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Thermodynamics of associated solutions. Prediction of ternary excess molar enthalpies of alcohol mixtures containing an active non-associating component

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Abstract

Ternary excess molar enthalpies of 1-propanol + triethylamine + *n*-heptane, 1-propanol + 1-hexanol + 3-pentanone and 1-propanol + 1-heptanol + 3-pentanone have been predicted using the UNIQUAC associated-solution model with binary parameters alone. For 1-propanol + triethylamine + *n*-heptane, the UNIQUAC associated-solution model gives better predicted results than those obtained from the ERAS model of Heintz and the NRTL equation. For the two other ternary systems, the UNIQUAC associated-solution model is superior to the group-contribution model of Nitta–Chao.

LIST OF SYMBOLS

A, B, C	1-propanol, triethylamine or 1-hexanol or 1-heptanol, and *n*-heptane or 3-pentanone
a_{JI}	binary energy parameter
A_i, B_j	*i*mer of 1-propanol and *j*mer of 1-hexanol or 1-heptanol
A_iB	complex containing *i* molecules of 1-propanol and one molecule of triethylamine
A_iB_j	complex containing *i* molecules of 1-propanol and *j* molecules of 1-hexanol or 1-heptanol
A_iB_jC	complex containing *i* molecules of 1-propanol, *j* molecules of 1-hexanol or 1-heptanol and one molecule of 3-pentanone

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A_iC	complex containing i molecules of 1-propanol and one molecule of 3-pentanone
B_iC	complex containing i molecules of 1-hexanol or 1-heptanol and one molecule of 3-pentanone
C_{JI}, D_{JI}	coefficients of eqn. (7)
H_m^E	excess molar enthalpy
h_A, h_B	enthalpies of hydrogen-bonded formation of 1-propanol and 1-hexanol or 1-heptanol
h_{AB}, h_{AC}, h_{BC}	enthalpies of complex formation between unlike molecules
K_A, K_B	association constants of 1-propanol and 1-hexanol or 1-heptanol
K_{AB}, K_{AC}, K_{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 eqn. (19)
S_I	sum as defined by eqn. (20)
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

Greek letters

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	1-propanol, triethylamine or 1-hexanol or 1-heptanol, and *n*-heptane or 3-pentanone
A_1, B_1, C_1	monomers of components A, B and C
AB, AC, BC	binary complexes
I, J, K	components
i, j, k, l	i, j, k and $l$mers of 1-propanol and 1-hexanol or 1-heptanol

Superscripts

^{0}	pure alcohol state
*	reference state, here taken as 50°C

INTRODUCTION

It has been found that the UNIQUAC associated-solution model is useful in predicting ternary excess molar enthalpies, not only for alcohol mixtures composed of completely miscible binary mixtures, but also for ternary alcohol mixtures which contain binary mixtures with partial miscibility [1–7]. Furthermore, the model has been successfully applied for tenary aniline + alcohol + benzene mixtures [8–11]. The number of ternary alcohol mixtures previously studied is not huge. The workability of the model needs to be examined using new experimental results on ternary alcohol mixtures, including one or two strongly polar non-associating components. Recently, Bender et al. [12] reported the excess molar enthalpies H^E of 1-propanol + triethylamine + *n*-heptane mixtures and its three binary mixtures, and compared their experimental ternary H^E results with those calculated from the ERAS (extended real associated solution) model of Heintz [13] and the NRTL equation [14]. López and co-workers [15, 16] reported two sets of ternary experimental H^E data for 1-propanol + 1-hexanol or 1-heptanol + 3-pentanone and their component binaries, and presented a comparison of experimental results and theoretical calculations derived from the group-contribution Nitta–Chao model [17] for the two ternary systems. These three sets of ternary H^E data provide a good means of checking the prediction ability of the UNIQUAC associated-solution model.

THE UNIQUAC ASSOCIATED-SOLUTION MODEL

One of the three ternary systems to be studied here contains only one alcohol, and the two others include two alcohols. We must use two different expressions of excess molar enthalpy for these systems.

1-Propanol+triethylamine+n-heptane system

We assume that 1-propanol (A) self-associates to produce linear *i*mers by chain reactions ($A_i + A_1 = A_{i+1}$), and the resultant *i*mers of 1-propanol form chemical complexes with triethylamine (B) according to the reaction $A_i + B = A_iB$. *n*-Heptane does not form any chemical complexes with 1-propanol and triethylamine, as expected from its chemical nature. The two equilibrium constants K_A and K_{AB} for these two reactions are independent of the degree of association and depend on temperature

$$K_A = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\Phi_{A_1}}\frac{i}{i+1}$$

$$= K_A^* \exp\left(-\frac{h_A}{R}\left(\frac{1}{T}-\frac{1}{T^*}\right)\right) \qquad (1)$$

$$K_{\mathrm{AB}} = \frac{\Phi_{\mathrm{A}_i\mathrm{B}}}{\Phi_{\mathrm{A}_i}\Phi_{\mathrm{B}_1}}\frac{i}{ir_{\mathrm{A}} + r_{\mathrm{B}}}$$
$$= K^*_{\mathrm{AB}}\exp\left(-\frac{h_{\mathrm{AB}}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right) \tag{2}$$

where $\Phi_{\mathrm{A}_{i+1}}$, Φ_{A_i}, Φ_{A_1}, $\Phi_{\mathrm{A}_i\mathrm{B}}$ and Φ_{B_1} are the segment fractions of the chemical species A_{i+1}, A_i, A_1, $\mathrm{A}_i\mathrm{B}$ and B_1, h_{A} and h_{AB} are the molar enthalpies of hydrogen bond and complex formation, r_{A} and r_{B} are the pure-component molecular size parameters, R is the gas constant, and the superscript * indicates the reference state (here taken as 50°C). The final expression of the ternary excess molar enthalpy is given by

$$H^{\mathrm{E}}_{\mathrm{m}} = h_{\mathrm{A}}K_{\mathrm{A}}X_{\mathrm{A}}(\Phi_{\mathrm{A}_1} - \Phi^0_{\mathrm{A}_1}) + h_{\mathrm{AB}}K_{\mathrm{AB}}\Phi_{\mathrm{B}_1}r_{\mathrm{A}}x_{\mathrm{A}}\frac{(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1})}{(1 + r_{\mathrm{A}}K_{\mathrm{AB}}\Phi_{\mathrm{B}_1})}$$
$$- R\sum_I^3 q_I x_I \frac{\sum_J^3 \theta_J(\partial\tau_{JI}/\partial(1/T))}{\sum_J^3 \theta_J\tau_{JI}} \tag{3}$$

where q is the pure-component molecular area parameter; the segment fraction Φ, the surface fraction θ and the binary coefficient τ_{JI} are given by

$$\Phi_I = x_I r_I \Big/ \sum_J^3 x_J r_J \tag{4}$$

$$\theta_I = x_I q_I \Big/ \sum_J^3 x_J q_J \tag{5}$$

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

The energy parameters are assumed to change linearly with temperature

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15), \quad a_{IJ} = C_{IJ} + D_{IJ}(T - 273.15) \tag{7}$$

The monomer segment fractions Φ_{A_1} and Φ_{B_1} are solved simultaneously from the mass balance equations

$$\Phi_{\mathrm{A}} = \frac{\Phi_{\mathrm{A}_1}}{(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1})^2}(1 + r_{\mathrm{A}}K_{\mathrm{AB}}\Phi_{\mathrm{B}_1}) \tag{8}$$

$$\Phi_{\mathrm{B}} = \Phi_{\mathrm{B}_1}\left(1 + \frac{r_{\mathrm{B}}K_{\mathrm{AB}}\Phi_{\mathrm{A}_1}}{(1 - K_{\mathrm{A}}\Phi_{\mathrm{A}_1})}\right) \tag{9}$$

The monomer segment fraction of the pure alcohol is expressed by

$$\Phi^0_{\mathrm{A}_1} = [2K_{\mathrm{A}} + 1 - (1 + 4K_{\mathrm{A}})^{0.5}]/2K^2_{\mathrm{A}} \tag{10}$$

1-Propanol + 1-hexanol or 1-heptanol + 3-pentanone systems

We assume that the multi-cross association between an *i*mer of 1-propanol (A) and a *j*mer of 1-hexanol or 1-heptanol (B) yields $(A_iB_j)_k$, $(B_iA_j)_k$, $A_i(B_jA_k)_l$ and $B_i(A_jB_k)_l$ according to the reaction $A_iB_jA_k + B_l = A_iB_jA_kB_l$, and that the equilibrium constant is independent of the degrees of the self-association and cross-association

$$K_{AB} = \frac{\Phi_{A_iB_jA_kB_l}}{\Phi_{A_iB_jA_k}\Phi_{B_l}} \frac{r_{A_iB_jA_k} r_{B_l}}{r_{A_iB_jA_kB_l} r_A r_B} \tag{11}$$

The resultant alcohol polymers and copolymers and 3-pentanone (C) produce additional chemical complexes A_iC, B_iC, $(A_iB_j)_kC$, $(B_iA_j)_kC$, $A_i(B_jA_k)_lC$ and $B_i(A_jB_k)_lC$. The equilibrium constants for these chemical complex-forming reactions are assumed to be independent of the degrees of the self-association and cross-association.

The ternary H^E_m is expressed by

$$H^E_m = h_A x_A\left(\frac{\bar{U}_A \Phi_{A_1}}{\Phi_A} - \bar{U}^0_A \Phi^0_{A_1}\right) + h_B x_B\left(\frac{\bar{U}_B \Phi_{B_1}}{\Phi_B} - U^0_A \Phi^0_{B_1}\right)$$

$$+ (h_A \bar{U}_A + h_{AC} U_A)\frac{r_A K_{AC} \Phi_{C_1} x_A \Phi_{A_1}}{\Phi_A}$$

$$+ (h_B \bar{U}_B + h_{BC} U_B)\frac{r_B K_{BC} \Phi_{C_1} x_B \Phi_{B_1}}{\Phi_B}$$

$$+ \Bigg[h_A\Bigg\{\frac{\bar{U}_A x_A \Phi_{A_1}}{\Phi_A}(2 - r_A r_B K^2_{AB} \Phi_{A_1} \Phi_{B_1} U_A U_B)(1 + r_A K_{AC} \Phi_{C_1})$$

$$+ \frac{\bar{U}_A}{U_A K_{AB}}\left[\frac{x_A}{r_B \Phi_A}(1 + r_A K_{AC} \Phi_{C_1}) + \frac{x_B}{r_A \Phi_B}(1 + r_B K_{BC} \Phi_{C_1})\right]$$

$$+ \frac{\bar{U}_A U_B x_B \Phi_{B_1}}{U_A \Phi_B}(1 + r_B K_{BC} \Phi_{C_1})\Bigg\}$$

$$+ h_B\Bigg\{\frac{\bar{U}_B x_B \Phi_{B_1}}{\Phi_B}(2 - r_A r_B K^2_{AB} \Phi_{A_1} \Phi_{B_1} U_A U_B)(1 + r_B K_{BC} \Phi_{C_1})$$

$$+ \frac{\bar{U}_B}{U_B K_{AB}}\left[\frac{x_A}{r_B \Phi_A}(1 + r_A K_{AC} \Phi_{C_1}) + \frac{x_B}{r_A \Phi_B}(1 + r_B K_{BC} \Phi_{C_1})\right]$$

$$+ \frac{\bar{U}_B U_A x_A \Phi_{A_1}}{U_B \Phi_A}(1 + r_A K_{AC} \Phi_{C_1})\Bigg\}$$

$$
\begin{aligned}
&+h_{\mathrm{AB}}\left\{\left[\frac{x_{\mathrm{A}}}{r_{\mathrm{B}}\Phi_{\mathrm{A}}}(1+r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1})+\frac{x_{\mathrm{B}}}{r_{\mathrm{A}}\Phi_{\mathrm{B}}}(1+r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\right]\right.\\
&\times\frac{(1+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})}{K_{\mathrm{AB}}}\\
&\left.+\frac{2U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}}(1+r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1})+\frac{2U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}(1+r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\right\}\\
&+\left\{h_{\mathrm{AC}}r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1}\left(\frac{U_{\mathrm{A}}x_{\mathrm{A}}\Phi_{\mathrm{A}_1}}{\Phi_{\mathrm{A}}}+\frac{x_{\mathrm{A}}}{r_{\mathrm{A}}K_{\mathrm{AB}}\Phi_{\mathrm{A}}}\right)\right.\\
&\left.+h_{\mathrm{BC}}r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1}\left(\frac{U_{\mathrm{B}}x_{\mathrm{B}}\Phi_{\mathrm{B}_1}}{\Phi_{\mathrm{B}}}+\frac{x_{\mathrm{B}}}{r_{\mathrm{B}}K_{\mathrm{AB}}\Phi_{\mathrm{B}}}\right)\right\}\\
&\left.\times(1-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})\right]\frac{r_{\mathrm{A}}r_{\mathrm{B}}K_{AB}^2\Phi_{A_1}\Phi_{B_1}U_{\mathrm{A}}U_{\mathrm{B}}}{(1-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2\Phi_{\mathrm{A}_1}\Phi_{\mathrm{B}_1}U_{\mathrm{A}}U_{\mathrm{B}})^2}\\
&-R\sum_{I}^{3}q_Ix_I\frac{\sum_{J}^{3}\theta_J\frac{\partial\tau_{JI}}{\partial(1/T)}}{\sum_{J}^{3}\theta_J\tau_{JI}}
\end{aligned}
\tag{12}
$$

where the quantities $\bar{U}_I$ and U_I are defined as

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

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

and the value of $\bar{U}_I$ at pure alcohol states $\bar{U}_I^0$ is

$$\bar{U}_I^0=K_I\Phi_{I_1}^0/(1-K_I\Phi_{I_1}^0)^2 \tag{15}$$

The monomer segment fractions of the components, Φ_{A_1}, Φ_{B_1} and Φ_{C_1}, are solved simultaneously from eqns. (16)–(18)

$$
\begin{aligned}
\Phi_{\mathrm{A}}=&(1+r_{\mathrm{A}}K_{\mathrm{AC}}\Phi_{\mathrm{C}_1})\bar{S}_{\mathrm{A}}+\frac{r_{\mathrm{A}}K_{\mathrm{AB}}\bar{S}_{\mathrm{A}}S_{\mathrm{B}}}{(1-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2}\\
&\times\{2+r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})+r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}\\
&+\Phi_{\mathrm{C}_1}[(r_{\mathrm{A}}K_{\mathrm{AC}}+r_{\mathrm{B}}K_{\mathrm{BC}})+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}\\
&\times(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}]\}
\end{aligned}
\tag{16}
$$

$$
\begin{aligned}
\Phi_{\mathrm{B}}=&(1+r_{\mathrm{B}}K_{\mathrm{BC}}\Phi_{\mathrm{C}_1})\bar{S}_{\mathrm{B}}+\frac{r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\bar{S}_{\mathrm{B}}}{(1-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})^2}\\
&\times\{2+r_{\mathrm{A}}K_{\mathrm{AB}}S_{\mathrm{B}}(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}^2S_{\mathrm{A}}S_{\mathrm{B}})+r_{\mathrm{B}}K_{\mathrm{AB}}S_{\mathrm{A}}\\
&+\Phi_{\mathrm{C}_1}[(r_{\mathrm{A}}K_{\mathrm{AC}}+r_{\mathrm{B}}K_{\mathrm{BC}})+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{BC}}S_{\mathrm{B}}\\
&\times(2-r_{\mathrm{A}}r_{\mathrm{B}}K_{AB}^2S_{\mathrm{A}}S_{\mathrm{B}})+r_{\mathrm{A}}r_{\mathrm{B}}K_{\mathrm{AB}}K_{\mathrm{AC}}S_{\mathrm{A}}]\}
\end{aligned}
\tag{17}
$$

$$\Phi_{C} = \Phi_{C_1}\{1 + r_{C}K_{AC}S_{A} + r_{C}K_{BC}S_{B} + \frac{r_{A}r_{B}r_{C}K_{AB}^{2}S_{A}S_{B}}{(1 - r_{A}r_{B}K_{AB}^{2}S_{A}S_{B})} \times \left[\frac{K_{AC}}{r_{B}K_{AB}} + \frac{K_{BC}}{r_{A}K_{AB}} + K_{AC}S_{A} + K_{BC}S_{B}\right]\right\} \tag{18}$$

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

$$\bar{S}_{I} = \Phi_{I_1}/(1 - K_{I}\Phi_{I_1})^{2} \tag{19}$$

$$S_{I} = \Phi_{I_1}/(1 - K_{I}\Phi_{I_1}) \tag{20}$$

CALCULATED RESULTS

Table 1 shows the association parameters and molecular structural parameters for the pure components. We used two sets of association parameters: **I**, association constants at 50°C, K_A^*, were taken from Brandani [18] and a single value of $h_A = -23.2\ \text{kJ mol}^{-1}$ was taken for all alcohols [19]; **II**, K_A^* and h_A were obtained from Nagata [5]. The pure-component molecular structural parameters r and q were calculated by the method of Vera et al. [20]. Table 2 gives the solvation constants and enthalpies of complex formation used in this work. Table 3 presents the binary calculated results and the calculated values are compared with the experimental results in Figs. 1–3.

Figures 4 and 5 compare selected experimental H^E results with theoretical calculations based on the ERAS, NRTL [12] and UNIQUAC associated-solution models for 1-propanol + triethylamine + n-heptane. The solid lines through the triangles depicted in Figs. 4 and 5 represent the compositions for which experimental results were taken. Bender et al. [12] stated that predictions of H^E made by the ERAS model and the NRTL model are of comparable quality in the case of curves A, C, D and E in Figs. 4 and

TABLE 1

Association parameters and molecular structural parameters for pure components

Component	Type [a]	K_A^* (50°C)	$-h_A$/(kJ mol^{-1})	r	q
1-Propanol	**I**	87.0	23.2	2.23	1.98
	II	89.9	23.6		
1-Hexanol	**I**	40.8	23.2	3.85	3.28
	II	59.6	22.4		
1-Heptanol	**I**	40.7	23.2	4.39	3.71
	II	49.8	22.1		
n-Heptane				4.15	3.52
3-Pentanone				3.14	2.72
Triethylamine				4.02	3.41

[a] **I**, association constants were taken from Brandani [18], and $h_A = -23.2\ \text{kJ mol}^{-1}$ was used for all alcohols [19]; **II**, K_A^* and h_A were taken from Nagata [5].

TABLE 2

Solvation constants and enthalpies of complex formation

System (A + B)	Type [a]	K^*_{AB}(50°C)	$-h_{AB}$/(kJ mol^{-1})
1-Propanol + triethylamine	**I**	4	23.6
	II	4	23.6
1-Propanol + 1-hexanol	**I**	20	23.2
	II	24	23.0
1-Propanol + 1-heptanol	**I**	20	23.2
	II	24	22.85
1-propanol + 3-pentanone	**I**	10	21.0
	II	10	21.0
1-Hexanol + 3-pentanone	**I**	5	21.0
	II	5	21.0
1-Heptanol + 3-pentanone	**I**	5	21.0
	II	5	21.0

[a] **I**, association constants were taken from Brandani [18], and $h_A = -23.2$ kJ mol^{-1} was used for all alcohols [19]; **II**, K^*_A and h_A were taken from Nagata [5] and $h_{AB} = (h_A + h_B)/2$.

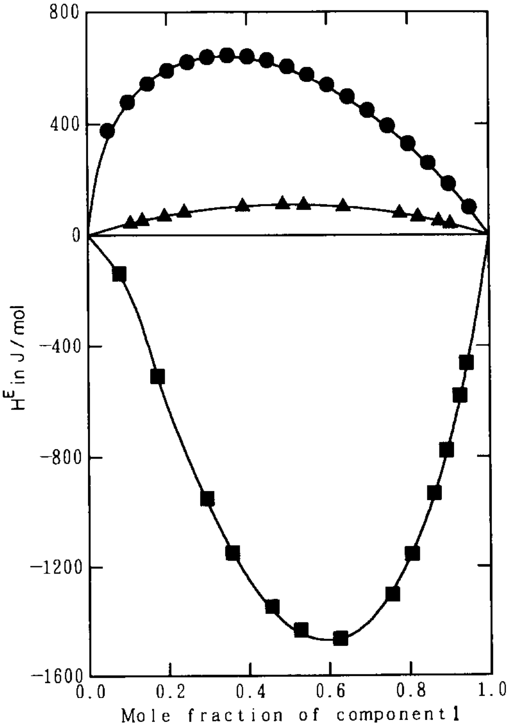

Fig. 1. Molar excess enthalpies for the three binary systems at 25°C. Experimental data: ●, 1-propanol + *n*-heptane [12] (smoothed data); ▲, triethylamine + *n*-heptane [12]; ■, 1-propanol + triethylamine [12]; ——, calculated using K^*_A (50°C) = 89.9 and $h_A = -23.6$ kJ mol^{-1}.

TABLE 3

Calculated results of excess molar enthalpies for binary systems at 25°C

System (A + B)	Type[a]	No. of data points	Abs. arith. mean dev./ (J mol^{-1})	Parameters				Ref.
				C_{BA}/K	D_{BA}	C_{AB}/K	D_{AB}	
1-Propanol	**I**	13	8.61	987.73	1.7722	−156.75	0.0974	12
+ triethylamine	**II**		7.11	766.99	1.3933	−183.97	0.0511	
1-Propanol	**I**	19	4.44	191.66	0.7144	150.34	0.4789	12
+ *n*-heptane	**II**		4.47	214.36	0.7924	165.64	0.5360	
Triethylamine + *n*-heptane		12	0.60	264.52	0.9504	63.19	0.1798	12
1-Propanol	**I**	16	0.62	−59.08	−0.4566	67.78	0.5175	16
+ 1-hexanol	**II**		0.15	−64.83	−0.1702	94.07	0.2377	
1-Propanol	**I**	18	0.51	34.73	−0.8317	−22.50	0.7835	16
+ 1-Heptanol	**II**		0.81	35.48	−0.6744	−15.00	0.6535	
1-Propanol	**I**	22	8.22	300.60	0.4061	381.80	−0.2969	15
+ 3-pentanone	**II**		7.21	260.41	0.2982	411.21	−0.1738	
1-Hexanol	**I**	20	8.49	313.60	0.4868	418.68	−0.2963	16
+ 3-pentanone	**II**		8.62	272.43	0.2369	439.02	−0.1321	
1-Heptanol	**I**	20	5.94	297.24	0.3656	465.42	−0.1866	16
+ 3-pentanone	**II**		8.16	308.11	0.3068	449.46	−0.2184	

[a] **I**, association constants were taken from Brandani [18], and $h_A = -23.2$ kJ mol^{-1} was used for all alcohols [19]; **II**, K_A^* and h_A were taken from Nagata [5].

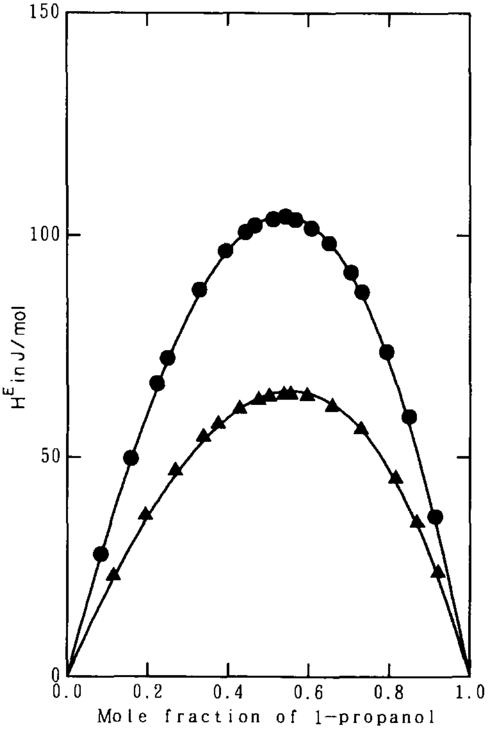

Fig. 2. Molar excess enthalpies for two alcohol + alcohol systems at 25°C. Experimental data: ●, 1-propanol + 1-heptanol [16]; ▲, 1-propanol + 1-hexanol [16]; ——, calculated using K_A^* (1-propanol) = 87.0, K_B^* (1-hexanol) = 40.8 and K_B^* (1-heptanol) = 40.7 at 50°C, and $h_A = h_B = -23.2$ kJ mol^{-1}.

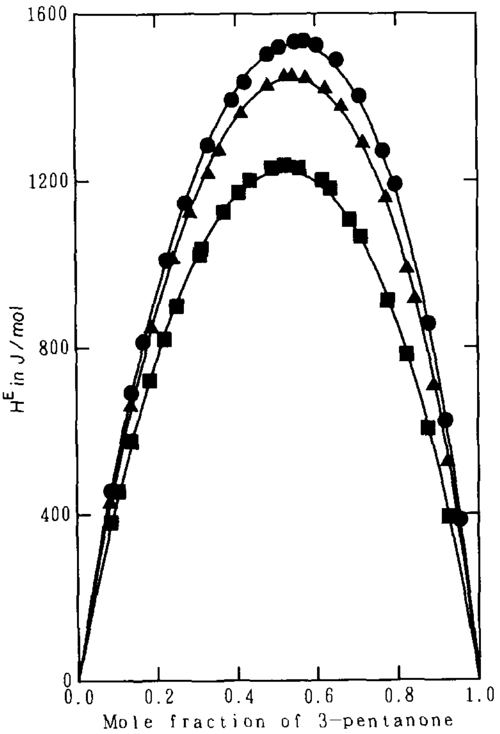

Fig. 3. Molar excess enthalpies for three binary systems at 25°C. Experimental data: ●, 1-heptanol + 3-pentanone [16]; ▲, 1-hexanol + 3-pentanone [16]; ■, 1-propanol + 3-pentanone [15]; ——, calculated using K_A^* (1-propanol) = 87.0, K_B^* (1-hexanol) = 40.8 and K_B^* (1-heptanol) = 40.7 at 50°C, and $h_A = h_B = -23.2$ kJ mol^{-1}.

5, and the ERAS model is superior in the case of curve B. In contrast, the UNIQUAC associated-solution model is superior to the ERAS model in all cases.

Figures 6 and 7 also compare experimental H^E results with predicted values obtained from the Nitta–Chao [17] and UNIQUAC associated-solution models for 1-propanol + 1-hexanol or 1-heptanol + 3-pentanone. Again the UNIQUAC associated-solution model works better than the Nitta–Chao model.

Table 4 gives the ternary predicted results for the three systems. The two sets of parameters give nearly the same results.

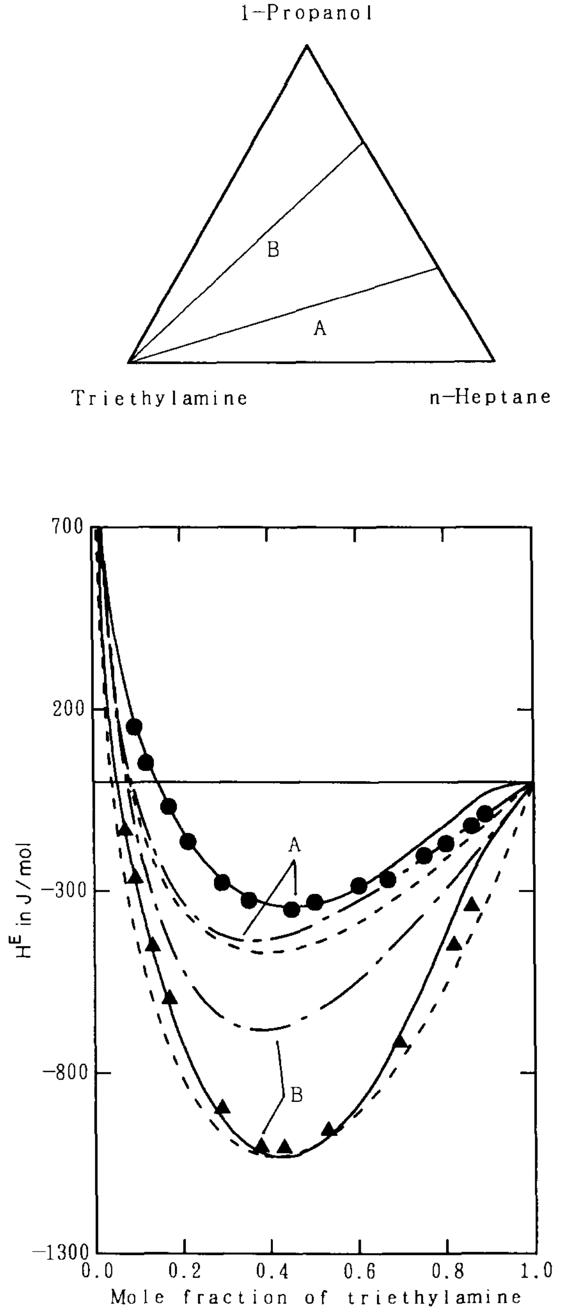

Fig. 4. Comparison between experimental and calculated excess enthalpies for ternary mixtures of $x_1$1-propanol + $x_2$triethylamine + x_3n-heptane prepared by mixing pure triethylamine with constant ratios of x_1/x_3 at 25°C. ●, ▲: Experimental data of Bender et al. [12]. Calculated: ——, UNIQUAC associated-solution model using $K_A^* = 89.9$ (50°C) and $h_A = -23.6$ kJ mol^{-1}; ---, ERAS model; — — —, NRTL model.

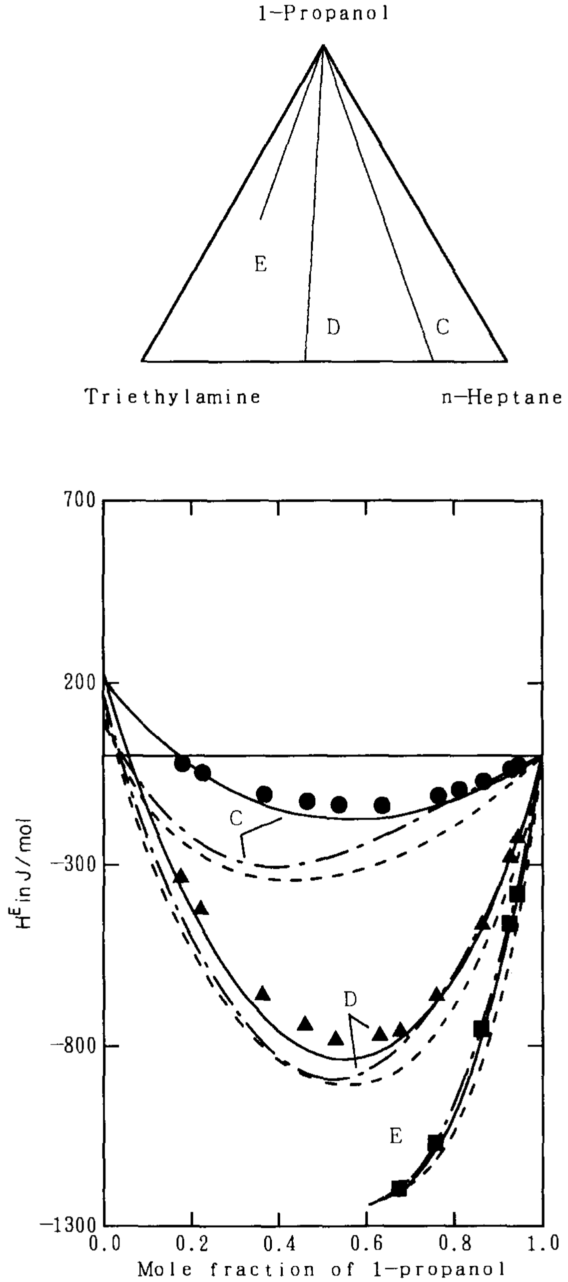

Fig. 5. Comparison between experimental and calculated excess enthalpies for ternary mixtures of $x_1$1-propanol + $x_2$triethylamine + x_3*n*-heptane prepared by mixing pure 1-propanol with constant ratios of x_2/x_3 at 25°C. ●, ▲, ■: Experimental data of Bender et al. [12]. Calculated: ——, UNIQUAC associated-solution model using $K_A^* = 89.9$ (50°C) and $h_A = -23.6$ kJ mol^{-1}; ---, ERAS model; — — —, NRTL model.

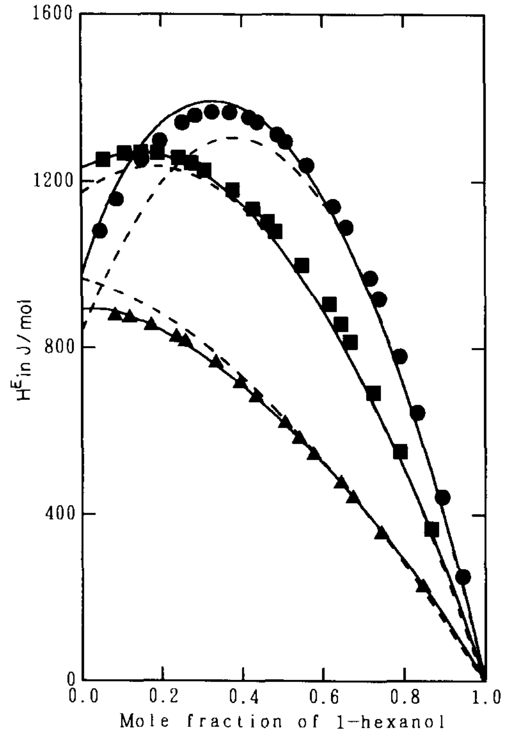

Fig. 6. Comparison between experimental and calculated excess enthalpies at 25°C of the pseudo-binary. Experimental data of López et al. [16]: ●, (x_1+x_2)(0.2495 1-propanol + 0.7505 3-pentanone) + $x_3$1-hexanol; ■, (x_1+x_2)(0.5000 1-propanol + 0.5000 3-pentanone) + $x_3$1-hexanol; ▲, (x_1+x_2)(0.7505 1-propanol + 0.2495 3-pentanone) + $x_3$1-hexanol. Calculated: ——, UNIQUAC associated-solution model using $K_A^* = 87.0$ (50°C) and $h_A = -23.2$ kJ mol^{-1} for 1-propanol, and $K_B^* = 40.8$ kJ mol^{-1} and $h_B = -23.2$ kJ mol^{-1} for 1-hexanol; ---, Nitta–Chao model.

TABLE 4

Predicted results of ternary excess molar enthalpies at 25°C

System (A + B + C)	Type [a]	No. of data points	Deviations [b]		Ref.
			AAD (J mol^{-1})	ARD (%)	
1-Propanol + triethylamine	**I**	75	27.57	17.59	12
+ *n*-heptane	**II**		29.61	15.65	
1-Propanol + 1-hexanol	**I**	54	16.03	1.78	16
+ 3-pentanone	**II**		16.27	1.80	
1-Propanol + 1-heptanol	**I**	60	22.22	2.42	16
+ 3-pentanone	**II**		20.90	2.42	

[a] **I**, association constants were taken from Brandani [18], and $h_A = 23.2$ kJ mol^{-1} was used for all alcohols [19]; **II**, association parameters were taken from Nagata [5].

[b] AAD, absolute arithmetic mean deviation; ARD, absolute relative deviation.

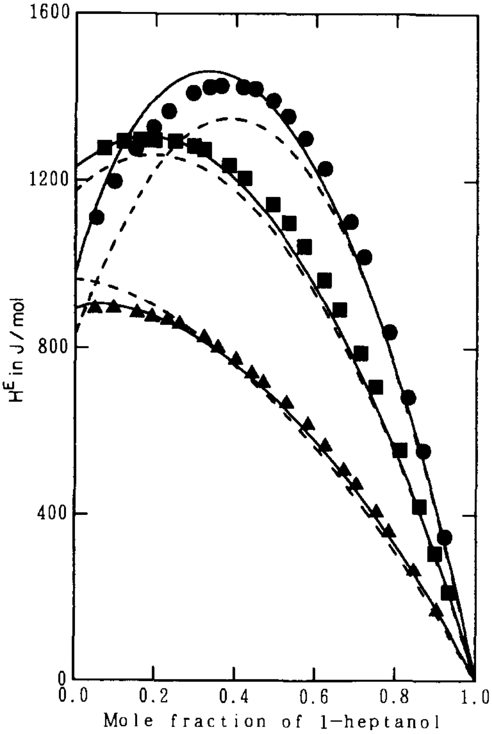

Fig. 7. Comparison between experimental and calculated excess enthalpies at 25°C of the pseudo-binary. Experimental data of López et al. [16]: ●, $(x_1 + x_2)$(0.2495 1-propanol + 0.7505 3-pentanone) + $x_3$1-heptanol; ■, $(x_1 + x_2)$(0.5000 1-propanol + 0.5000 3-pentanone) + $x_3$1-heptanol; ▲, $(x_1 + x_2)$(0.7505 1-propanol + 0.2495 3-pentanone) + x_3 1-heptanol. Calculated: ——, UNIQUAC associated-solution model using $K_A^* = 87.0$ (50°C) and $h_A = -23.2$ kJ mol^{-1} for 1-propanol, and $K_B^* = 40.7$ kJ mol^{-1} and $h_B = -23.2$ kJ mol^{-1} for 1-heptanol; ---, Nitta–Chao model.

We may conclude that the UNIQUAC associated-solution model is better than the ERAS, NRTL and Nitta–Chao models in predicting ternary H^E values for the three systems studied here.

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