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Thermodynamics of associated solutions. Correlation of ternary excess molar enthalpies for aniline + alkanol + benzene or acetone mixtures using the UNIQUAC associated-solution model

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Abstract

Ternary excess molar enthalpies are reported for 1-propanol + aniline + acetone at 25°C. The UNIQUAC associated-solution model with ternary parameters is used to correlate ternary excess molar enthalpies for aniline + alkanol + benzene or acetone mixtures. The model gives appreciably smaller deviations between the calculated and experimental results than those obtained using polynomial equations.

Keywords: Acetone; Alkanol; Aniline; Association; Benzene; Excess molar enthalpy; Model; Ternary system; Thermodynamics; UNIQUAC

List of symbols

A, B, C	aniline, alkanol, and benzene or acetone
a_{JI}	binary interaction parameter for J–I pair
A_i, B_i	*i*mers of aniline and alkanol
$\mathrm{A}_i\mathrm{B}_j\mathrm{C}$	complex containing *i* molecules of aniline, *j* molecules of alkanol and one molecule of benzene or acetone
$\mathrm{A}_i\mathrm{C}$	complex containing *i* molecules of aniline and one molecule of benzene or acetone

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B_iC	complex containing i molecules of alkanol and one molecule of benzene or acetone
C_{JI}, D_{JI}	parameters of Eq. (18)
F	ternary function
H^E	excess molar enthalpy
$H^E_{12}, H^E_{13} H^E_{23}$	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 alkanol
h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules
K°_A, K°_B	association constants of aniline and alkanol
$K^\circ_{AB}, K^\circ_{AC}, K^\circ_{BC}$	solvation constants between unlike molecules
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 Eq. (24)
S_I	sum as defined by Eq. (25)
s	standard deviation
T	absolute temperature
$\bar{U}_I$	quantity as defined by Eq. (15)
U_I	quantity as defined by Eq. (16)
x_I	liquid mole fraction of component I

Greek letters

γ_I	activity coefficient of component I
θ_I	area fraction of component I
τ_{JI}	binary parameter as defined by $\exp(-a_{JI}/T)$
τ_{JKI}	ternary parameter
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I

Subscripts

A, B, C	aniline, alkanol and benzene or acetone
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 alkanol or indices
phys	physical

Superscripts

$^\circ$	pure liquid state
*	reference state, here mainly taken as 323.15 K
$'$	differential with respect to $1/T$

1. Introduction

Many equations have been developed to predict ternary excess molar enthalpies H^E of liquid mixtures from binary information and to correlate the same ternary data by adding a ternary contribution term. Two general approaches have been used to represent H^E for ternary mixtures [1,2]: polynomial equations and local composition equations.

The following expression is a commonly used form of polynomial equation

$$H^E = H^E_{12} + H^E_{13} + H^E_{23} + x_1 x_2 x_3 F \tag{1}$$

where H^E_{IJ} is the excess molar enthalpy function for the I–J binary system and F is a function of the liquid-phase composition. Eq. (1) has reasonable flexibility in selecting the excess function for the binaries. The functional form of F is unknown. Usually rather simple expressions including several adjustable parameters are sufficient to fit ternary data.

Local composition equations include the expression for H^E written for a ternary (or *n*-component) system. The capability of local composition equation in H^E data reduction has been extensively studied [3–7]. The UNIQUAC associated-solution model has been successfully used to predict H^E for ternary alcohol mixtures using binary information alone [8–12]. Recently, the UNIQUAC associated-solution model has been modified to include ternary parameters in the correlation of ternary vapour–liquid equilibria [13]. In this work, ternary excess enthalpies for 1-propanol + aniline + acetone at 25°C are reported and the UNIQUAC associated-solution model with ternary parameters will be applied to the correlation of ternary H^E data for eight aniline + alkanol + benzene or acetone mixtures. The calculated results obtained here are compared with those derived from polynomial equations.

2. Experimental

Acetone (Wako Pure Chemical Industries, Ltd., guaranteed reagent grade) was dried over fresh potassium carbonate followed by fractional distillation in vacuum. Aniline and 1-propanol (Wako Pure Chemical Industries, Ltd., guaranteed reagent grade) were used directly. The densities of the chemicals used, measured with an Anton Paar densimeter (DMA40) at 25°C, agreed well with published values [14] as shown in Table 1. Excess molar enthalpies H^E for 1-propanol + aniline + acetone at 25°C were measured as described previously [15]. H^E data for three binary mixtures at 25°C are available from the literature, i.e. 1-propanol + aniline [16], 1-propanol + acetone [17], and aniline + acetone [18]; the two former systems are endothermic, the latter is exothermic and all three systems show considerably large deviations from ideality.

Table 1
Densities of pure components at 25°C

Component	Density in g cm^{-3}	
	Obs.	Lit. [14]
Acetone	0.78443	0.78440
Aniline	1.01750	1.01750
1-Propanol	0.79973	0.79960

Table 2
Experimental ternary excess molar enthalpies for 1-propanol(1) + aniline(2) + acetone(3) mixtures at 25°C

x_1	x_2	H^E in J mol^{-1}	x_1	x_2	H^E in J mol^{-1}	x_1	x_2	H^E in J mol^{-1}
$x'_2 = 0.2496$ [a]			$x'_2 = 0.5010$ [a]			$x'_2 = 0.7509$ [a]		
0.0500	0.2371	−590.0	0.0500	0.4759	−899.4	0.0500	0.7129	−541.1
0.1000	0.2247	−315.6	0.1000	0.4509	−639.9	0.1000	0.6754	−338.4
0.1500	0.2122	−72.4	0.1500	0.4259	−414.2	0.1500	0.6379	−162.7
0.2000	0.1997	137.5	0.2000	0.4008	−219.1	0.2000	0.6004	−7.9
0.2500	0.1872	317.9	0.2500	0.3758	−47.5	0.2500	0.5628	123.7
0.3000	0.1747	472.7	0.3000	0.3507	108.0	0.3000	0.5253	238.0
0.3500	0.1623	603.9	0.3500	0.3256	228.2	0.3500	0.4878	332.1
0.4000	0.1498	707.9	0.4000	0.3006	334.0	0.4000	0.4503	409.6
0.4500	0.1373	791.0	0.4500	0.2756	432.4	0.4500	0.4128	470.3
0.5000	0.1248	850.0	0.5000	0.2505	503.6	0.5000	0.3752	520.7
0.5500	0.1123	884.6	0.5500	0.2254	554.5	0.5500	0.3377	559.1
0.6000	0.0998	897.6	0.6000	0.2004	596.2	0.6000	0.3002	570.1
0.6500	0.0874	884.7	0.6500	0.1754	607.3	0.6500	0.2627	564.5
0.7000	0.0749	850.6	0.7000	0.1503	605.1	0.7000	0.2251	544.4
0.7500	0.0624	792.7	0.7500	0.1253	579.1	0.7500	0.1876	503.0
0.8000	0.0499	709.2	0.8000	0.1002	519.8	0.8000	0.1501	443.3
0.8500	0.0374	591.2	0.8500	0.0751	445.6	0.8500	0.1126	363.8
0.9000	0.0250	439.3	0.9000	0.0501	332.1	0.9000	0.0751	266.6
0.9500	0.0125	252.8	0.9500	0.0251	187.7	0.9500	0.0375	139.3

[a] Ternary mixtures were obtained by mixing pure 1-propanol with [x'_2 aniline + $(1 - x'_2)$ acetone].

3. Experimental results

Table 2 shows the experimental H^E data for 1-propanol + aniline + acetone at 25°C. H^E data for the three binary mixtures were correlated with the following polynomial equation

$$H^E = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} / [1 - k(x_1 - x_2)] \tag{2}$$

Table 3
Binary parameters of Eq. (2), root-mean-square deviations and standard deviations s

Mixture (1 + 2)	A_1	A_2	A_3	A_4	k	RMSD[a] in J mol^{-1}	s
1-Propanol + aniline	3132.82	−2640.31	430.13	−263.97	0.6536	0.4	0.5
1-Propanol + acetone	5561.65	49.48	856.60	−40.97		4.1	4.6
Aniline + acetone	−4798.77	−876.81	756.47	−215.47		7.8	

[a] Root-mean-square deviation.

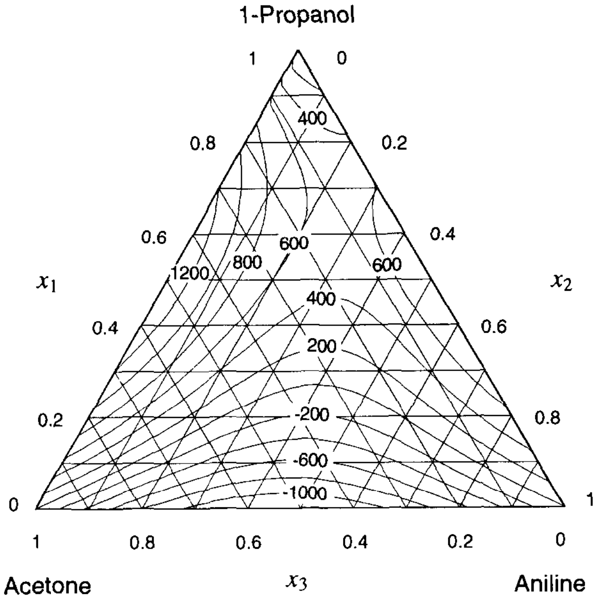

Fig. 1. Curves of constant excess molar enthalpies for 1-propanol(1) + aniline(2) + acetone(3) at 25°C• ——, calculated from Eq. (3).

Table 3 gives the parameters of Eq. (2) and the standard deviations s.

The ternary polynomial equation is expressed by

$$H^{E}_{123} = H^{E}_{12} + H^{E}_{13} + H^{E}_{23} + x_1 x_2 x_3 \Delta_m \tag{3}$$

$$\Delta_m/RT = B_0 - B_1 x_1 - B_2 x_2 - B_3 x_1^2 - B_4 x_2^2 - B_5 x_1 x_2 \tag{4}$$

and has been fitted to the ternary H^Es. The parameters of Eq. (4) are: $B_0 = 3.1685$, $B_1 = 9.0389$, $B_2 = 15.8774$, $B_3 = -0.2459$, $B_4 = -15.3717$, and $B_5 = -6.2354$; and the absolute arithmetic-mean deviation is 9.6 J mol^{-1} and $s = 13.3$. Contours of the ternary H^E values calculated from Eqs. (3) and (4) are shown in Fig. 1.

4. Solution model

In a ternary mixture containing aniline (A), an alkanol (B) and benzene or acetone (C), the UNIQUAC associated-solution model assumes that pure aniline and alkanol self-associate to form linear chains A_i and B_i, and that these pure open chains solvate multiply to yield open crossed chains $(A_iB_j)_k$, $A_i(B_jA_k)_l$, $(B_iA_j)_k$, and $B_i(A_jB_k)_l$, and then the resulting open homo- and hetero-chains and benzene or acetone (C) further solvate to produce additional chemical 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 i, j, k and l range from one to infinity. The equilibrium constants for all chemical-complex-forming reactions are assumed to be independent of the degrees of association and solvation and are defined by

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

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

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

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

$$K_{AB}^\circ = \frac{\Phi_{A_iB_jA_kB_l}}{\Phi_{A_iB_jA_k}\Phi_{B_l}}\frac{r_{A_iB_jA_k}r_{B_l}}{r_{A_iB_jA_kB_l}r_Ar_B} \qquad \text{for } A_iB_jA_k + B_l = A_iB_jA_kB_l$$

$$= \frac{\Phi_{B_iA_jB_kA_l}}{\Phi_{B_iA_jB_k}\Phi_{A_l}}\frac{r_{B_iA_jB_k}r_{A_l}}{r_{B_iA_jB_kA_l}r_Br_A} \qquad \text{for } B_iA_jB_k + A_l = B_iA_jB_kA_i$$

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

$$K_{AC}^\circ = \frac{\Phi_{A_iC}}{\Phi_{A_i}\Phi_{C_1}}\frac{i}{ir_A + r_C} \qquad \text{for } A_i + C_1 = A_iC$$

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

$$K_{BC}^\circ = \frac{\Phi_{B_iC}}{\Phi_{B_i}\Phi_{C_1}}\frac{i}{ir_B + r_C} \qquad \text{for } B_i + C_1 = B_iC$$

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

The ternary H^{E} is given by the sum of the chemical and physical contributions

$$H^{\mathrm{E}} = H^{\mathrm{E}}_{\mathrm{chem}} + H^{\mathrm{E}}_{\mathrm{phys}} \tag{10}$$

$$\begin{aligned}
H^{\mathrm{E}}_{\mathrm{chem}} ={}& h_{\mathrm{A}} x_{\mathrm{A}}\left(\frac{\bar{U}_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} - \bar{U}^{\circ}_{\mathrm{A}}\Phi^{\circ}_{\mathrm{A}_1}\right) + h_{\mathrm{B}} x_{\mathrm{B}}\left(\frac{\bar{U}_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} - \bar{U}^{\circ}_{\mathrm{B}}\Phi^{\circ}_{\mathrm{B}_1}\right)\\
&+ (h_{\mathrm{A}}\bar{U}_{\mathrm{A}} + h_{\mathrm{AC}}U_{\mathrm{A}})\frac{r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}}\\
&+ (h_{\mathrm{B}}\bar{U}_{\mathrm{B}} + h_{\mathrm{BC}}U_{\mathrm{B}})\frac{r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}\\
&+ \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^{\circ 2}_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})(1 + r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1})\\
&+ \frac{\bar{U}_{\mathrm{A}}}{U_{\mathrm{A}}K^{\circ}_{\mathrm{AB}}}\left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}(1 + r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1}) + \frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}(1 + r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\right]\\
&+ \frac{\bar{U}_{\mathrm{A}}U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{U_{\mathrm{A}}\Phi_{\mathrm{B}}}(1 + r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\Bigg\}\\
&+ h_{\mathrm{B}}\Bigg\{\frac{\bar{U}_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}(2 - r_{\mathrm{A}}r_{\mathrm{B}}K^{\circ 2}_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})(1 + r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\\
&+ \frac{\bar{U}_{\mathrm{B}}}{U_{\mathrm{B}}K^{\circ}_{\mathrm{AB}}}\left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}(1 + r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1}) + \frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}(1 + r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\right]\\
&+ \frac{\bar{U}_{\mathrm{B}}U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{U_{\mathrm{B}}\Phi_{\mathrm{A}}}(1 + r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1})\Bigg\} + h_{\mathrm{AB}}\Bigg\{\Bigg[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}(1 + r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1})\\
&+ \frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}(1 + r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\Bigg]\frac{(1 + r_{\mathrm{A}}r_{\mathrm{B}}K^{\circ 2}_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})}{K^{\circ}_{\mathrm{AB}}}\\
&+ \frac{2U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}}(1 + r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1}) + \frac{2U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}(1 + r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\Bigg\}\\
&+ \Bigg[h_{\mathrm{AC}}r_{\mathrm{A}}K^{\circ}_{\mathrm{AC}}\Phi_{\mathrm{C}_1}\left(\frac{U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}} + \frac{x_{\mathrm{A}}}{r_{\mathrm{A}}K^{\circ}_{\mathrm{AB}}\Phi_{\mathrm{A}}}\right)\\
&+ h_{\mathrm{BC}}r_{\mathrm{B}}K^{\circ}_{\mathrm{BC}}\Phi_{\mathrm{C}_1}\left(\frac{U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}} + \frac{x_{\mathrm{B}}}{r_{\mathrm{B}}K^{\circ}_{\mathrm{AB}}\Phi_{\mathrm{B}}}\right)\Bigg]\\
&\times (1 - r_{\mathrm{A}}r_{\mathrm{B}}K^{\circ 2}_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})\Bigg]\frac{r_{\mathrm{A}}r_{\mathrm{B}}K^{\circ 2}_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_2}U_{\mathrm{A}}U_{\mathrm{B}}}{(1 - r_{\mathrm{A}}r_{\mathrm{B}}K^{\circ 2}_{\mathrm{AB}}\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})^2}
\end{aligned} \tag{11}$$

$$\begin{aligned}
H^{\mathrm{E}}_{\mathrm{phys}} ={}& -R\Bigg[q_{\mathrm{A}}x_{\mathrm{A}}\frac{\theta_{\mathrm{B}}\tau'_{\mathrm{BA}} + \theta_{\mathrm{C}}\tau'_{\mathrm{CA}} + \theta_{\mathrm{B}}\theta_{\mathrm{C}}\tau'_{\mathrm{BCA}}}{\theta_{\mathrm{A}} + \theta_{\mathrm{B}}\tau_{\mathrm{BA}} + \theta_{\mathrm{C}}\tau_{\mathrm{CA}} + \theta_{\mathrm{B}}\theta_{\mathrm{B}}\tau_{\mathrm{BCA}}}\\
&+ q_{\mathrm{B}}x_{\mathrm{B}}\frac{\theta_{\mathrm{A}}\tau'_{\mathrm{AB}} + \theta_{\mathrm{C}}\tau'_{\mathrm{CB}} + \theta_{\mathrm{A}}\theta_{\mathrm{C}}\tau'_{\mathrm{ACB}}}{\theta_{\mathrm{A}}\tau_{\mathrm{AB}} + \theta_{\mathrm{B}} + \theta_{\mathrm{C}}\tau_{\mathrm{CB}} + \theta_{\mathrm{A}}\theta_{\mathrm{C}}\tau_{\mathrm{ACB}}}\\
&+ q_{\mathrm{C}}x_{\mathrm{C}}\frac{\theta_{\mathrm{A}}\tau'_{\mathrm{AC}} + \theta_{\mathrm{B}}\tau'_{\mathrm{BC}} + \theta_{\mathrm{A}}\theta_{\mathrm{B}}\tau'_{\mathrm{ABC}}}{\theta_{\mathrm{A}}\tau_{\mathrm{AC}} + \theta_{\mathrm{B}}\tau_{\mathrm{BC}} + \theta_{\mathrm{C}} + \theta_{\mathrm{A}}\theta_{\mathrm{B}}\tau_{\mathrm{ABC}}}\Bigg]
\end{aligned} \tag{12}$$

where the segment fraction Φ_I, the surface fraction θ_I, the symbols $\bar{U}_\mathrm{I}$ and U_I and the binary parameter τ_JI are expressed by

$$\Phi_\mathrm{I} = x_\mathrm{I}/r_\mathrm{I} \Big/ \sum_\mathrm{J} x_\mathrm{J} r_\mathrm{J} \tag{13}$$

$$\theta_\mathrm{I} = x_\mathrm{I}/q_\mathrm{I} \Big/ \sum_\mathrm{J} x_\mathrm{J} q_\mathrm{J} \tag{14}$$

$$\bar{U}_\mathrm{I} = K_\mathrm{I}^\circ \Phi_{\mathrm{I}_1}/(1 - K_\mathrm{I}^\circ \Phi_{\mathrm{I}_1})^2 \tag{15}$$

$$U_\mathrm{I} = 1/(1 - K_\mathrm{I}^\circ \Phi_{\mathrm{I}_1}) \tag{16}$$

$$\tau_\mathrm{JI} = \exp(-a_\mathrm{JI}/T) \tag{17}$$

The energy parameter a_JI is assumed to change linearly with temperature.

$$a_\mathrm{JI} = C_\mathrm{JI} + D_\mathrm{JI}(T - 273.15) \tag{18}$$

The values of Φ_{I_1} and $\bar{U}_\mathrm{I}^\circ$ in the pure liquid state are expressed by

$$\Phi_{\mathrm{I}_1}^\circ = [1 + 2K_\mathrm{I}^\circ - (1 + 4K_\mathrm{I}^\circ)^{0.5}]/2K_\mathrm{I}^{\circ 2} \tag{19}$$

$$\bar{U}_\mathrm{I}^\circ = K_\mathrm{I}^\circ \Phi_{\mathrm{I}/1}^\circ/(1 - K_\mathrm{I}^\circ \Phi_{\mathrm{I}_1})^2 \tag{20}$$

$\tau'_\mathrm{JI} = \partial \tau_\mathrm{JI}/\partial(1/T)$ and $\tau'_\mathrm{JKI} = \partial \tau_\mathrm{JKI}/\partial(1/T)$.

The monomeric segment fractions of the components, Φ_{A_1}, Φ_{B_1} and Φ_{C_1}, are obtained by simultaneous solution of Eqs. (21)–(23)

$$\begin{aligned}
\Phi_\mathrm{A} = {} & (1 + r_\mathrm{A} K_\mathrm{AC}^\circ \Phi_{\mathrm{C}_1})\bar{S}_\mathrm{A} + \frac{r_\mathrm{A} K_\mathrm{AB}^\circ \bar{S}_\mathrm{A} S_\mathrm{B}}{(1 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B})^2} \\
& \times \{2 + r_\mathrm{B} K_\mathrm{AB}^\circ S_\mathrm{A}(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B}) + r_\mathrm{A} K_\mathrm{AB}^\circ S_\mathrm{B} \\
& + \Phi_{\mathrm{C}_1}[(r_\mathrm{A} K_\mathrm{AC}^\circ + r_\mathrm{B} K_\mathrm{BC}^\circ) + r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^\circ K_\mathrm{AC}^\circ S_\mathrm{A} \\
& \times (2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B}) + r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^\circ K_\mathrm{BC}^\circ S_\mathrm{B}]\}
\end{aligned} \tag{21}$$

$$\begin{aligned}
\Phi_\mathrm{B} = {} & (1 + r_\mathrm{B} K_\mathrm{BC}^\circ \Phi_{\mathrm{C}_1})\bar{S}_\mathrm{B} + \frac{r_\mathrm{B} K_\mathrm{AB}^\circ S_\mathrm{A} \bar{S}_\mathrm{B}}{(1 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B})^2} \\
& \times \{2 + r_\mathrm{A} K_\mathrm{AB}^\circ S_\mathrm{B}(2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B}) + r_\mathrm{B} K_\mathrm{AB}^\circ S_\mathrm{A} \\
& + \Phi_{\mathrm{C}_1}[(r_\mathrm{A} K_\mathrm{AC}^\circ + r_\mathrm{B} K_\mathrm{BC}^\circ) + r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^\circ K_\mathrm{BC}^\circ S_\mathrm{B} \\
& \times (2 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B}) + r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^\circ K_\mathrm{AC}^\circ S_\mathrm{A}]\}
\end{aligned} \tag{22}$$

$$\begin{aligned}
\Phi_\mathrm{C} = {} & \Phi_{\mathrm{C}_1}\left\{1 + r_\mathrm{C} K_\mathrm{AC}^\circ S_\mathrm{A} + r_\mathrm{C} K_\mathrm{BC}^\circ S_\mathrm{B} + \frac{r_\mathrm{A} r_\mathrm{B} r_\mathrm{C} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B}}{(1 - r_\mathrm{A} r_\mathrm{B} K_\mathrm{AB}^{\circ 2} S_\mathrm{A} S_\mathrm{B})}\right. \\
& \left. \times \left[\frac{K_\mathrm{AC}^\circ}{r_\mathrm{B} K_\mathrm{AB}^\circ} + \frac{K_\mathrm{BC}^\circ}{r_\mathrm{A} K_\mathrm{AB}^\circ} + K_\mathrm{AC}^\circ S_\mathrm{A} + K_\mathrm{BC}^\circ S_\mathrm{B}\right]\right\}
\end{aligned} \tag{23}$$

where the sums $\bar{S}_\mathrm{I}$ and S_I are defined as

$$\bar{S}_\mathrm{I} = \Phi_{\mathrm{I}_1}/(1 - K_\mathrm{I}^\circ \Phi_{\mathrm{I}_1})^2 \tag{24}$$

$$S_\mathrm{I} = \Phi_{\mathrm{I}_1}/(1 - K_\mathrm{I}^\circ \Phi_{\mathrm{I}_1}) \tag{25}$$

Tables 4 and 5 contain all the pure component and binary parameters necessary for the correlation of the ternary H^E values of the eight mixtures studied here [19–25]. Table 4 gives the association parameters K_A° and h_A for aniline and alkanols, the pure-component molecular structural constants r and q, and the solvation parameters K_{AB}° and h_{AB}, for binary mixtures. All h_A and h_{AB} values were assumed to be independent of temperature. Table 5 shows the coefficients C_{JI} and D_{JI} of Eq. (18) and the deviations between the experimental and calculated H^E data for all component binary mixtures. The values of the ternary parameters τ_{JKI} and τ'_{JKI} were obtained by minimizing the sum of the deviations between the experimental and calculated values using the simplex method of Nelder and Mead [26]. Table 6 gives the calculated ternary results derived from the present approach and from polynomial equations, which are usually used for smoothing binary and ternary excess properties as reported in the literature, and were also employed in Refs.

Table 4
Association parameters and molecular structural parameters for pure components and solvation parameters for mixtures

Component	K_A° at 50°C	$-h_A$ in kJ mol^{-1}	r	q
Aniline	15.0	15.4	2.98	2.38
Methanol	173.9	23.2	1.15	1.12
Ethanol	110.4	23.2	1.69	1.55
1-Propanol	87.0	23.2	2.23	1.98
2-Propanol	49.1	23.2	2.23	1.98
1-Butanol	69.5	23.2	2.77	2.42
2-Butanol	31.1	23.2	2.77	2.42
Acetone			2.06	1.85
Benzene			2.56	2.05

Mixture (A + B)	T in °C	K_{AB}°	$-h_{AB}$ in kJ mol^{-1}
Aniline + methanol	25	25.0	20.7
Aniline + ethanol	25	25.0	20.7
Aniline + 1-propanol	25	23.0	20.7
Aniline + 2-propanol	25	22.0	20.7
Aniline + 1-butanol	25	22.0	17.5
Aniline + 2-butanol	25	16.0	17.5
Aniline + acetone	50	6.0	14.2
Aniline + benzene	50	1.0	10.8
Methanol + acetone	50	60.0	21.0
Methanol + benzene	50	4.0	8.3
Ethanol + benzene	50	3.0	8.3
1-Propanol + acetone	50	35.0	21.0
1-Propanol + benzene	50	2.5	8.3
2-Propanol + benzene	50	2.5	8.3
1-Butanol + benzene	50	2.5	8.3
2-Butanol + benzene	50	2.5	8.3

Table 5
Binary parameters C_{JI} and D_{JI} and absolute arithmetic mean deviation at 25°C

Mixture (A + B)	Number of data points	Parameters				Abs. arith. mean dev. in J mol^{-1}
		C_{BA} in K	C_{AB} in K	D_{BA}	D_{AB}	
Aniline + methanol	16	−36.86	340.20	0.3662	0.3748	4.0
Aniline + ethanol	20	331.5	262.6	1.4910	−0.3368	4.4
Aniline + 1-propanol	15	−1.861	158.77	0.0394	−0.8525	4.6
Aniline + 2-propanol	15	201.14	132.20	0.2183	−0.9316	1.8
Aniline + 1-butanol	16	82.09	225.57	0.3845	0.3985	2.5
Aniline + 2-butanol	16	364.13	321.96	0.3196	0.8742	1.0
Aniline + acetone	13	−313.33	−1.6971	−1.7788	1.6055	15.5
Aniline + benzene	14	−188.1	519.51	−1.0731	2.1112	4.5
Methanol + acetone	22	−516.60	−262.35	−2.2853	−1.1245	12.7
Methanol + benzene	10	1260.7	−109.3	2.174	−0.3827	1.7
Ethanol + benzene	10	952.4	−26.58	2.2554	0.1347	3.2
1-Propanol + acetone	19	−458.80	−250.43	−2.2957	−1.1797	7.7
1-Propanol + benzene	10	807.5	355.0	2.055	1.3727	5.7
2-Propanol + benzene	10	1428.72	299.17	3.0317	0.7810	7.3
1-Butanol + benzene	10	539.17	1709.20	1.4761	11.1116	9.2
2-Butanol + benzene	18	1914.84	335.34	−0.6689	0.5887	8.2

[19–25]. The two methods included the six ternary parameters. The present approach is much better than that using polynomial equations.

5. Conclusions

The proposed form for expressing H^E data for ternary associated mixtures has the advantage of a local composition model: no guesswork is necessry for the extension to ternary systems from the constituent binaries. It is found that the

Table 6
Ternary calculated results at 25°C

Mixture (A + B + C)	Ternary parameters		Deviations			
			AAMD[a] in J mol^{-1}		RMSD[b] in J mol^{-1}	
			I[c]	II[d]	I[c]	II[d]
Aniline+ methanol+ benzene	$\tau_{BCA} = 0.3587$	$\tau'_{BCA} = 2.6717$	5.1	7.2	57	8.1
	$\tau_{ACB} = 0.2411$	$\tau'_{ACB} = -24.0165$				
	$\tau_{ABC} = -0.4962$	$\tau'_{ABC} = -15.2474$				
Aniline+ ethanol+ benzene	$\tau_{BCA} = -0.7535$	$\tau'_{BCA} = 20.9153$	5.7	8.6	6.9	9.7
	$\tau_{ACB} = 0.0080$	$\tau'_{ACB} = -5.0498$				
	$\tau_{ABC} = -0.7527$	$\tau'_{ABC} = 5.6353$				
Aniline+ 1-propanol+ benzene	$\tau_{BCA} = 1.9246$	$\tau'_{BCA} = -21.5430$	9.3	7.3	10.8	8.1
	$\tau_{ACB} = 0.1498$	$\tau'_{ACB} = -26.0643$				
	$\tau_{ABC} = -0.7678$	$\tau'_{ABC} = -23.0639$				
Aniline+ 2-propanol benzene	$\tau_{BCA} = -2.2278$	$\tau'_{BCA} = -71.1337$	3.3	7.9	3.8	9.0
	$\tau_{ACB} = -0.2113$	$\tau'_{ACB} = 54.0770$				
	$\tau_{ABC} = 2.0854$	$\tau'_{ABC} = 176.5265$				
Aniline+ 1-butanel+ benzene	$\tau_{BCA} = 16.9875$	$\tau'_{BCA} = 520.6063$	4.9	10.1	6.1	11.5
	$\tau_{ACB} = -0.6004$	$\tau'_{ACB} = -87.3787$				
	$\tau_{ABC} = 1.0997$	$\tau'_{ABC} = -93.2947$				
Aniline+ 2-butanol+ benzene	$\tau_{BCA} = -2.8295$	$\tau'_{BCA} = 99.3316$	3.2	9.9	4.2	10.9
	$\tau_{ACB} = 0.0557$	$\tau'_{ACB} = -51.2059$				
	$\tau_{ABC} = 4.1187$	$\tau'_{ABC} = 212.9269$				
Aniline+ methanol+ acetone	$\tau_{BCA} = 0.4893$	$\tau'_{BCA} = -570.9823$	10.6	15.4	13.4	20.4
	$\tau_{ACB} = -10.2918$	$\tau'_{ACB} = 1285.8769$				
	$\tau_{ABC} = 1.8904$	$\tau'_{ABC} = 288.5387$				
Aniline+ 1-propanol+ acetone	$\tau_{BCA} = 5.8558$	$\tau'_{BCA} = -352.6444$	9.9	9.6	12.7	13.3
	$\tau_{ACB} = -6.5051$	$\tau'_{ACB} = 1053.4407$				
	$\tau_{ABC} = -1.7587$	$\tau'_{ABC} = -236.5626$				

[a] Absolute arithmetic-mean deviation. [b] Root-mean-square deviation. [c] This work. [d] Polynomial equation [19-25].

method with six ternary parameters can represent H^E data significantly better than polynomial expressions with six ternary parameters. The proposed method may be useful in the correlation of H^E data for markedly non-ideal ternary mixtures involving an alkanol and aniline.

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