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Thermodynamics of associated solutions. Prediction of excess molar enthalpies of ternary mixtures containing methanol, an active non-associating component and *n*-heptane from binary data

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Abstract

The UNIQUAC associated-solution model is used to predict ternary excess enthalpies of methanol + benzene + *n*-heptane and methanol + methyl *tert*-butyl ether + *n*-heptane from binary information. The model assumes that the excess enthalpy is expressed as the sum of chemical and physical terms. The chemical contribution term is due to the association of alcohol and the solvation between alcohol *i*-mer and a solvating component and the physical contribution term represents non-specific interactions between unlike molecules in solution.

LIST OF SYMBOLS

a_{AB}, a_{BA}	binary energy parameters
C_I, D_I	coefficients of eqn. (13)
h_A	molar enthalpy of a hydrogen bond
h_{AB}	molar enthalpy of complex formation
H^E	excess molar enthalpy
K_A	association constant
K_{AB}	solvation constant between alcohol *i*-mer and a solvating molecule
q_I	molecular surface parameter of pure component I
r_I	molecular size parameter of pure component I
R	universal gas constant

Greek letters

α, β	two liquid phases
γ_I	activity coefficient of component I

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θ_I	surface fraction of component I
τ_{AB}, τ_{BA}	binary parameters as defined by eqn. (12)
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I

Subscripts

A, B, C	alcohol, an active non-associating component and an inert component
AB	chemical complex A_iB
chem	chemical
phys	physical

Superscripts

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

INTRODUCTION

The thermodynamic properties of associated solutions have been dealt with using so-called chemical models. Usually these models contain two contribution terms: chemical and physical. One of the most useful chemical models is the UNIQUAC associated-solution model [1–14]. This model has good prediction performance for excess enthalpy data for ternary mixtures composed of completely miscible binary mixtures but has not been tested for ternary mixtures which involve binary mixtures with partial miscibility. So it would be interesting to study the predictive ability of the model for such ternary mixtures. Ternary experimental excess enthalpies have been published for methanol + benzene + *n*-heptane at 30°C [15] and methanol + methyl *tert*-butyl ether (MTBE) + *n*-heptane at 25 and 40°C [16]. Similar data for the binary mixtures constituting the two ternary mixtures are also available from the literature: methanol + benzene [15]; methanol + *n*-heptane [17,18]; methanol + MTBE [18]; benzene + *n*-heptane [15]; MTBE + *n*-heptane [18]. The mixture methanol + *n*-heptane shows phase separation in the temperature range studied.

THE UNIQUAC ASSOCIATED-SOLUTION MODEL

A brief summary of the model is described here. According to the model assumptions, the alcohol molecules form open chains by successive reactions such as $A_i + A_1 = A_{i+1}$ and an active non-associating component B produces chemical complexes by the reaction $A_i + B_1 = A_iB$. The two equilibrium constants K_A and K_{AB} depend only on temperature and are independent of the chain length

$$K_A = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\Phi_{A_1}} \frac{i}{i+1} = K_A^* \exp\left[-\frac{h_A}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{1}$$

$$K_{AB} = \frac{\Phi_{A_iB}}{\Phi_{A_i}\Phi_{B_1}} \frac{1}{ir_A + r_B} = K_{AB}^* \exp\left[-\frac{h_{AB}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{2}$$

where Φ_{A_i}, $\Phi_{A_{i+1}}$, Φ_{A_1}, Φ_{A_iB}, Φ_{B_1} are the segment fractions of A_i, A_{i+1}, A_1, A_iB and B_1, h_A and h_{AB} are the enthalpies of hydrogen bonding and complex formation, r_A and r_B are pure component segment parameters, and R is the universal gas constant.

The excess enthalpy of binary mixtures involving an associating component A and a non-associating component B is given by the sum of two contribution terms: chemical and physical

$$H^E = H^E_{chem} + H^E_{phys} \tag{3}$$

The chemical contribution term H^E_{chem} for the alcohol (methanol) + inert component (n-heptane) is

$$H^E_{chem} = h_A K_A x_A\left(\Phi_{A_1} - \Phi^0_{A_1}\right) \tag{4}$$

where x_A is the mole fraction of the alcohol, Φ_{A_1} and $\Phi^0_{A_1}$ are the segment fractions of the monomeric alcohol in the mixture and in the pure alcohol respectively.

$$\Phi_{A_1} = \left[2K_A\Phi_A + 1 - (4K_A\Phi_A + 1)^{0.5}\right]/2K_A^2\Phi_A \tag{5}$$

where the nominal segment fractions are given by

$$\Phi_A = r_Ax_A/(r_Ax_A + r_Bx_B) \quad \Phi_B = r_Bx_B/(r_Ax_A + r_Bx_B) \tag{6}$$

When $\Phi_A = 1$, Φ_{A_1} reduces to $\Phi^0_{A_1}$.

The H^E_{chem} of binary mixtures including the alcohol and an active non-associating component (benzene or MTBE) is described by

$$H^E_{chem} = h_A K_A x_A\left(\Phi_{A_1} - \Phi^0_{A_1}\right) + h_{AB}K_{AB}\Phi_{B_1}r_Ax_A\frac{\left(1 - K_A\Phi_{A_1}\right)}{\left(1 + r_AK_{AB}\Phi_{B_1}\right)} \tag{7}$$

In eqn. (7) the monomer segment fractions Φ_{A_1} and Φ_{B_1} are obtained from simultaneous solution of the following mass balance equations

$$\Phi_A = \frac{\Phi_{A_1}}{(1 - K_A\Phi_{A_1})^2}(1 + r_A K_{AB}\Phi_{B_1}) \tag{8}$$

$$\Phi_B = \Phi_{B_1}\left[1 + \frac{r_B K_{AB}\Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] \tag{9}$$

The physical contribution term H^E_{phys} represents non-specific interactions between unlike molecules in each binary mixture.

$$H^E_{phys} = -R\left[q_A x_A \frac{\theta_B(\partial\tau_{BA}/\partial(1/T))}{\theta_A + \theta_B\tau_{BA}} + q_B x_B \frac{\theta_A(\partial\tau_{AB}/\partial(1/T))}{\theta_B + \theta_A\tau_{AB}}\right] \tag{10}$$

with the surface fractions θ_A and θ_B and the binary coefficients τ_{BA} and τ_{AB} given by

$$\theta_A = q_A x_A/(q_A x_A + q_B x_B) \qquad \theta_B = q_B x_B/(q_A x_A + q_B x_B) \tag{11}$$

$$\tau_{BA} = \exp(-a_{BA}/T) \qquad \tau_{AB} = \exp(-a_{AB}/T) \tag{12}$$

The energy parameters are assumed to be a linear function of temperature.

$$a_{BA} = C_A + D_A(T - 273.15) \qquad a_{AB} = C_B + D_B(T - 273.15) \tag{13}$$

The H^E of the ternary system composed of an associating component A (methanol) + an active non-associating component B (benzene or MTBE) + an inert component C (*n*-heptane) is calculated by combining eqn. (7) for H^E_{chem} and eqn. (14) for H^E_{phys}

$$H^E_{phys} = -R\sum_I q_I x_I \frac{\sum_J \theta_J(\partial\tau_{JI}/\partial(1/T))}{\sum_J \theta_J\tau_{JI}} \tag{14}$$

Two sets of the association parameters for methanol were used: **I**, $K_A = 173.9$ at 50°C [19] and $h_A = -23.2$ kJ mol^{-1} [20]; **II**, $K_A = 125.1$ at 50°C and $h_A = -23.6$ kJ mol^{-1} [10]. The solvation parameters for two

TABLE 1

Structural parameters for pure components

Component	r	q
Benzene	2.56	2.05
n-Heptane	4.15	3.52
Methanol	1.15	1.12
Methyl *tert*-butyl ether (MTBE)	3.26	2.81

TABLE 2

Calculated results for binary excess enthalpy data

System (A+B)	Temp. (°C)	Number of data points	Type [a]	Abs. arith. mean dev. ($J\ mol^{-1}$)	Parameters				Ref.
					C_A (K)	C_B (K)	D_A	D_B	
Methanol + benzene	30	13	I	16.2	20.40	117.66	0.5373	0.3613	15
			II	16.1	57.32	156.06	1.0855	0.3021	
Methanol + *n*-heptane	25	7 [b]	I	2.4	4.57	70.35	3.2071	−2.5844	18
			II	6.6	13.83	56.31	4.0888	−2.9347	
	30	8	I	12.7	−13.35	87.34	2.8568	−2.4092	17
			II	9.4	−10.85	77.21	3.8017	−2.8555	
	40	10 [b]	I	7.2	−8.28	70.86	2.7489	−2.1303	18
			II	5.1	−9.75	62.69	3.5763	−2.4681	
Methanol + MTBE	25	14	I	9.2	−11.93	212.18	0.7854	−0.4686	18
			II	9.9	14.53	143.88	1.5076	−1.0930	
	40	20	I	9.5	−9.16	173.95	0.9613	−0.6910	18
			II	9.2	8.53	126.56	1.6422	−1.1941	
Benzene + *n*-heptane	30	15		12.3	361.60	−12.85	75.7770	−0.6303	15
MTBE + *n*-heptane	25	20		1.8	667.01	−8.82	2.4235	−0.2398	18
	40	16		1.7	531.32	−4.58	1.9388	−0.2148	18

[a] **I**, One-constant model with association constants taken from Brandani [19]; **II**, One-constant model with association constants taken from Nagata [10].

[b] Data points from the two-liquid region are excluded in data reduction.

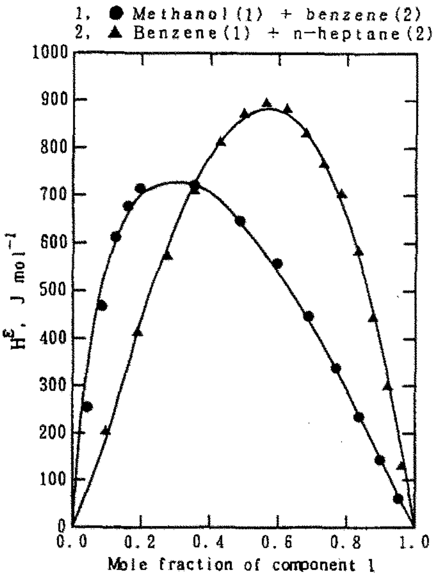

Fig. 1. Molar excess enthalpies for methanol + benzene and benzene + *n*-heptane at 30°C. Experimental data of Battler and Rowley [15]: 1, methanol + benzene (●); 2, benzene + *n*-heptane (▲); calculated (———) using $K_A = 125.1$ (50°C) and $h_A = -23.6$ kJ mol^{-1}.

binary mixtures are $K_{AB} = 4$ at 50°C and $h_{AB} = -8.3$ kJ mol^{-1} [5] for methanol + benzene and $K_{AB} = 10$ at 50°C and $h_{AB} = -18.4$ kJ mol^{-1} for methanol + MTBE. The pure-component molecular structural parameters

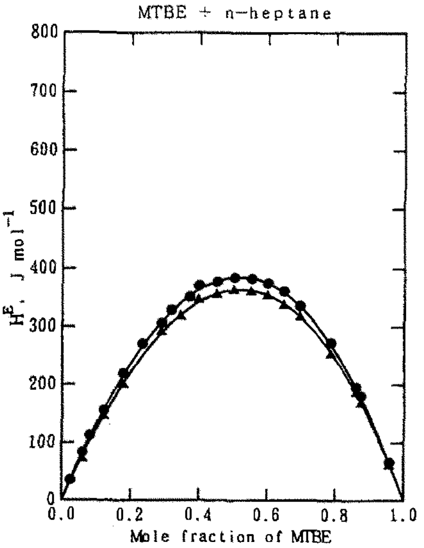

Fig. 2. Molar excess enthalpies for MTBE + *n*-heptane. Experimental data of Tusel-Langer et al. [18]: (●), 25°C; (▲), 40°C; calculated (———).

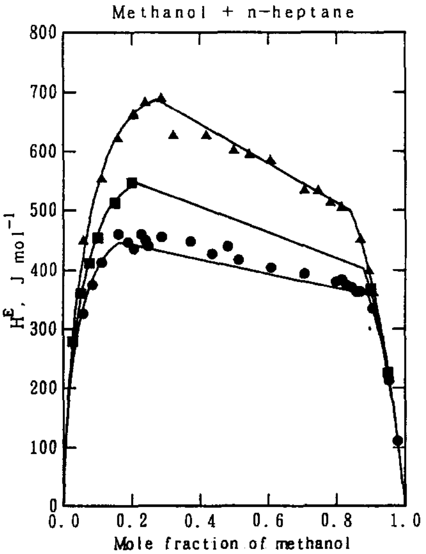

Fig. 3. Molar excess enthalpies for methanol + *n*-heptane. Experimental: (●), 25°C [18]; (■), 30°C [17]; (▲), 40°C [18]; calculated (———) using $K_A = 125.1$ (50°C) and $h_A = -23.6$ kJ mol^{-1}.

r and *q* were calculated by the method of Vera et al. [21] and are listed in Table 1.

The binary calculated results are given in Table 2 and the experimental

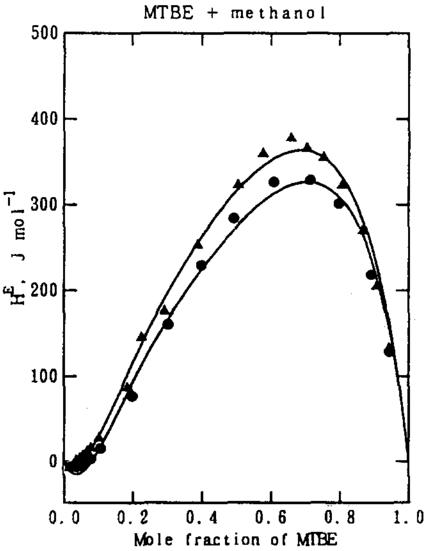

Fig. 4. Molar excess enthalpies for methanol + MTBE. Experimental data of Tusel-Langer et al. [18]: (●), 25°C; (▲), 40°C; calculated (———) using $K_A = 125.1$ (50°C) and $h_A = -23.6$ kJ mol^{-1}.

TABLE 3

Calculated results of ternary data

System A + B + C	Temp. (°C)	Number of data points	Deviations [a]				Ref.
			AAD (J mol^{-1})		ARD (%)		
			I [b]	II [c]	I	II	
Methanol + benzene + n-heptane	30	13	34.9	31.7	7.0	7.2	15
Methanol + MTBE	25	121	32.4	24.0	6.2	5.1	16
+ n-heptane	40	113	32.0	26.2	5.8	5.1	16

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

[b] $K_A = 173.9$ at 50°C and $h_A = -23.2$ kJ mol^{-1}.

[c] $K_A = 125.1$ at 50°C and $h_A = -23.6$ kJ mol^{-1}.

values are compared with the calculated results derived from the UNIQUAC associated-solution model in Figs. 1–4. In the binary mixtures benzene + n-heptane and MTBE + n-heptane the excess enthalpies were calculated with eqn. (10) for the physical contribution term and good agreement is obtained. For the mixture MTBE + methanol the UNIQUAC associated-solu-

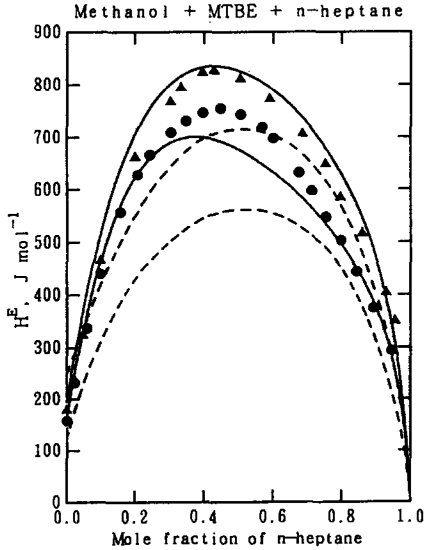

Fig. 5. Comparison between experimental and calculated excess enthalpies for ternary mixtures of [x_1 n-heptane + x_2 MTBE + $(1 - x_1 - x_2)$ methanol], which were prepared by mixing pure methanol with [x_2' MTBE + $(1 - x_2')$$n$-heptane], with x_2 MTBE = 0.3 at 25° and 40°C. Experimental data of Tusel-Langer and Lichtenthaler [16]: (●), 25°C; (▲), 40°C. Calculated: (———), uniquac associated-solution model using $K_A = 125.1$ (50°C) and $h_A = -23.6$ kJ mol^{-1}; (------), ERAS model.

tion model describes the S-shaped dependence on composition quite well in comparison to the ERAS (Extended Real Associated Solution) model and the NRTL equation [16,18,22]. For the mixture methanol + n-heptane the experimental excess enthalpies in the region of partial miscibility were not used in parameter determination, in which mutual solubilities were taken from Sørensen and Arlt [23] and the energy parameters satisfy the thermodynamic criterion that the activities of components should be equal in the two liquid phases α and β.

$$(x_i\gamma_i)^\alpha = (x_i\gamma_i)^\beta \qquad i = 1,2 \tag{15}$$

The UNIQUAC associated-solution model can be used to predict the excess enthalpies of ternary mixtures by using the binary parameters without any additional parameters. Table 3 shows the ternary predicted results, showing that the association constant of Nagata [10] provides smaller deviations between the experimental and calculated values than that of Brandani [19]. As shown in Fig. 5, the ERAS model provides, for all ternary data points of methanol + MTBE + n-heptane, calculated excess enthalpy values which are clearly too small and the discrepancy between the experimental and calculated excess enthalpy values is up to 20–30% [16]. The UNIQUAC associated-solution model improves the discrepancy significantly.

We may conclude that the UNIQUAC associated-solution model can be used in the prediction of excess enthalpies for ternary associated mixtures containing one binary system of partial miscibility.

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