

## Excess enthalpy surfaces for *n*-heptane + carboxylic acid, amylamine and *n*-octanol mixtures by the NRTL model

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### Abstract

The temperature and composition dependences of the excess enthalpy,  $h^E$ , have been calculated using the NRTL model for mixtures of *n*-heptane with the hydrogen-bonded liquids of acetic acid, propionic acid, amylamine and *n*-octanol. Reduced and partial molar excess enthalpies were also calculated. The temperature-dependent parameters of the NRTL model, estimated directly from  $h^E$  data for more than one isotherm, were used in the calculations. The overall deviations of all the experimental data points fall in the range 0.5–6.5% which shows highly satisfactory correlation of  $h^E$  data with the model. The temperature range for the mixtures is 285.15–330.15 K. The surfaces of excess enthalpy functions facilitate better understanding of the thermodynamic properties of the hydrogen-bonded mixtures. The NRTL model is a reliable thermodynamic model for studying the hydrogen-bonded mixtures in a qualitative and quantitative manner.

**Keywords:** Binary liquid mixtures; Excess enthalpy surfaces; NRTL model

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### 1. Introduction

The thermodynamic properties of alkane and hydrogen-bonded compounds, such as carboxylic acids, amines and alcohols, have attracted considerable attention. In particular, data for the excess enthalpies,  $h^E$ , of such mixtures are important for two reasons [1]. Firstly,  $h^E$  data reveal the structural changes of the mixture with changing composition and temperature. Secondly,  $h^E$  data are useful in developing and testing theoretical models for understanding the self-association of hydrogen-bonded components.

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For quite a long time, models based on activity coefficients have been the preferred method for calculating the thermodynamic properties of associating fluids. Such models are capable of yielding sufficient data of a high degree of accuracy and usually do not create numerical problems at low pressures [2]. The NRTL model is based on activity coefficients and is widely used in estimating the thermodynamic properties of various types of mixtures [3–5]. In a previous study [4], temperature-dependent interaction energy parameters of the NRTL model were estimated using  $h^E$  data at different temperatures. The mixtures considered in this study and the deviations obtained from the correlation of  $h^E$  data are shown in Table 1. Deviations between experimental (exp) and calculated (calc) values of  $h^E$  are defined as

$$D = \frac{1}{m} \left\{ \sum_i^m |(h_{\text{exp}}^E - h_{\text{calc}}^E)/h_{\text{exp}}^E| \right\} \times 100 \quad (1)$$

where  $m$  is the number of data points at each temperature [6]. Table 1 indicates that direct correlation of  $h^E$  data by the NRTL model yields reasonably low deviations and the overall deviations for the whole temperature range are in the range 0.5–6.5%. Therefore, an attempt has been made to calculate the surfaces of excess enthalpy functions to show the feasibility of the NRTL model in studying the self-association of hydrogen-bonded components and the structural changes with changing temperature and composition.

## 2. Excess enthalpy surfaces

Differentiation of  $g^E/T$  with respect to temperature is proportional to  $h^E$ , and is given by the Gibbs–Helmholtz equation at constant pressure  $P$  and liquid mole fraction  $x$

$$\frac{h^E}{T^2} = - \left( \frac{\partial (g^E/T)}{\partial T} \right)_{P,x} \quad (2)$$

Table 1  
Correlation of excess enthalpy data by the NRTL model

System [Reference]	$m$	$T$ (°C)	$D$
<i>n</i> -Heptane(1)–acetic acid(2) [7]	17	25	1.1
	14	35	0.9
<i>n</i> -Heptane(1)–propionic acid(2) [7]			1.0 <sup>a</sup>
	14	25	2.0
	15	35	3.0
<i>n</i> -Heptane(1)– <i>n</i> -amylamine(2) [8]			2.5 <sup>a</sup>
	19	15	0.4
	19	35	0.5
<i>n</i> -Heptane(1)– <i>n</i> -octanol(2) [9]			0.5 <sup>a</sup>
	9	15	7.3
	9	55	5.6
			6.5 <sup>a</sup>

<sup>a</sup> Overall deviation

For calculation of  $g^E$ , the NRTL model with temperature-dependent parameters in the following form was used

$$g_{21} - g_{11} = c_1 + c_2/(T - 273.15) \quad (3)$$

$$g_{12} - g_{22} = c_3 + c_4/(T - 273.15) \quad (4)$$

$$\alpha_{12} = \alpha_{21} = c_5 + c_6/(T - 273.15) \quad (5)$$

where  $g_{21} - g_{11}$  and  $g_{12} - g_{22}$  are the interaction energies in  $\text{J mol}^{-1}$  and  $\alpha_{12}$  are the non-randomness parameters. This form of the temperature dependence is particularly appropriate for evaluating the derivative functions from the expression for  $g^E$  [5]. The terms  $c_1 - c_4$  are the temperature-dependent interaction energy parameters, and  $c_5$  and  $c_6$  denote the temperature-dependent parameters of  $\alpha_{12}$  associated with the non-randomness of the molecules in liquid mixtures [3, 4]. It is commonly assumed that the NRTL parameters change with temperature in a linear form. However for mixtures showing strong association, such as those containing alcohols, it has been observed that the parameters should not be represented by linear relationships [4, 10, 11].

The equation for  $h^E$  obtained from Eq. (2) is given elsewhere [4]. The partial molar excess enthalpies of the hydrogen-bonded component 2,  $h_2^E$ , were calculated from

$$h_2^E = h^E - x_1(\partial h^E / \partial x_1)_{T,P} \quad (6)$$

The reduced excess enthalpies,  $h^E/(x_1 x_2)$  at liquid mole fractions  $x_1 = 0$  and  $x_2 = 0$  are identical to the partial molar excess heats of component 1 and 2 respectively at infinite dilution [11, 12].

The following quantity is some measure of the component  $i$ - $i$  interactions in terms of enthalpy [13]

$$n(\partial h_i^E / \partial n_i) = (1 - x_i)(\partial h_i^E / \partial x_i) \quad (7)$$

where  $n$  is the total number of moles, and  $n_i$  is the number of moles of component  $i$ .

### 3. Results and discussions

Enthalpy functions are sensitive to molecular complexation and provide a demanding test of the limitations and applications of the thermodynamic model [14]. In an inert hydrocarbon/hydrogen-bonded mixture, the molecular complexation includes clustering of hydrogen-bonded molecules, and is predicted assuming a balance between weak intermolecular van der Waals forces and relatively strong electrostatic forces. Carboxylic acids, amines and alcohols can form successive polymeric species due to hydrogen bonding leading to self-association in the mixtures. A reliable thermodynamic model is essential in studying complexation in such mixtures. The NRTL model with temperature-dependent parameters is employed to calculate the enthalpy functions in terms of composition and temperature. The excess enthalpy surfaces for the mixtures studied are shown in Fig. 1. Temperature intervals seen in the figures are

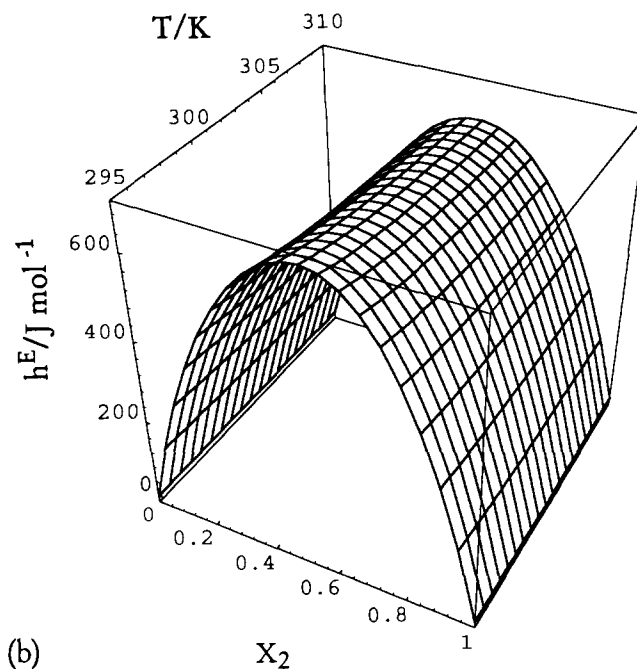
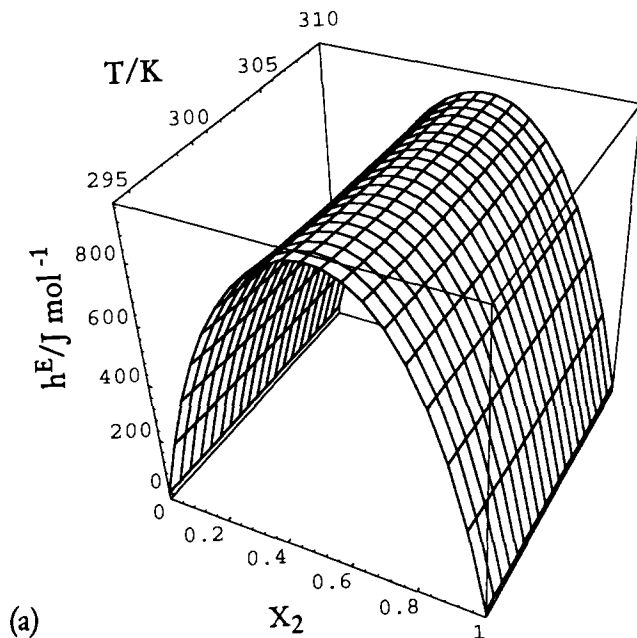


Fig. 1. Concentration and temperature dependences of excess enthalpy,  $h^E$ . (a) *n*-Heptane(1)-acetic acid(2), 295.15–310.15 K. (b) *n*-Heptane(1)-propionic acid(2), 295.15–310.15 K. (c) *n*-Heptane(1)-*n*-amylamine(2), 285.15–310.15 K. (d) *n*-Heptane(1)-*n*-octanol(2), 285.15–330.15 K.

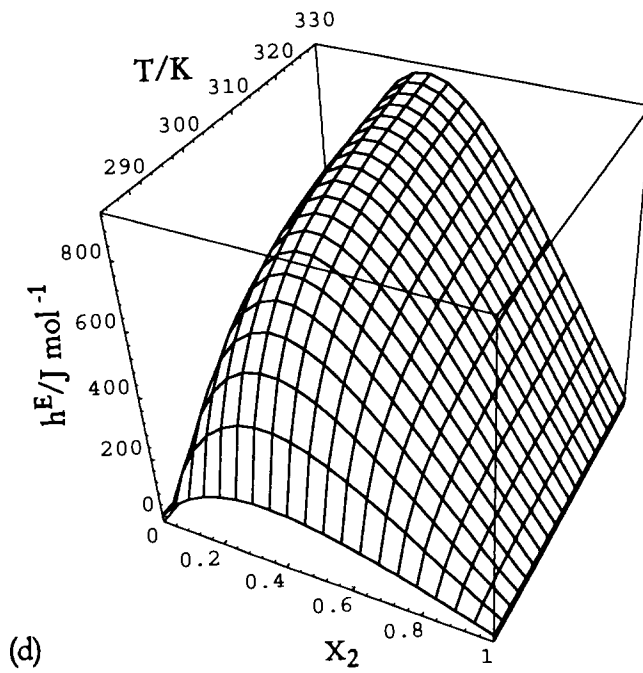
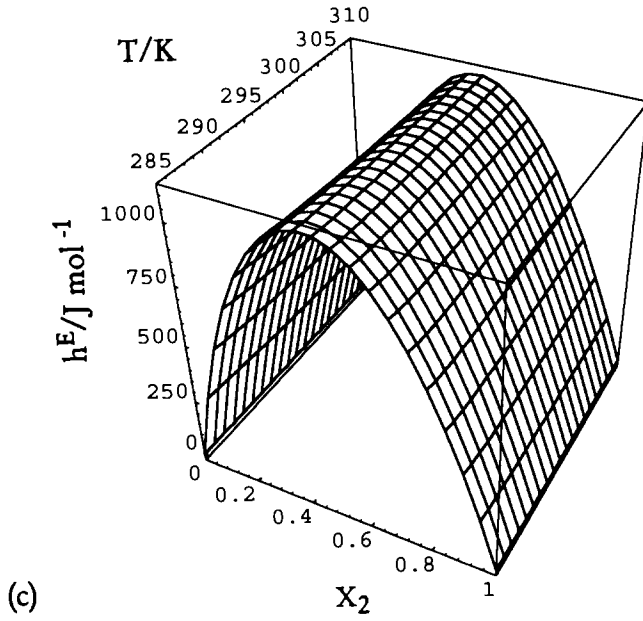


Fig. 1 (continued)

slightly outside the temperature intervals of the experimental data used in estimating the parameters. This is due to the extrapolating ability of the NRTL model, and to using  $20 \times 20$  grid points for a better representation of the functions. The effect of temperature on  $h^E$  surfaces is rather small for *n*-heptane/carboxylic acid and amylamine mixtures, while it is considerable for the *n*-heptane/*n*-octanol mixture which is typical for alkane/alkanol mixtures [15].

The concentration and temperature dependences of the reduced excess enthalpies,  $h^E/(x_1x_2)$ , are shown in Fig. 2. The mixtures containing carboxylic acids show similar behaviour, whereas the mixtures containing amylamine and alcohol show rather strong composition and temperature dependences.

Partial molar excess enthalpy calculations in the range of  $x_2 = 0.001 - 0.4$  are shown in Fig. 3. At infinite dilution of hydrogen-bonded components, the enthalpy values are higher for the mixtures containing amine and alcohol than for the mixtures containing carboxylic acids. For the mixture *n*-heptane/*n*-octanol,  $h_2^E$  shows a strong temperature dependence.

The interactions between the hydrogen-bonded components ( $x_2 = 0.001 - 0.4$ ) in terms of enthalpy are shown in Fig. 4. In the dilute region of hydrogen-bonded components, interactions reach a maximum which decrease gradually as the *n*-heptane concentration decreases. For the mixture *n*-heptane/*n*-octanol, similar interactions show rather strong concentration and temperature dependences.

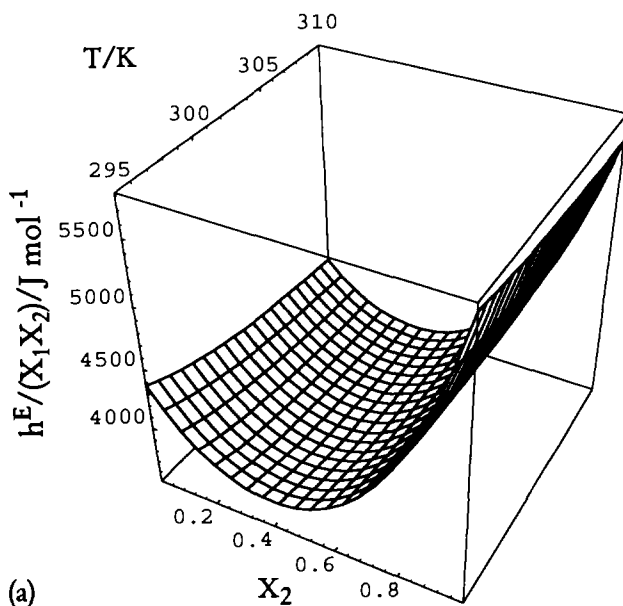


Fig. 2. Concentration and temperature dependences of reduced excess enthalpy,  $h^E/x_1x_2$ . (a) *n*-Heptane(1)-acetic acid(2), 295.15–310.15 K. (b) *n*-Heptane(1)-propionic acid(2), 295.15–310.15 K. (c) *n*-Heptane(1)-*n*-amylamine(2), 285.15–310.15 K. (d) *n*-Heptane(1)-*n*-octanol(2), 285.15–330.15 K.

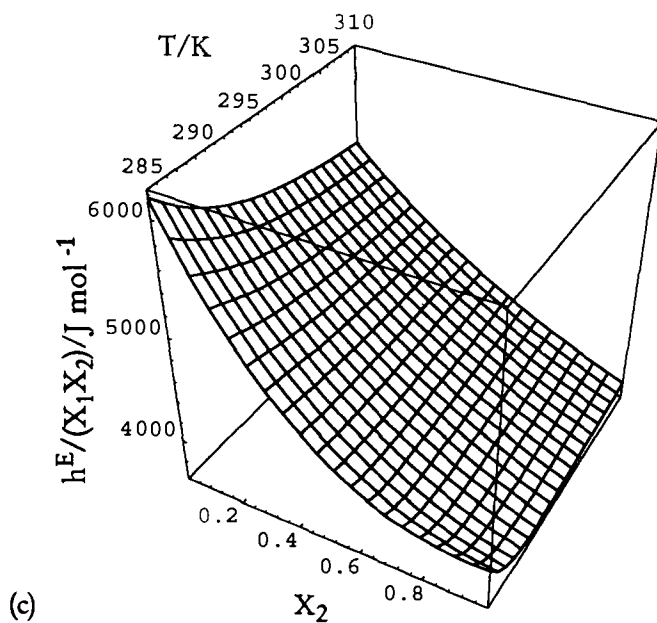
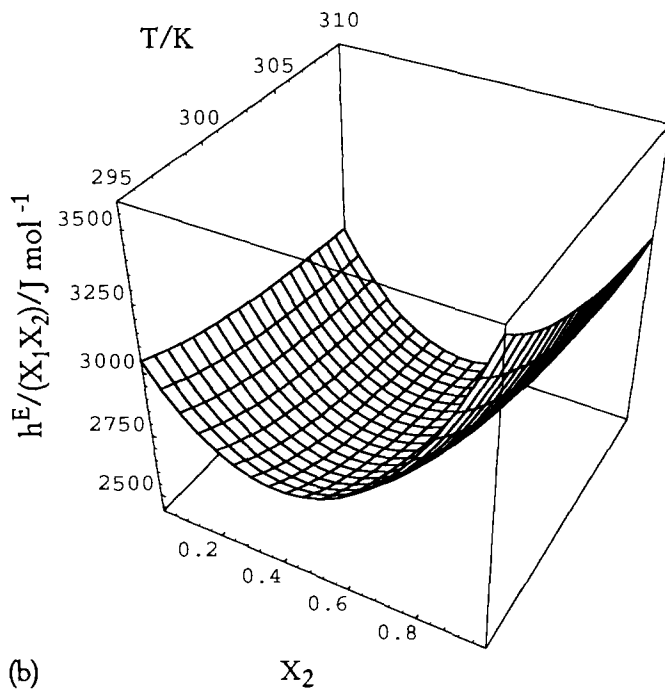


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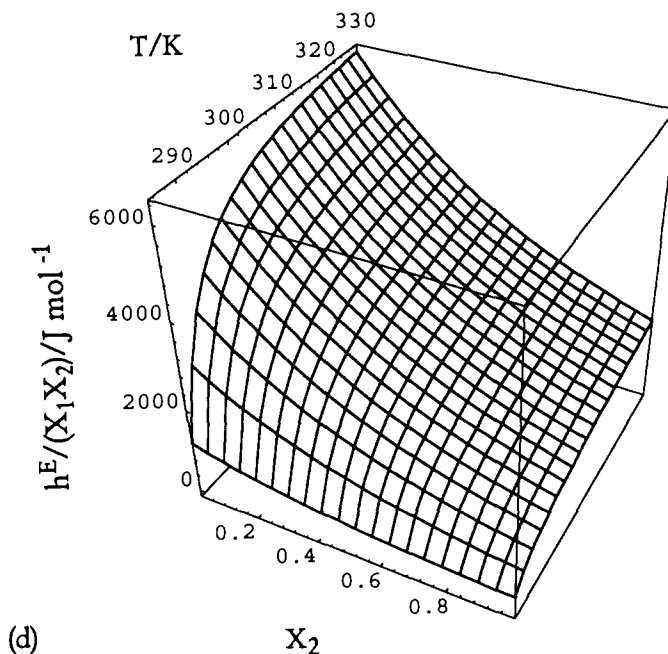


Fig. 2 (continued)

Calculations of enthalpy functions in the infinite dilution region by the NRTL model may not be satisfactory for hydrogen-bonded components [12]. This is mainly due to the error in experimental data at infinite dilution. As the estimated parameters are based upon the whole concentration range and directly related to the accuracy of the experimental data of the hydrogen-bonded components, necessary care should be exercised for the enthalpy calculations in the infinite dilution region. In this region, changes in enthalpy functions can be extremely steep [12].

#### 4. Conclusions

Concentration and temperature dependences of enthalpy functions have been calculated by the NRTL model with temperature-dependent parameters. Enthalpy functions are especially useful in understanding self-association of hydrogen-bonded components and structural changes in the mixtures. Surfaces of enthalpy functions facilitate a better understanding of thermodynamic fluctuations which can be explained in a qualitative and quantitative manner. The NRTL model is a reliable thermodynamic tool for studying the thermodynamic properties of mixtures containing hydrogen-bonded components.



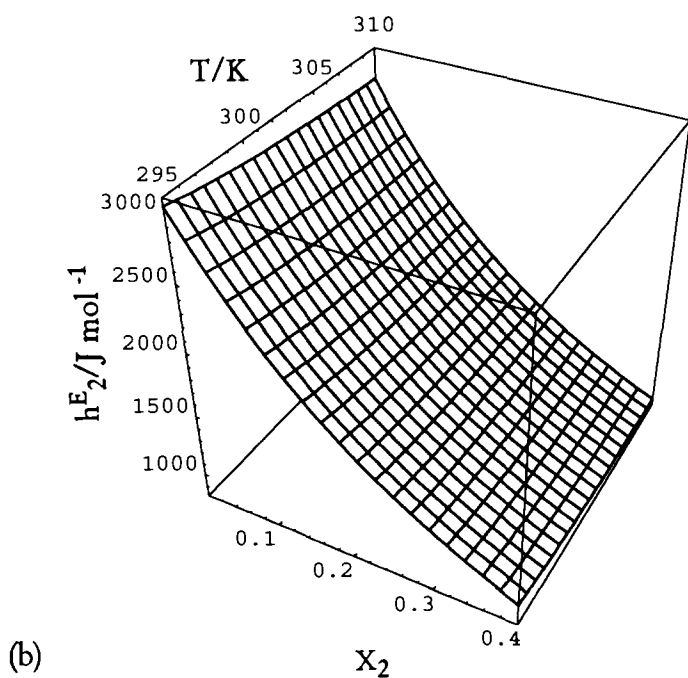
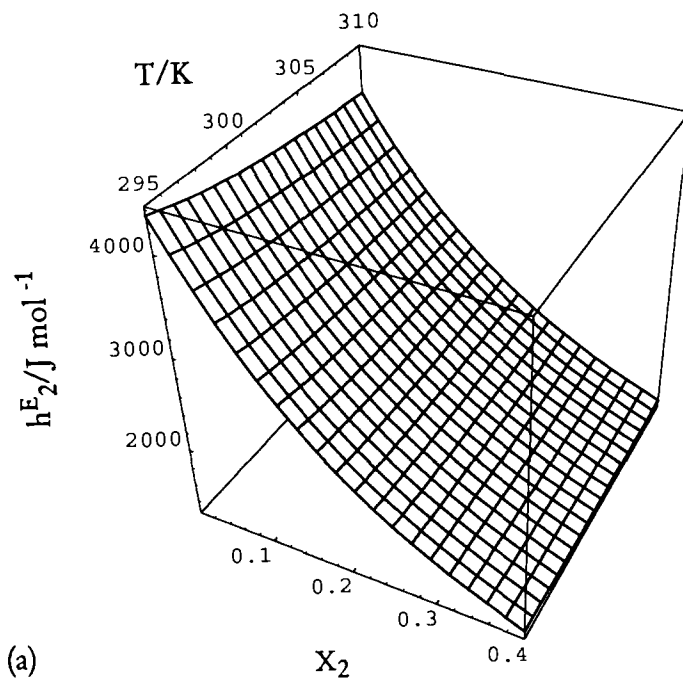


Fig. 3. Concentration and temperature dependences of partial molar excess enthalpy,  $h_2^E$ . (a) *n*-Heptane(1)-acetic acid(2), 295.15–310.15 K. (b) *n*-Heptane(1)-propionic acid(2), 295.15–310.15 K. (c) *n*-Heptane(1)-*n*-amylamine(2), 285.15–310.15 K. (d) *n*-Heptane(1)-*n*-octanol(2), 285.15–330.15 K.

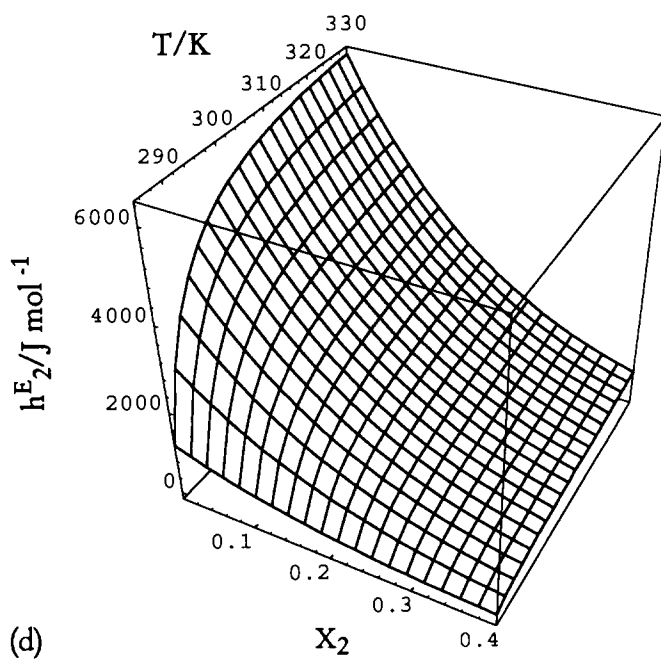
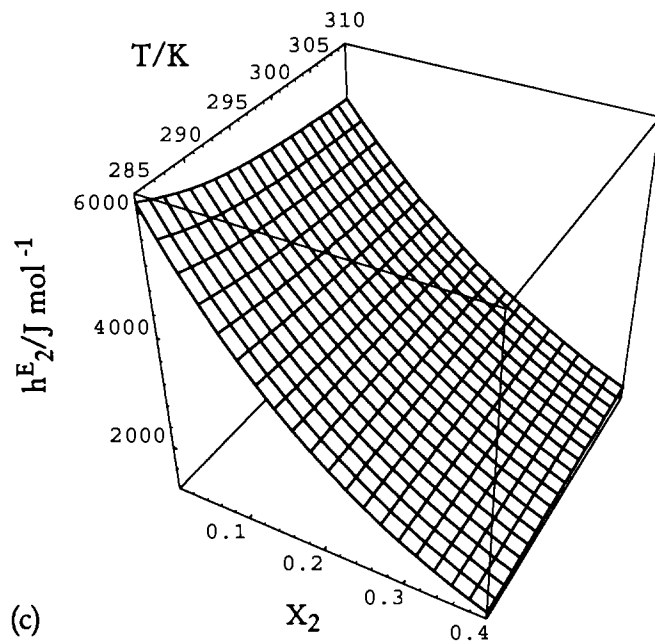


Fig. 3 (continued)

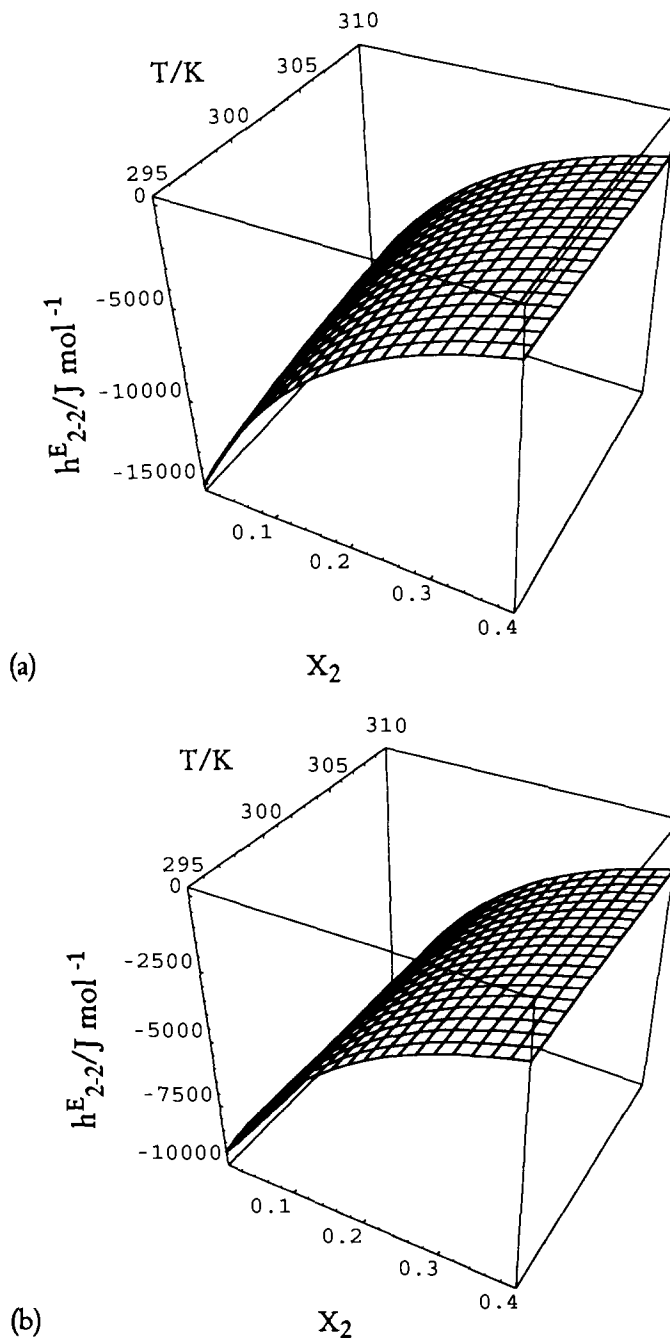


Fig. 4. Concentration and temperature dependences of interactions in terms of enthalpy between the hydrogen-bonded components,  $h_{2-2}^E$ . (a) *n*-Heptane(1)-acetic acid(2), 295.15–310.15 K. (b) *n*-Heptane(1)-propionic acid(2), 295.15–310.15 K. (c) *n*-Heptane(1)-*n*-amylamine(2), 285.15–310.15 K. (d) *n*-Heptane(1)-*n*-octanol(2), 285.15–330.15 K.

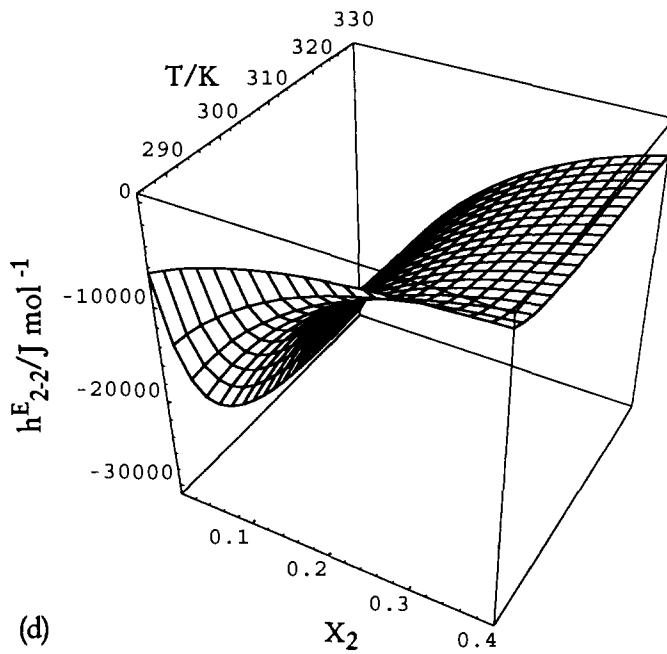
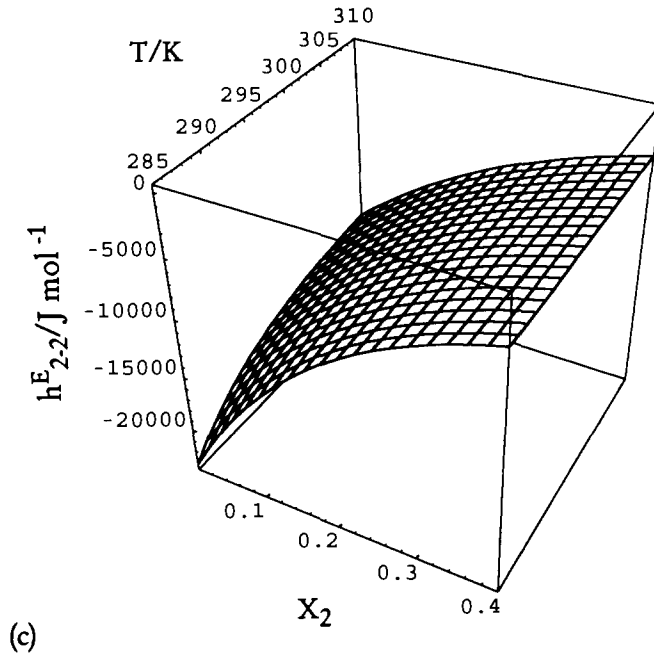


Fig. 4 (continued)

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