0.2	0.2528	166.0	−0.1	0.6400	392.9	1.1
0.0202	−6.9	0.1	0.3128	226.3	1.0	0.7160	376.3	0.2
0.0374	−7.6	−0.1	0.3692	277.1	1.9	0.7753	343.6	−0.5
0.0747	4.7	0.3	0.3775	281.5	−0.6	0.8352	289.9	−0.1
0.1078	25.8	0.0	0.4315	319.8	−1.9	0.9267	159.9	0.6
0.1468	58.6	−0.5	0.4942	356.8	−1.0	0.9641	85.2	0.5
0.1951	106.3	−0.3	0.5693	385.4	0.7			

[a] δ = experimental value minus calculated value.

The parameters of eqn. (4) were calculated by means of an equally weighted least-squares method: $B_1 = 1.7097$, $B_2 = 0.9836$, $B_3 = -0.5089$, $B_4 = 0.8554$, $B_5 = -0.0257$, and $l = -1.3183$; and the arithmetic-mean deviation AAD = 8.6 J mol^{-1}, the standard deviation $\sigma = 10.3$ J mol^{-1}, and the relative-mean deviation is 1.0%. Contours of the ternary $H_{m,123}^E$ calculated from eqn. (3) are plotted in Fig. 2.

DATA ANALYSIS

The UNIQUAC associated-solution model [3] was applied to analyse the experimental H_m^E values and the phase equilibrium data of binary and

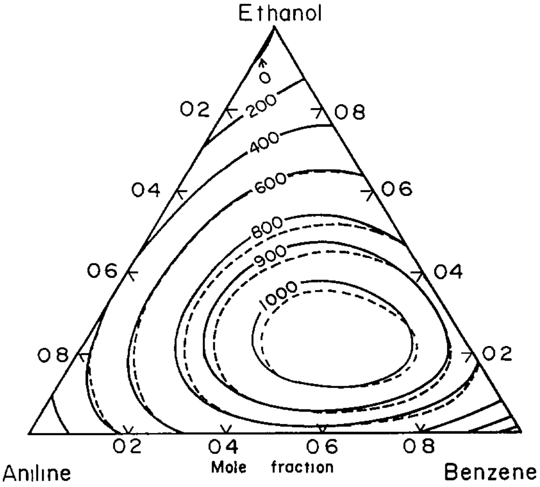

Fig. 2 Curves of constant excess molar enthalpies for the aniline(1)+ethanol(2)+benzene(3) system at 25°C (———), calculated from eqns. (3) and (4), (- - - - - -), calculated from the UNIQUAC associated-solution model.

ternary mixtures containing aniline (A), ethanol (B), and hydrocarbon (C) [2,3]. According to the model, many chemical species formed by successive chemical reactions due to the self-association and multisolvation of associ-

TABLE 2

Experimental ternary excess molar enthalpies H_m^E (J mol^{-1}) at 25°C for aniline(1)+ethanol(2)+benzene(3) [a]

x_1	x_3	H_m^E	δH_m^E [b]
$x_1' = 0.2502$			
0.2449	0.0209	218.3	2.4
0.2355	0.0585	312.0	6.0
0.2197	0.1216	456.6	9.7
0.2002	0.1998	615.0	12.2
0.1805	0.2786	749.8	10.8
0.1606	0.3580	858.9	6.0
0.1429	0.4288	933.2	0.9
0.1325	0.4703	967.6	−0.4
0.1198	0.5212	996.3	−3.7
0.1076	0.5697	1010.4	−7.0
0.0960	0.6164	1011.4	−9.9
0.0860	0.6564	1003.0	−10.9
0.0765	0.6943	985.0	−11.8
0.0715	0.7143	978.3	−5.3
0.0609	0.7567	942.0	−3.4
0.0530	0.7881	903.2	−4.1
0.0455	0.8180	854.2	−8.8
$x_1' = 0.5011$			
0.4855	0.0311	433.8	−4.1
0.4628	0.0763	534.8	−6.6
0.4362	0.1295	642.9	−8.1
0.4101	0.1816	738.9	−8.1
0.3856	0.2306	819.4	−7.3
0.3619	0.2779	886.4	−8.1
0.3376	0.3263	945.1	−9.0
0.3131	0.3751	993.7	−10.3
0.2876	0.4260	1033.2	−11.2
0.2654	0.4704	1057.0	−12.3
0.2508	0.4995	1068.0	−12.2
0.2326	0.5359	1075.3	−12.0
0.2129	0.5751	1074.8	−11.6
0.1956	0.6096	1065.8	−12.1
0.1768	0.6471	1049.5	−10.5
0.1599	0.6810	1025.8	−9.6
0.1446	0.7115	998.2	−7.6
0.1319	0.7368	969.7	−6.1
0.1189	0.7627	934.5	−5.0
0.1063	0.7878	894.2	−4.6
0.0946	0.8183	850.1	−5.9
0.0827	0.8350	798.5	−10.9

TABLE 2 (continued)

x_1	x_3	H_m^E	δH_m^E [b]
$x_1' = 0.7510$			
0.7339	0.0227	411.2	−1.0
0.6982	0.0703	513.3	−1.9
0.6570	0.1252	619.3	−2.9
0.6133	0.1833	719.8	−2.1
0.5659	0.2564	814.5	0.3
0.5178	0.3105	894.0	3.0
0.4731	0.3700	953.5	6.8
0.4288	0.4290	996.3	10.2
0.3852	0.4871	1022.1	13.3
0.3465	0.5386	1030.4	15.8
0.3261	0.5658	1026.6	14.9
0.2919	0.6113	1012.6	15.3
0.2571	0.6577	985.8	17.0
0.2232	0.7028	943.6	16.6
0.1970	0.7377	901.2	17.5
0.1760	0.7656	859.1	17.4
0.1480	0.8030	790.3	15.4
0.1236	0.8354	717.5	9.4
0.1055	0.8595	653.2	−9.1

[a] Obtained by mixing pure benzene with x_1'aniline + $(1 - x_1')$ethanol.

[b] δ = experimental value minus calculated value.

ating molecules may exist: A_i, B_i, $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$, and $B_i(A_jB_k)_l$, where the subscripts i, j, k, and l range from one to infinity. Furthermore, these pure polymers and copolymers produce additional complexes with benzene (C): A_iC, B_iC, $(A_iB_j)_kC$, $(B_iA_j)_kC$, $A_i(B_jA_k)_lC$, and $B_i(A_jB_k)_lC$. All the equilibrium constants are independent of the degree of association and solvation. The model gives the ternary H_m^E as

$$H_m^E = h_A x_A \left(\frac{\bar{U}_A \Phi_{A1}}{\Phi_A} - \bar{U}_A^\circ \Phi_{A1}^\circ \right) + h_B x_B \left(\frac{\bar{U}_B \Phi_{B1}}{\Phi_B} - \bar{U}_B^\circ \Phi_{B1}^\circ \right)$$

TABLE 3

Coefficients A_i of eqns. (1) and (2) and standard deviation σ

System (1+2)	A_1	A_2	A_3	A_4	A_5	A_6	k	σ (J mol^{-1})
Aniline + ethanol	1441.93	1648.12	341.01	406.13			−0.5010	0.9
Aniline + benzene	3003.51	−721.57	447.94	−333.36				1.3
Ethanol + benzene	3.2733	2.1376	0.2546	0.6895	−0.0321	0.0388		

$$
\begin{aligned}
&+\left(h_{\mathrm{A}}\bar{U}_{\mathrm{A}}+h_{\mathrm{AC}}U_{\mathrm{A}}\right)\frac{r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C1}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{\Phi_{\mathrm{A}}}\\
&+\left(h_{\mathrm{B}}\bar{U}_{\mathrm{B}}+h_{\mathrm{BC}}U_{\mathrm{B}}\right)\frac{r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C1}}x_{\mathrm{B}}\Phi_{B1}}{\Phi_{\mathrm{B}}}+\Bigg(h_{\mathrm{A}}\Bigg\{\frac{\bar{U}_{\mathrm{A}}}{K_{\mathrm{AB}}U_{\mathrm{A}}}\\
&\times\left(\frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}+\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}\right)+\frac{\bar{U}_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{\Phi_{\mathrm{A}}}\left(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}\Phi_{\mathrm{A1}}\Phi_{\mathrm{B1}}U_{\mathrm{A}}U_{\mathrm{B}}\right)\\
&+\frac{\bar{U}_{\mathrm{A}}U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B1}}}{U_{\mathrm{A}}\Phi_{\mathrm{B}}}+\Phi_{\mathrm{C1}}\Bigg[\left(\frac{r_{\mathrm{B}}K_{\mathrm{BC}}x_{\mathrm{B}}}{r_{\mathrm{A}}K_{\mathrm{AB}}\Phi_{\mathrm{B}}}+\frac{r_{\mathrm{A}}K_{\mathrm{AC}}x_{\mathrm{A}}}{r_{\mathrm{B}}K_{\mathrm{AB}}\Phi_{\mathrm{A}}}\right)\frac{\bar{U}_{\mathrm{A}}}{U_{\mathrm{A}}}\\
&+\frac{r_{\mathrm{A}}K_{\mathrm{AC}}\bar{U}_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{\Phi_{\mathrm{A}}}\left(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}\Phi_{\mathrm{A1}}\Phi_{\mathrm{B1}}U_{\mathrm{A}}U_{\mathrm{B}}\right)\\
&+\frac{r_{\mathrm{B}}K_{\mathrm{BC}}\bar{U}_{\mathrm{A}}U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B1}}}{U_{\mathrm{A}}\Phi_{\mathrm{B}}}\Bigg]\Bigg\}+h_{\mathrm{B}}\Bigg\{\frac{\bar{U}_{\mathrm{B}}}{K_{\mathrm{AB}}U_{\mathrm{B}}}\left(\frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}+\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}\right)\\
&+\frac{\bar{U}_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B1}}}{\Phi_{\mathrm{B}}}\left(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}\Phi_{\mathrm{A1}}\Phi_{\mathrm{B1}}U_{\mathrm{A}}U_{\mathrm{B}}\right)\\
&+\frac{U_{\mathrm{A}}\bar{U}_{\mathrm{B}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{U_{\mathrm{B}}\Phi_{\mathrm{A}}}+\Phi_{\mathrm{C1}}\Bigg[\left(\frac{r_{\mathrm{B}}K_{\mathrm{BC}}x_{\mathrm{B}}}{r_{\mathrm{A}}K_{\mathrm{AB}}\Phi_{\mathrm{B}}}+\frac{r_{\mathrm{A}}K_{\mathrm{AC}}x_{\mathrm{A}}}{r_{\mathrm{B}}K_{\mathrm{AB}}\Phi_{\mathrm{A}}}\right)\frac{\bar{U}_{\mathrm{B}}}{U_{\mathrm{B}}}\\
&+\frac{r_{\mathrm{B}}K_{\mathrm{BC}}\bar{U}_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B1}}}{\Phi_{\mathrm{B}}}\left(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}\Phi_{\mathrm{A1}}\Phi_{\mathrm{B1}}U_{\mathrm{A}}U_{\mathrm{B}}\right)\\
&+\frac{r_{\mathrm{A}}K_{\mathrm{AC}}\bar{U}_{\mathrm{B}}U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{U_{\mathrm{B}}\Phi_{\mathrm{A}}}\Bigg]\Bigg\}\\
&+h_{\mathrm{AB}}\Bigg\{\left(\frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}+\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}\right)\frac{\left(1+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}\Phi_{\mathrm{A1}}\Phi_{\mathrm{B1}}U_{\mathrm{A}}U_{\mathrm{B}}\right)}{K_{\mathrm{AB}}}\\
&+2\left(\frac{U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{\Phi_{\mathrm{A}}}+\frac{U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B1}}}{\Phi_{\mathrm{B}}}\right)\\
&+\Phi_{\mathrm{C1}}\Bigg[\left(\frac{r_{\mathrm{B}}K_{\mathrm{BC}}x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}+\frac{r_{\mathrm{A}}K_{\mathrm{AC}}x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}\right)\frac{\left(1+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}\Phi_{\mathrm{A1}}\Phi_{\mathrm{B1}}U_{\mathrm{A}}U_{\mathrm{B}}\right)}{K_{\mathrm{AB}}}\\
&+2\left(\frac{r_{\mathrm{A}}K_{\mathrm{AC}}U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A1}}}{\Phi_{\mathrm{A}}}+\frac{r_{\mathrm{B}}K_{\mathrm{BC}}U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B1}}}{\Phi_{\mathrm{B}}}\right)\Bigg]\Bigg\}
\end{aligned}
$$

$$+\left[h_{AC}r_AK_{AC}\Phi_{C1}\left(\frac{U_Ax_A\Phi_{A1}}{\Phi_A}+\frac{x_A}{r_AK_{AB}\Phi_A}\right)+h_{BC}r_BK_{BC}\Phi_{C1}\right.$$

$$\left.\times\left(\frac{U_Bx_B\Phi_{B1}}{\Phi_B}+\frac{x_B}{r_AK_{AB}\Phi_B}\right)\right]\left(1-r_Ar_BK_{AB}^2\Phi_{A1}\Phi_{B1}U_AU_B\right)\Bigg)$$

$$\times\frac{r_Ar_BK_{AB}^2\Phi_{A1}\Phi_{B1}U_AU_B}{\left(1-r_Ar_BK_{AB}^2\Phi_{A1}\Phi_{B1}U_AU_B\right)^2}-R\sum_I q_Ix_I\frac{\sum_J\theta_J\frac{\partial\tau_{JI}}{\partial(1/T)}}{\sum_J\theta_J\tau_{JI}} \tag{5}$$

where

$$\Phi_I=x_Ir_I/\sum_J x_Jr_J \tag{6}$$

$$\theta_I=x_Iq_I/\sum_J x_Jq_J \tag{7}$$

$$\bar{U}_A=K_A\Phi_{A1}/(1-K_A\Phi_{A1})^2 \tag{8}$$

$$\bar{U}_B=K_B\Phi_{B1}/(1-K_B\Phi_{B1})^2 \tag{9}$$

$$U_A=1/(1-K_A\Phi_{A1}) \tag{10}$$

$$U_B=1/(1-K_B\Phi_{B1}) \tag{11}$$

$$\tau_{JI}=\exp(-a_{JI}/T) \tag{12}$$

$$a_{JI}=C_{JI}+D_{JI}(T-273.15) \tag{13}$$

The monomer segment fraction in pure aniline and alcohol are given by

$$\Phi_{A1}^{\circ}=\left[1+2K_A-(1+4K_A)^{0.5}\right]/2K_A^2 \tag{14}$$

$$\Phi_{B1}^{\circ}=\left[1+2K_B-(1+4K_B)^{0.5}\right]/2K_B^2 \tag{15}$$

and then

$$\bar{U}_A^{\circ}=K_A\Phi_{A1}^{\circ}/(1-K_A\Phi_{A1}^{\circ})^2 \tag{16}$$

$$\bar{U}_B^{\circ}=K_B\Phi_{B1}^{\circ}/(1-K_B\Phi_{B1}^{\circ})^2 \tag{17}$$

The monomer segment fractions Φ_{A1}, Φ_{B1}, and Φ_{C1} are solved simultaneously from the mass balance equations (eqns. (18)–(20))

$$\Phi_A=(1+r_AK_{AC}\Phi_{C1})\bar{S}_A+\frac{r_AK_{AB}\bar{S}_AS_B}{\left(1-r_Ar_BK_{AB}^2S_AS_B\right)^2}$$

$$\times\left\{2+r_BK_{AB}S_A(2-r_Ar_BK_{AB}^2S_AS_B)+r_AK_{AB}S_B\right.$$

$$+\Phi_{C1}\left[(r_AK_{AC}+r_BK_{BC})+r_Ar_BK_{AB}K_{AC}S_A\right.$$

$$\left.\left.\times(2-r_Ar_BK_{AB}^2S_AS_B)+r_Ar_BK_{AB}K_{BC}S_B\right]\right\} \tag{18}$$

$$\begin{aligned}\Phi_{\mathrm{B}} = {} & (1 + r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C1}})\bar{S}_{\mathrm{B}} + \frac{r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}S_{\mathrm{A}}S_{\mathrm{B}}\right)^{2}} \\ & \times\left\{2 + r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}\left(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}S_{\mathrm{A}}S_{\mathrm{B}}\right) + r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\right. \\ & + \Phi_{\mathrm{C1}}\left[(r_{\mathrm{A}}K_{\mathrm{AC}} + r_{\mathrm{B}}K_{\mathrm{BC}}) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}\right. \\ & \left.\left.\times\left(2 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}S_{\mathrm{A}}S_{\mathrm{B}}\right) + r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}\right]\right\} \end{aligned} \tag{19}$$

$$\begin{aligned}\Phi_{\mathrm{C}} = {} & \Phi_{\mathrm{C1}}\left\{1 + r_{\mathrm{C}}K_{\mathrm{AC}}S_{\mathrm{A}} + r_{\mathrm{C}}K_{\mathrm{BC}}S_{\mathrm{B}} + \frac{r_{\mathrm{A}}r_{\mathrm{B}}r_{\mathrm{C}}K_{\mathrm{AB}}^{2}S_{\mathrm{A}}S_{\mathrm{B}}}{\left(1 - r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^{2}S_{\mathrm{A}}S_{\mathrm{B}}\right)}\right. \\ & \left.\times\left[\frac{K_{\mathrm{AC}}}{r_{\mathrm{B}}K_{\mathrm{AB}}} + \frac{K_{\mathrm{BC}}}{r_{\mathrm{A}}K_{\mathrm{AB}}} + K_{\mathrm{AC}}S_{\mathrm{A}} + K_{\mathrm{BC}}S_{\mathrm{B}}\right]\right\} \end{aligned} \tag{20}$$

$$\bar{S}_{\mathrm{A}} = \Phi_{\mathrm{A1}}/(1 - K_{\mathrm{A}}\Phi_{\mathrm{A1}})^{2} \tag{21}$$

$$\bar{S}_{\mathrm{B}} = \Phi_{\mathrm{B1}}/(1 - K_{\mathrm{B}}\Phi_{\mathrm{B1}})^{2} \tag{22}$$

$$S_{\mathrm{A}} = \Phi_{\mathrm{A1}}/(1 - K_{\mathrm{A}}\Phi_{\mathrm{A1}}) \tag{23}$$

$$S_{\mathrm{B}} = \Phi_{\mathrm{B1}}/(1 - K_{\mathrm{B}}\Phi_{\mathrm{B1}}) \tag{24}$$

The association parameters of the pure components are as follows: for aniline, $K_{\mathrm{A}} = 15$ at 50°C and $h_{\mathrm{A}} = -15.4$ kJ mol^{-1} [8]; for ethanol, $K_{\mathrm{B}} = 110.4$ at 50°C and $h_{\mathrm{B}} = -23.2$ kJ mol^{-1} [9]. The solvation parameters are: for aniline–ethanol, $K_{\mathrm{AB}} = 25$ at 25°C and $h_{\mathrm{AB}} = -20.7$ kJ mol^{-1}; for aniline–benzene, $K_{\mathrm{AC}} = 1$ at 50°C and $h_{\mathrm{AC}} = -10.8$ kJ mol^{-1} [8]; for ethanol–benzene, $K_{\mathrm{BC}} = 3$ at 50°C and $h_{\mathrm{AC}} = -8.3$ kJ mol^{-1} [9]. The pure-component structural parameters r and q were estimated by the method of Vera et al. [10] and are listed in Table 4. All h values were assumed to be independent of temperature and the van't Hoff relation fixes the temperature dependence of the equilibrium constants. Table 5 gives the coefficients of eqn. (17), C_{JI} and D_{JI}, obtained by fitting the model to the binary $H_{\mathrm{m}}^{\mathrm{E}}$ results using the simplex method [11] and the absolute arithmetic mean and standard deviations between the calculated and experimental values. The predicted ternary $H_{\mathrm{m}}^{\mathrm{E}}$ results for fifty-eight data points derived from the binary parameters alone, show that the

TABLE 4

Values of the pure component structural parameters

Component	r	q	Component	r	q
Aniline	2.98	2.38	*n*-Hexane	3.61	3.09
Ethanol	1.69	1.55	*n*-Heptane	4.15	3.52
Benzene	2.56	2.05			

TABLE 5

Parameters C_{JI} and D_{JI} for binary systems at 25°C

System (1+2)	Number of data points	Parameters				Deviation [a] (J mol^{-}	
		C_{21} (K)	C_{12} (K)	D_{21}	D_{12}	AAD	σ
Aniline +ethanol	20	331.5	262.6	1.491	−0.3368	4.4	5.5
Aniline +benzene	14	−188.1	519.5	−1.073	−2.111	4.5	9.0
Ethanol +benzene	10	952.4	−26.58	2.255	0.1347	3.2	4.4

[a] AAD = absolute arithmetic-mean deviation, σ = standard deviation

absolute arithmetic mean, root-mean-square, and absolute relative deviations are 12.4 J mol^{-1}, 15.1 J mol^{-1}, and 1.7%, respectively. These values are comparable to those for ternary mixtures containing alcohols and one hydrocarbon [12].

Prediction of ternary LLE for the aniline + ethanol + *n*-hexane or *n*-heptane systems was performed to demonstrate the good ability of the model. Binary phase equilibrium data were taken from the literature: VLE data, for aniline + ethanol at 40°C [13]; for ethanol + *n*-hexane at 25°C [14]; for ethanol + *n*-heptane at 30°C [15]; mutual solubilities, aniline + *n*-hexane or *n*-heptane at 25°C [1].

The activity coefficients of aniline (A) and the saturated hydrocarbon (C) [2] are given by

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A1}}{\Phi^{\circ}_{A1} x_A}\right) + r_A\left(\frac{1}{V^{\circ}_A} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right) q_A\left[\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right] + q_A\left[1 - \ln\left(\sum_J \theta_J \tau_{JA}\right) - \sum_J \frac{\theta_J \tau_{AJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{25}$$

$$\ln \gamma_C = \ln\left(\frac{\Phi_{C1}}{x_C}\right) + 1 - \frac{r_C}{V} - \left(\frac{Z}{2}\right) q_C\left[\ln\frac{\Phi_C}{\theta_C} + 1 - \frac{\Phi_C}{\theta_C}\right] + q_C\left[1 - \ln\left(\sum_J \theta_J \tau_{JC}\right) - \sum_J \frac{\theta_J \tau_{CJ}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{26}$$

where

$$\frac{1}{V} = \frac{S_A}{r_A} + \frac{S_B}{r_B} + \left(\frac{2}{r_A r_B K_{AB}} + \frac{S_A}{r_A} + \frac{S_B}{r_B}\right)\frac{r_A r_B K_{AB}^2 S_A S_B}{\left(1 - r_A r_B K_{AB}^2 S_A S_B\right)} + \frac{\Phi_{C1}}{r_C} \tag{27}$$

TABLE 6

Results of binary vapour–liquid equilibrium data reduction

System (1 + 2)	Temp. (°C)	Number of data points	Root-mean-square deviations				Parameters	
			δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	a_{12} (K)	a_{21} (K)
Aniline + ethanol	40	13	0.37	0.00	0.0		44.95	14.28
Ethanol + *n*-hexane	25	9	0.34	0.01	0.0	2	78.76	−11.96
Ethanol + *n*-heptane	30	22	0.73	0.00	0.0		39.73	20.92
Aniline + *n*-hexane	25	MS [a]					200.8	9.744
Aniline + *n*-heptane	25	MS					176.8	16.80

[a] MS = mutual solubilities.

and

$$V^{\circ}_{A} = r_A/(1 - K_A\Phi^{\circ}_{A1}) \tag{28}$$

The activity coefficient of ethanol was also derived from eqns. (25) and (28), changing the subscript from A to B. The monomer segment fractions Φ_{A1} and Φ_{B1} were obtained from eqns. (18) and (19), in which $K_{AC} = K_{BC} = 0$ and $\Phi_{C1} = \Phi_C$.

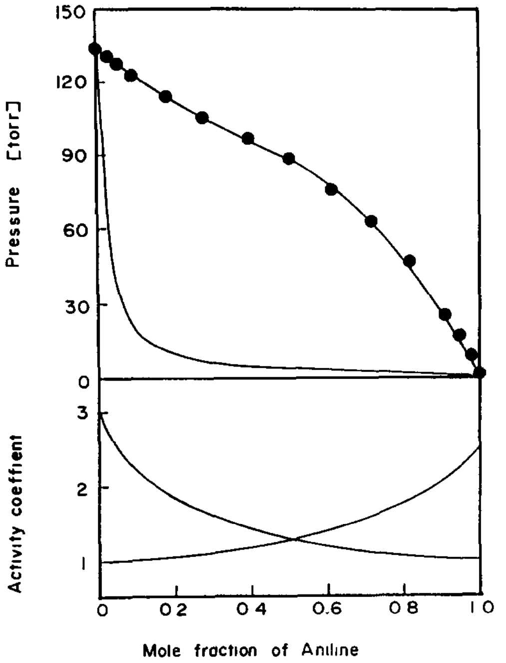

Fig 3 Vapour–liquid equilibrium for the aniline + ethanol system at 40°C; (●), experimental data of Maher and Smith [13], (———), calculated from the UNIQUAC associated-solution model

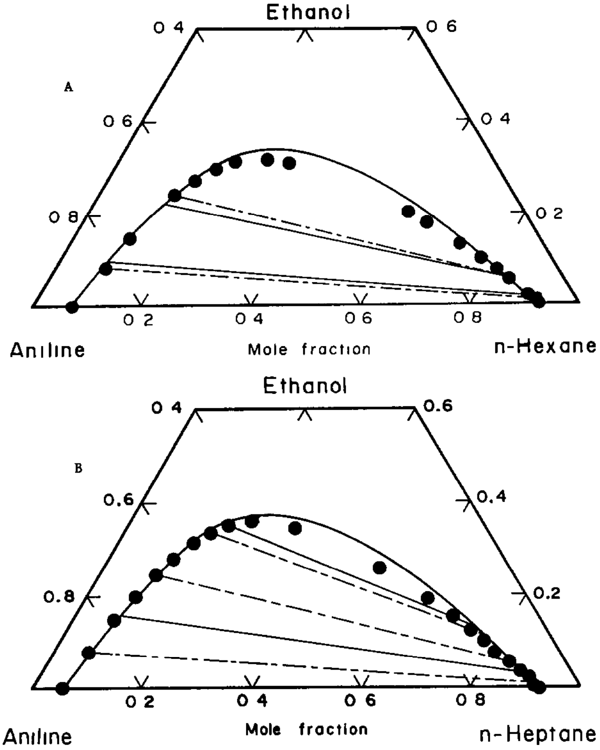

Fig 4 Ternary liquid–liquid equilibria at 25°C (●- — - — -●), experimental tie-line data of Nagata [1]; (A), aniline + ethanol + *n*-hexane, (B), aniline + ethanol + *n*-heptane, (———), calculated from the UNIQUAC associated-solution model.

Binary VLE data reduction was carried out using a computer program similar to that described by Prausnitz et al. [16]; vapour phase non-ideality and the Poynting correction were also taken into account. The binary parameters of the model for partially miscible mixtures were obtained from the mutual solubilities by solving eqn. (29) for each component in the equilibrated phases I and II.

$$(x_i\gamma_i)^{\mathrm{I}} = (x_i\gamma_i)^{\mathrm{II}} \qquad (29)$$

Table 6 gives the results of binary phase equilibrium data reduction. Figure 3 shows VLE data for the aniline + ethanol system at 40°C. Ternary predicted LLE results agree well with the experimental data for the aniline + ethanol + *n*-hexane or *n*-heptane systems at 25°C, as shown in Fig. 4.

CONCLUSION

The excess molar enthalpy and phase equilibrium data of binary and ternary mixtures of aniline with ethanol and the hydrocarbon have been successfully correlated with the UNIQUAC associated-solution model which has only binary parameters.

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