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Thermodynamics of associated solutions. Prediction of excess molar enthalpies of acetone + bromoform + saturated hydrocarbon mixtures using a chemical model

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Abstract

A chemical model based on mole-fraction statistics is used to predict ternary excess molar enthalpies for acetone + bromoform + saturated hydrocarbon mixtures, in which the hydrocarbon is cyclohexane, *n*-hexane, *n*-heptane, or *n*-decane, from binary information alone. The model used gives significantly smaller deviations between the calculated and experimental results than the chemical models proposed by Singh et al.

LIST OF SYMBOLS

A, B, C	acetone, bromoform, saturation hydrocarbon
a_{IJ}	binary interaction parmeter for I–J pair
C_{JI}, D_{JI}	parameters of eqn. (12)
G_{IJ}	coefficient as defined by $\exp(-\alpha_{IJ}\tau_{IJ})$
H^E	excess molar enthalpy
h_{AB}	enthalpy of formation of chemical complex AB
K_{AB}	equilibrium constant of formation of chemical complex AB
R	gas constant
S	stoichiometric sum
T	absolute temperature
x_I	liquid mole fraction of component I

Greek letters

α_{IJ}	non-randomness parameter of NRTL equation for I–J pair
τ_{IJ}	parameter as defined by a_{IJ}/T

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Subscripts

A, B, C	acetone, bromoform and saturated hydrocarbon
A_1, B_1, C_1	monomers of components A, B, and C
AB	complex formation between acetone and bromoform
chem	chemical
phys	physical

Superscript

E	excess

INTRODUCTION

Singh et al. [1, 2] have measured the excess molar enthalpies of four ternary mixtures, namely, acetone + bromoform + cyclohexane, acetone + bromoform + *n*-hexane, acetone + bromoform + *n*-heptane, and acetone + bromoform + *n*-decane, at 308.15 K as well as enthalpic data for the binary mixtures. Singh et al. [2] used these experimental results to test the applications and limitations of two associated solution models containing either a mole-fraction-based or a volume-fraction-based equilibrium constant with two sets of weighting factors for predicting excess molar enthalpies of systems containing a single AB molecular complex. The two equilibrium constants for AB and AB_2 of acetone + bromoform complexes were usually determined from vapour–liquid equilibrium data, which were not available from the literature for the acetone + bromoform mixture. Therefore, Singh et al. assumed only a single AB molecular complex, neglecting non-specific interactions in the acetone + bromoform system, and obtained significant deviations between calculated and experimental values at many ternary compositions.

In this work, we present results calculated from another chemical model for comparison with those given by Singh et al. [2].

SOLUTION MODEL

In an acetone(A) + bromoform(B) + saturated hydrocarbon(C) mixture, we assume a 1:1 complex formation between acetone and bromoform and define the equilibrium constant in terms of mole fractions of chemical species

$$K_{AB} = x_{AB}/x_{A_1}x_{B_1} \quad \text{for } A_1 + B_1 = AB \tag{1}$$

Non-specific interactions between each pair of three components are given by applying the Gibbs–Helmholtz relation to the NRTL equation [3].

The ternary excess molar enthalpy H^E is expressed as the sum of chemical and physical contribution terms

$$H^E = H^E_{\mathrm{chem}} + H^E_{\mathrm{phys}} \tag{2}$$

$$H^E_{\mathrm{chem}} = h_{AB} K_{AB} x_{A_1} x_{B_1} / S \tag{3}$$

where h_{AB} is the enthalpy of formation of the chemical complex AB and the stoichiometric sum S is given by

$$S = x_{A_1} + x_{B_1} + x_{C_1} + 2K_{AB} x_{A_1} x_{B_1} \tag{4}$$

The nominal mole fractions of components are related to the monomeric mole fractions of the components

$$x_A = (x_{A_1} + K_{AE} x_{A_1} x_{B_1})/S \tag{5}$$

$$x_B = (x_{B_1} + K_{AB} x_{A_1} x_{B_1})/S \tag{6}$$

$$x_C = x_{C_1}/S \tag{7}$$

The sum of the mole fractions of all chemical species present in the mixture must be unity

$$x_{A_1} + x_{B_1} + x_{C_1} + K_{AB} x_{A_1} x_{B_1} = 1 \tag{8}$$

Equations (4)–(8) are used to obtain x_{A1}, and x_{C1}, if the equilibrium constant K_{AB} is known

$$H^E_{\mathrm{phys}} = R \sum_I x_I \left[\frac{\sum_J x_J \dfrac{\partial(\tau_{JI} G_{JI})}{\partial(1/T)}}{\sum_K G_{KI} x_K} - \frac{\sum_J \tau_{JI} G_{JI} x_J \sum_K x_K \dfrac{\partial G_{KJ}}{\partial(1/T)}}{\left(\sum_K G_{KI} x_K\right)^2} \right] \tag{9}$$

where

$$\tau_{JI} = a_{JI}/T \tag{10}$$

$$G_{JI} = \exp(-\alpha_{JI} \tau_{JI}) \tag{11}$$

In fitting the model to binary excess molar enthalpy results, the energy parameters are assumed to be linearly temperature dependent, i.e.

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \tag{12}$$

The non-randomness parameter $\alpha_{JI}(=\alpha_{IJ})$ is taken as 0.3 for the three binaries.

CALCULATED RESULTS

Binary mixtures

The value of K_{AB} at 308.15 K obtained from NMR studies is 2.38 [4]; an h_{AB} value of -6.57 kJ mol^{-1} [2] was used in this work. The parameters of eqn. (12) were obtained by minimizing the sum of the deviations between calculated and experimental values using a simplex method [5]. Table 1

TABLE 1

Binary results of excess molar enthalpy data reduction at 308.15 K

System(A + B)	Number of data points	Parameters					Abs. arith. mean dev./ (J mol^{-1})	Root-mean-squared dev./ (J mol^{-1})	Ref.
		C_{BA}/K	C_{AB}/K	D_{BA}	D_{AB}	α_{AB}			
Acetone + bromoform	16	−347.16	−754.56	−1.4007	−2.5679	0.3	29.2	32.2	2
Acetone + cyclohexane	15	91.06	−943.14	−2.5977	−3.6378	0.3	5.0	6.0	2
Acetone + *n*-hexane	15	349.64	520.76	−2.4498	1.0462	0.3	2.4	2.9	1
Acetone + *n*-heptane	16	−550.65	−370.39	−2.4841	−2.9614	0.3	3.0	3.4	2
Acetone + *n*-decane	16	−486.71	−481.08	−3.0377	−2.8247	0.3	9.9	11.5	2
Bromoform + cyclohexane	16	−391.19	887.05	−3.0970	4.0677	0.3	3.1	3.5	2
Bromoform + *n*-hexane	16	−531.51	813.72	−3.7718	6.4116	0.3	13.8	16.2	1
Bromoform + *n*-heptane	16	−16.33	−263.20	−10.553	17.038	0.3	3.2	4.2	2
Bromoform + *n*-decane	16	−226.02	225.95	−5.2430	5.9318	0.3	3.6	3.8	2

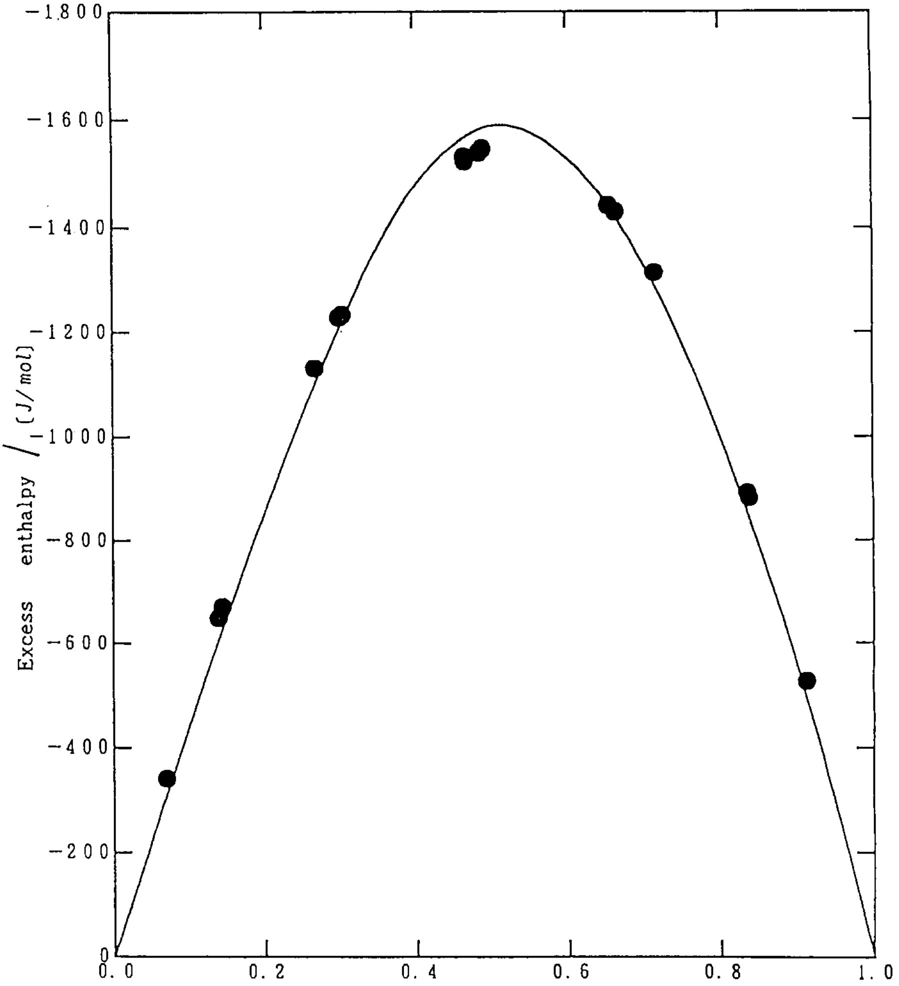

Fig. 1. Binary excess molar enthalpies for the acetone + bromoform system at 308.15 K: ●, ref. 2; ——, calculated in this work.

shows the binary results of excess molar enthalpy data reduction and Figs. 1–3 compare the calculated results with the experimental values. The model is able to fit the experimental values well.

Ternary mixtures

The prediction of ternary excess molar enthalpies for four acetone + bromoform + saturated hydrocarbon systems was performed using the parameters listed in Table 1. Singh et al. [2] presented four sets of ternary predicted results for each system using a mole-fraction-based association constant or a volume-fraction-based association constant, with weighting factors approximated with molar volumes and evaluated from measured binary data. Their calculated results revealed that there is

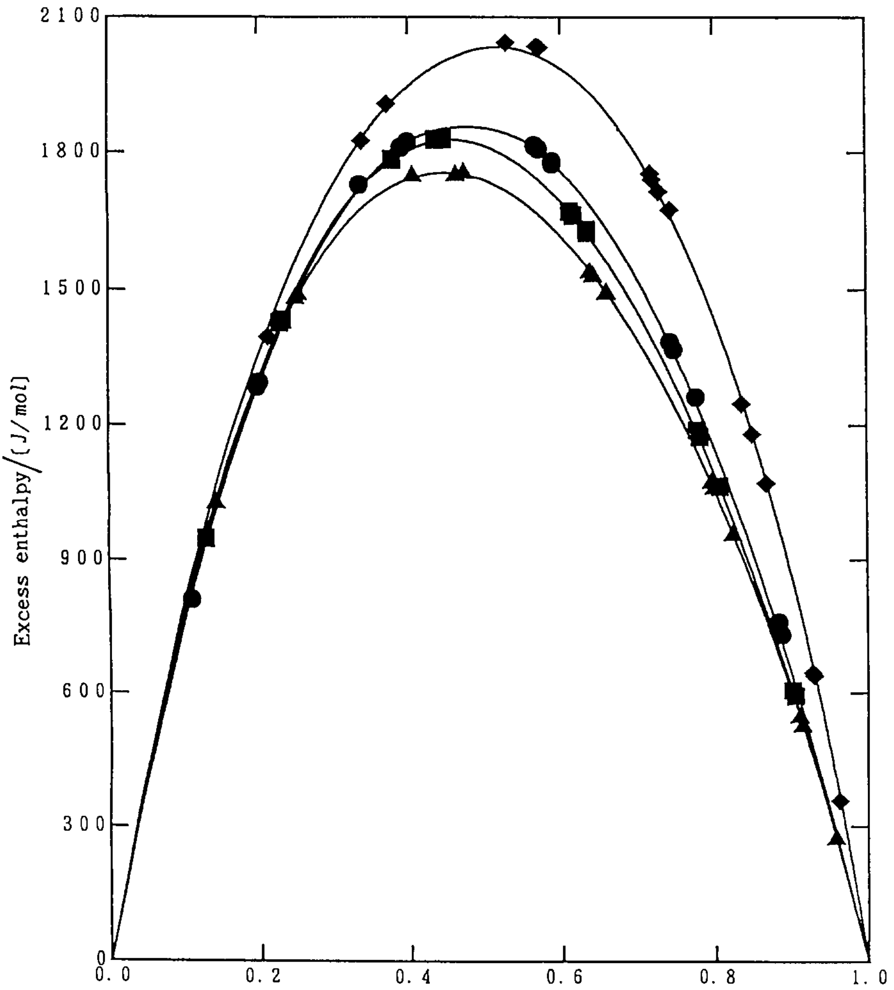

Fig. 2. Binary excess molar enthalpies for four acetone + saturated hydrocarbon systems at 308.15 K: ●, acetone + cyclohexane [2]; ■, acetone + *n*-hexane [1]; ▲, acetone + *n*-heptane [2]; ◆, acetone + *n*-decane [2]; ——, calculated in this work.

TABLE 2

Ternary predicted results for four systems at 308.15 K

System	Number of data points	Abs. arith. mean dev./(J mol^{-1})		Ref.
		This work	Singh [a]	
Acetone + bromoform + cyclohexane	25	29.2	162.0	2
Acetone + bromoform + *n*-hexane	25	38.9	198.1	1
Acetone + bromoform + *n*-heptane	24	59.3	77.5	2
Acetone + bromoform + *n*-decane	26	15.4	46.7	2

[a] Equation (1) of ref. 2 with weighting factors calculated from binary excess enthalpy data.

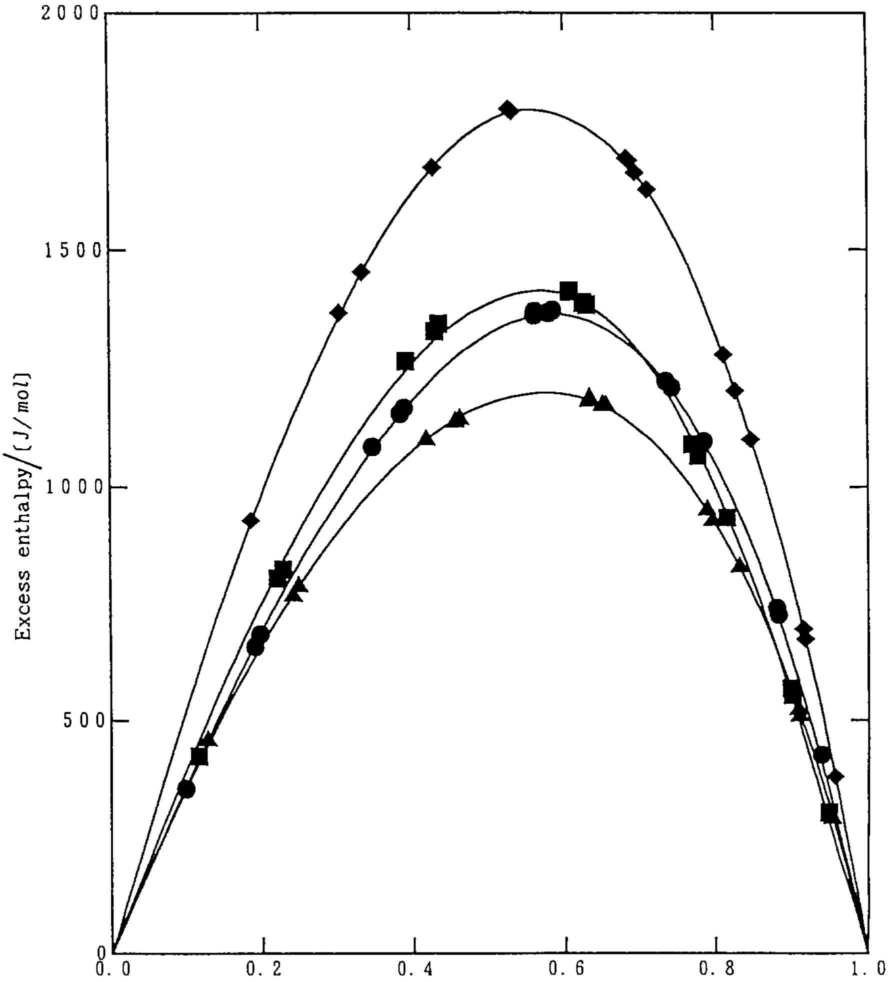

Fig. 3. Binary excess molar enthalpies for four bromoform + saturated hydrocarbon systems at 308.15 K: ●, bromoform + cyclohexane [2]; ■, bromoform + *n*-hexane [1]; ▲, bromoform + *n*-heptane [2]; ◆, bromoform + *n*-decane [2]; ——, calculated in this work.

significant difference between the various weighting factor approximations or concentrational forms of the association constant. Therefore, we compare our calculated results with only one set of the calculated results given by Singh et al. in Table 2, which indicates that the present method provides predicted results that are better than those of Singh et al.

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