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Excess enthalpy surfaces for alkanol–alkane mixtures by the UNIQUAC model

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Abstract

Temperature and composition dependences of excess enthalpy surfaces and composition fluctuations were calculated using the UNIQUAC model and the Kirkwood–Buff theory of statistical mechanics for seven alkanol–alkane mixtures. Surfaces of partial molar excess enthalpies and enthalpy of dilution were also calculated. Temperature-dependent parameters of the UNIQUAC model in the range of 278.15–333.15 K were used in the calculations. The thermodynamic surfaces facilitate better understanding of thermodynamic properties of alkanol–alkane mixtures over the whole mole fraction range in a certain temperature interval. The UNIQUAC model is capable of representing the thermodynamic properties of associating mixtures at low pressures.

Keywords: Alkanol–alkane mixtures; Composition fluctuations; Excess enthalpy; Kirkwood–Buff theory; Uniquac model

1. Introduction

The thermodynamic properties of alkanol–alkane binary liquid mixtures have attracted considerable attention among researchers. In particular, the excess enthalpy, h^E data of such mixtures are essential in two respects: firstly, h^E data reveal the structural changes of a mixture with changing composition and temperatures; secondly, h^E data are useful to develop and test theoretical models for understanding the self association of alcohols. The key binary mixtures, as Roux et al. [1] suggest, are those comprising an alkanol and alkane either of different size or with the same number of carbon atoms, such as methanol–*n*-heptane and ethanol–*n*-hexane.

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For a quite long time, models based on activity coefficients have been the preferred method for the calculation of thermodynamic properties of associating fluids. Such models are capable of a high degree of accuracy and usually do not create numerical problems at low pressures [2]. The UNIQUAC model is based on activity coefficients and is widely used in estimating the thermodynamic properties of various types of mixtures [3, 4]. In a previous study, temperature-dependent interaction parameters of the UNIQUAC model were estimated using h^E data at more than one different isotherm; these are given elsewhere [5]. The mixtures considered in this study and the deviations obtained from the correlation of h^E and excess Gibbs energy g^E data are shown in Tables 1 and 2. The deviations between the calculated (calcd) and experimental (exptl) data D are obtained from the relation [6]

$$D(f^E) = \frac{1}{m} \left\{ \sum_i^m |[(f_{\text{exptl}}^E - f_{\text{calcd}}^E)/f_{\text{exptl}}^E]_i| \right\} \times 100 \quad (1)$$

Table 1
Correlation of excess enthalpy h^E data by UNIQUAC model

System [Ref.]	m	$T/(^{\circ}\text{C})$	$D(h^E)$
Methanol(1)- <i>n</i> -heptane(2) [7]	8	30	4.9
	11	45	3.2
	17	60	4.2
			4.1 ^a
Ethanol(1)- <i>n</i> -hexane(2) [8]	24	10	7.2
	24	25	3.3
	25	45	12.8
Ethanol(1)-cyclohexane(2) [9]	10	5	7.8 ^a
	10	20	2.8
	10	35	2.2
	10	50	2.5
	10	60	0.8
			2.4
2-Propanol(1)- <i>n</i> -heptane(8) [10]	24	30	2.1 ^a
	22	45	10.3
	21	60	8.5
			8.0
<i>n</i> -Pentanol(1)- <i>n</i> -hexane(2) [11, 12]	9	25	8.9 ^a
	17	30	9.9
	17	45	10.9
<i>n</i> -Hexanol(1)- <i>n</i> -octane(2) [13]			8.7
			9.8 ^a
	9	15	4.7
	8	55	11.8
<i>n</i> -Octanol(1)- <i>n</i> -octane(2) [13]			8.2 ^a
	9	15	4.6
	9	55	1.9
		3.2 ^a	

^a Overall deviation.

Table 2
Correlation of excess Gibbs energy g^E data by the UNIQUAC model

System [Ref.]	m	$T/(^{\circ}\text{C})$	$D(g^E)$
Ethanol(1)–cyclohexane(2) [9]	8	5	5.3
	10	20	4.3
	9	35	3.8
	8	50	4.0
	8	60	4.7
			4.4 ^a
2-Propanol(1)– <i>n</i> -heptane(8) [10]	17	30	3.2
	17	45	3.1
	16	60	2.9
			3.1 ^a

^a Overall deviation.

where m indicates the number of data points at each isotherm, and f^E represents h^E or g^E . As Table 1 indicates, direct correlation of h^E data by the UNIQUAC model yields reasonably low deviations that are in the range 2.1–9.8% for the whole temperature range. The composition fluctuations are determined for the two mixtures ethanol–cyclohexane and 2-propanol–*n*-heptane using the Kirkwood–Buff theory of statistical mechanics. To calculate the derivative of the activity coefficients, the temperature-dependent parameters of the UNIQUAC model, estimated by regressing h^E and g^E data simultaneously [4], were used. Deviations between the calculated and experimental g^E data are shown in Table 2. As the overall deviations are reasonably low, an attempt was made to calculate the excess enthalpy surfaces and composition fluctuations to show the feasibility of applying the UNIQUAC model with associating mixtures and to understand the self association of alcohol molecules with changing temperature and composition.

2. Excess enthalpy surfaces

The rate of change of excess Gibbs free energy with respect to temperature T is proportional to h^E and is given by the Gibbs–Helmholtz equation at constant pressure P and liquid mole fraction x .

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

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

$$a_{21} = d_1 + d_2/T \quad (3)$$

$$a_{12} = d_3 + d_4/T \quad (4)$$

where a_{21} and a_{12} are the interaction parameters in K. The terms d_1 and d_3 in K, and d_2 and d_4 in K^2 are the coefficients related to the parameters a_{ij} . The UNIQUAC model contains the pure component structural parameters r and q . Anderson and Prausnitz [14] modified the UNIQUAC model slightly and introduced new values for the surface parameters q' for alcohols to be used in the residual part of the model.

The equations for h^E obtained from Eq. (2) is given elsewhere [5]. The partial molar excess enthalpies of alkanol molecules are calculated from

$$h_1^E = h^E + (1 - x_1)(\partial h^E / \partial x_1)_{T,P} \quad (5)$$

The surface of the enthalpy of dilution ΔH_{dil} is calculated as h^E/x_1 .

The following quantity is a measure of the component i - i interactions in terms of enthalpy [15]

$$n(\partial h_i^E / \partial h_i) = (1 - x_i)(\partial h_i^E / \partial x_i) \quad (6)$$

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

3. Molecular interactions

Understanding the trends in thermodynamic properties requires a study of the interactions between the molecules and their structure in mixtures. The Kirkwood–Buff theory of statistical mechanics [16] is one of the tools used to achieve this objective. This theory was originally formulated to obtain thermodynamic properties from pair-correlation functions, g_{ij} . However, when thermodynamic properties are available, this theory can be inverted to calculate the Kirkwood–Buff parameter G_{ij} defined as

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 dr \quad (7)$$

where r is the distance between the pair i and j .

For a mixture of ideal gases where no interactions between molecules exist, $g_{ij}(r)$ is unity due to the random distribution of molecules in the mixture and thus leads to a zero value for G_{ij} . In real mixtures, the quantity G_{ij} can take either positive or negative values, reflecting the total average excess or deficiency of i molecules in the surroundings of j molecules. In a binary mixture there are three G_{ij} integrals, namely G_{11} , G_{22} and G_{12} ($= G_{21}$), corresponding to the three possible interactions. These three quantities can be obtained in terms of the derivative of the activity coefficient with respect to composition A , partial molar volumes V_i , and isothermal compressibility, κ_T , according to the following relations

$$\rho G_{12} = RT\rho\kappa_T - V_i V_j / (AV^2) \quad (8)$$

$$\rho G_{ii} = \rho G_{12} - [(V_j / (AV)) - 1] / x_i \quad (9)$$

where R is the gas constant, ρ is the mixture density, V is the mixture molar volume, and A is obtained from

$$A = 1 + x_i d \ln \gamma_i / dx_i$$

In this study, the UNIQUAC model with temperature-dependent parameters is used to evaluate $d \ln \gamma_i / dx_i$ and the Costald [17] correlation is used to evaluate the volumes and the isothermal compressibility.

4. Results and discussion

The temperature intervals of the thermodynamic surfaces are slightly outside the temperature intervals of the experimental data used in estimating the model parameters. This is mainly due to the extrapolating capability of the UNIQUAC model, and a better representation of the thermodynamic surfaces that contain 20×20 and 10×10 grids. The surfaces of the heats of mixing are calculated for the whole concentration range, while the other surfaces are for the range 0.001–0.4 or less.

Concentration and temperature dependences of the heats of mixing for the alkanol–alkane mixtures are shown in Fig. 1. All the mixtures show rather strong composition

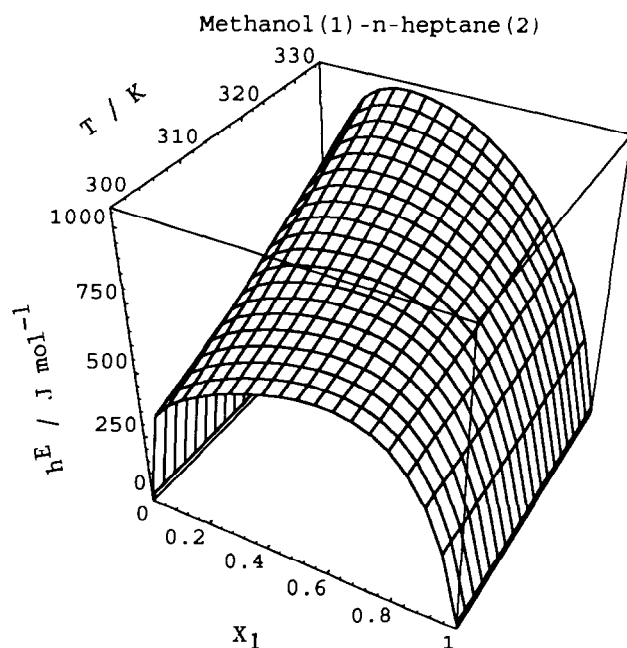


Fig. 1. Composition and temperature dependence of excess enthalpy h^E . (a) Methanol(1)–*n*-heptane(2), 300.15–335.15 K. (b) Ethanol(1)–*n*-hexane(2), 280.15–320.15 K. (c) Ethanol(1)–cyclohexane(2), 275.15–335.15 K. (d) 2-Propanol(1)–*n*-heptane(2), 300.15–335.15 K. (e) *n*-Pentanol–*n*-hexane(2), 295.15–320.15 K. (f) *n*-Hexanol(1)–*n*-octane(2), 285.15–330.15 K. (g) *n*-Octanol(1)–*n*-octane(2), 285.15–330.15 K.

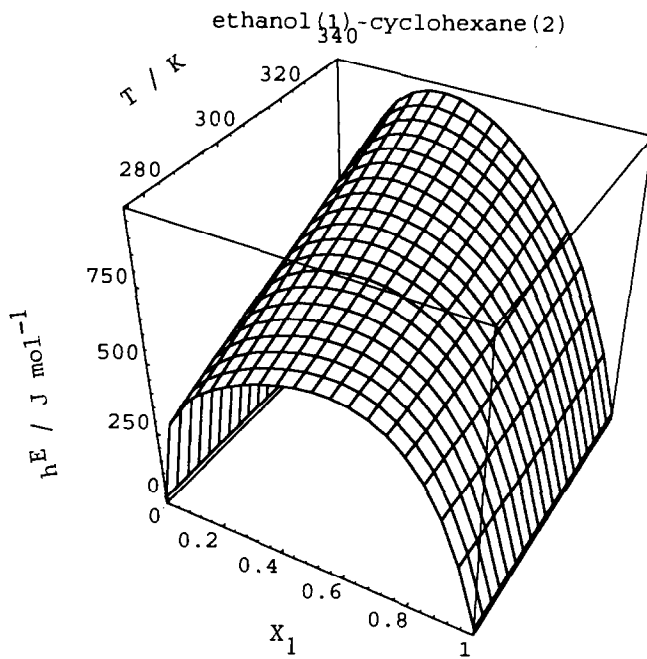
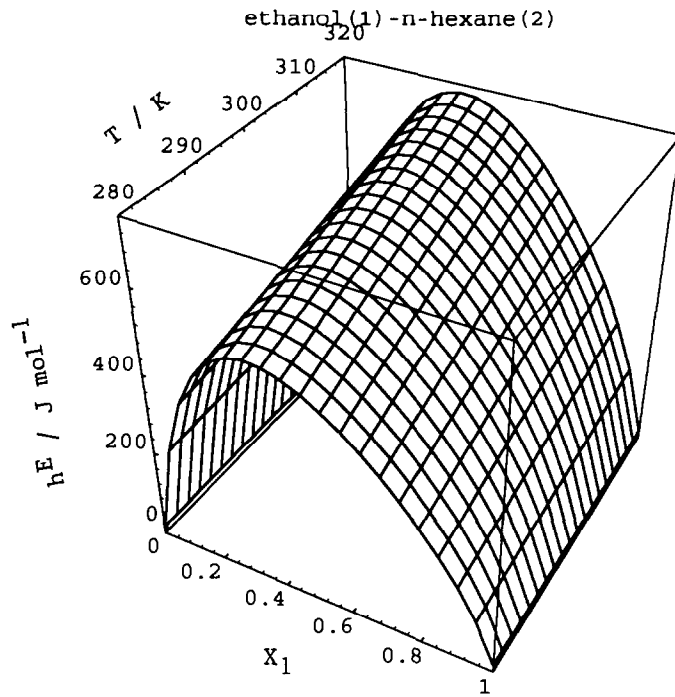


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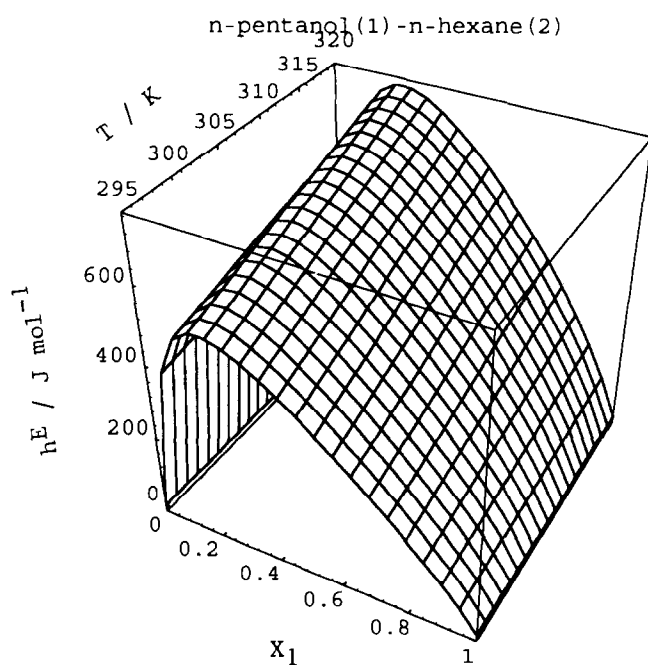
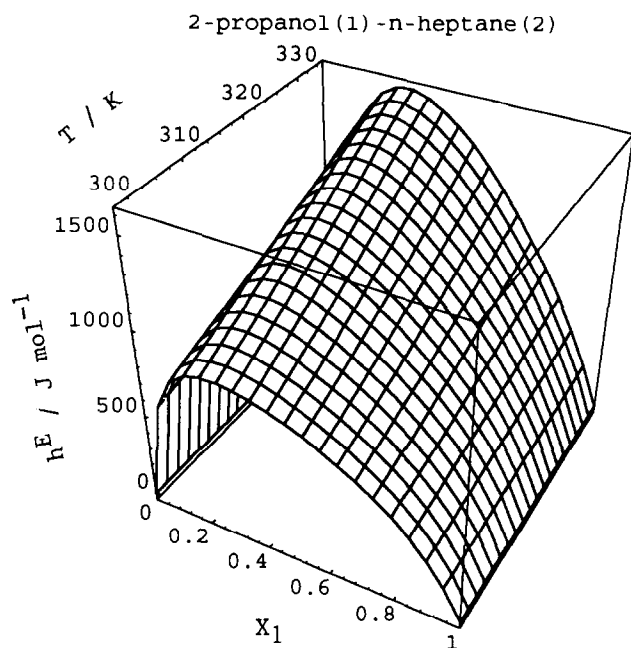


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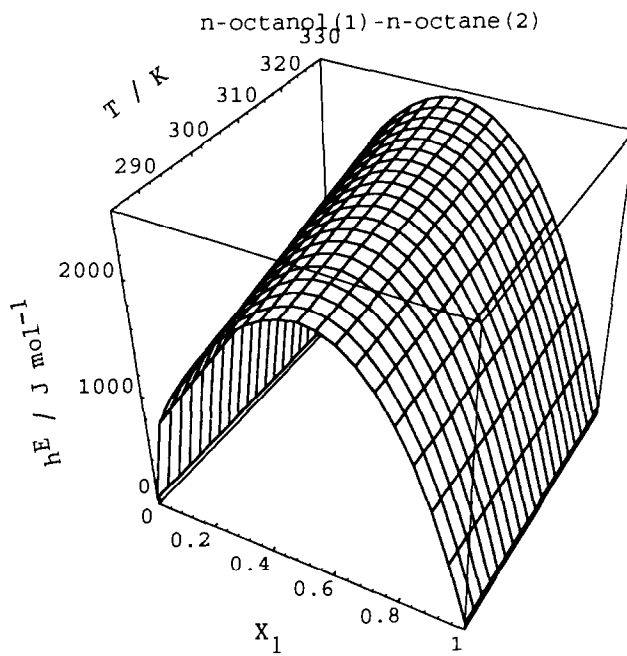
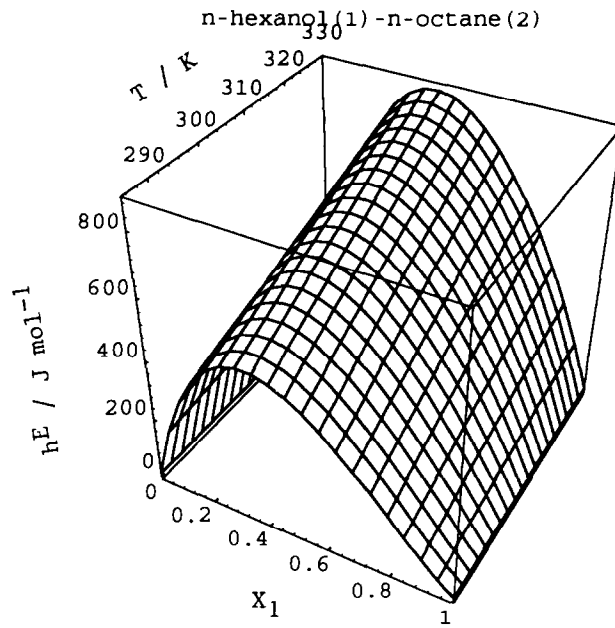


Fig. 1 (continued)

and temperature dependency. As the temperature increases, the value of h^E increases for all the mixtures [18]. The composition dependences at both ends of the temperature interval are especially different from each other for the mixtures methanol(1)–*n*-heptane(2) and ethanol(1)–cyclohexane(2).

Reliable thermodynamic data in the very dilute region is essential for understanding alkanol association. Furthermore the excess functions in the dilute range show a very strong dependence on both temperature and composition. Temperature-dependent parameters of the UNIQUAC model were estimated using the data for the whole composition range.

Interpretation of mixture non-ideality in alkanol–alkane mixtures is mainly predicated upon long-range and short-range molecular forces. The alkane-rich region is characterized by weakly bonded van der Vals complexes. The alkanol-rich region is characterized by hydrogen bonded complexes that exhibit relatively strong, specific and highly directional binding of a primarily electrostatic nature. At low alkanol concentrations, dimers would be the predominant polymeric species, with larger polymer chains becoming more significant with increasing alkanol concentrations [19]. The *n*-alkane order decreases with increasing temperature due to thermal motion and expansion of the liquid which bring about a loosening of the packing between chains [20].

The change in dilution enthalpy, h^E/x_1 , with temperature and alkanol composition in the range 0.001–0.4 is shown in Fig. 2. The value of h^E/x_1 represents the enthalpy

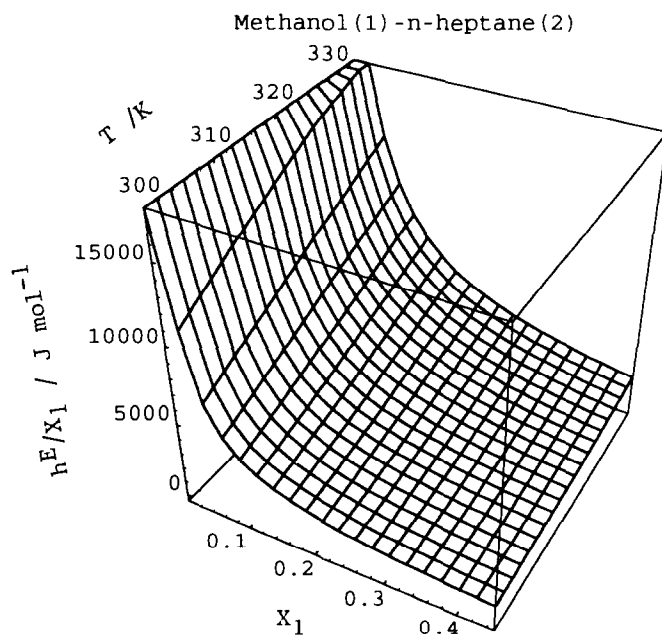


Fig. 2. Composition and temperature dependence of dilution enthalpy, h^E/x_1 . (a) Methanol(1)–*n*-heptane(2), 300.15–335.15 K. (b) Ethanol(1)–*n*-hexane(2), 280.15–320.15 K. (c) Ethanol(1)–cyclohexane(2), 275.15–335.15 K. (d) 2-Propanol(1)–*n*-heptane(2), 300.15–335.15 K. (e) *n*-Pentanol–*n*-hexane(2), 295.15–320.15 K. (f) *n*-Hexanol(1)–*n*-octane(2), 285.15–330.15 K. (g) *n*-Octanol(1)–*n*-octane(2), 285.15–330.15 K.

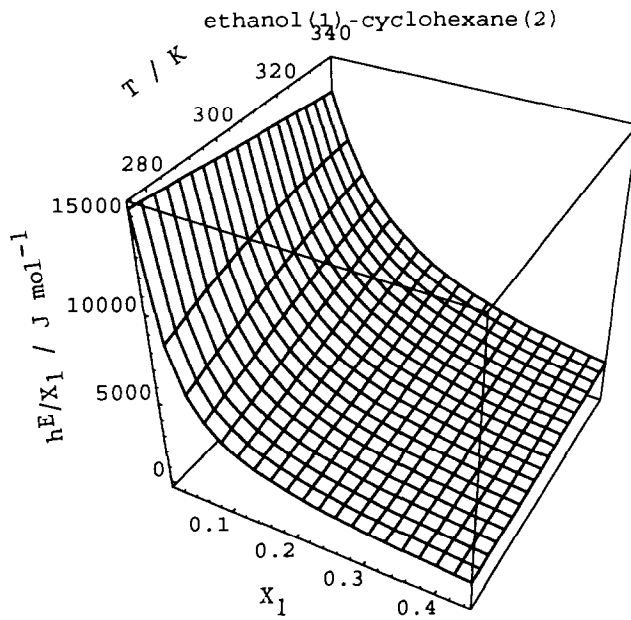
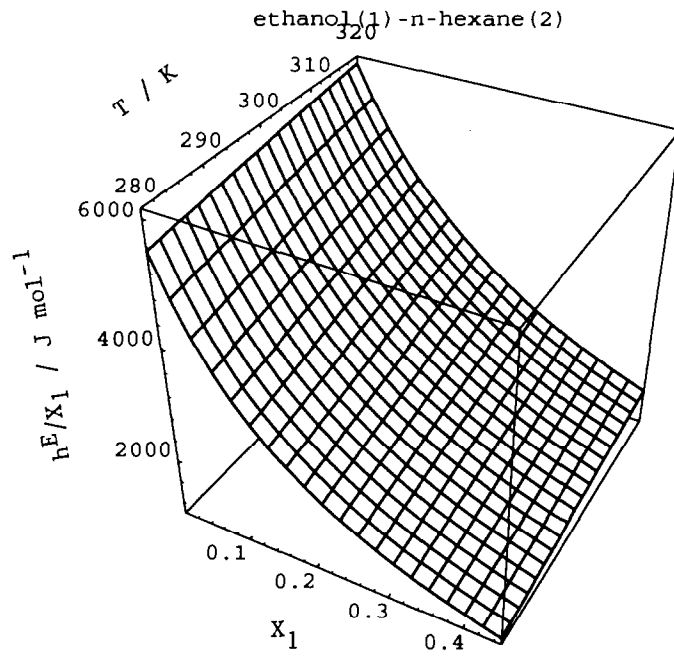


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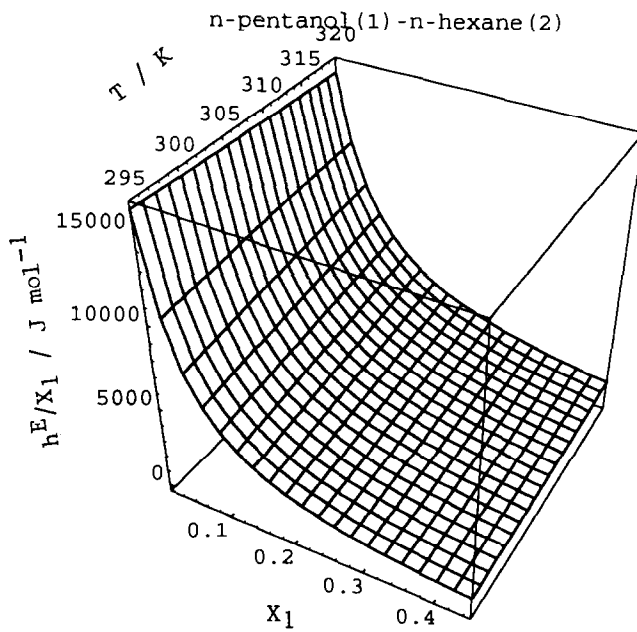
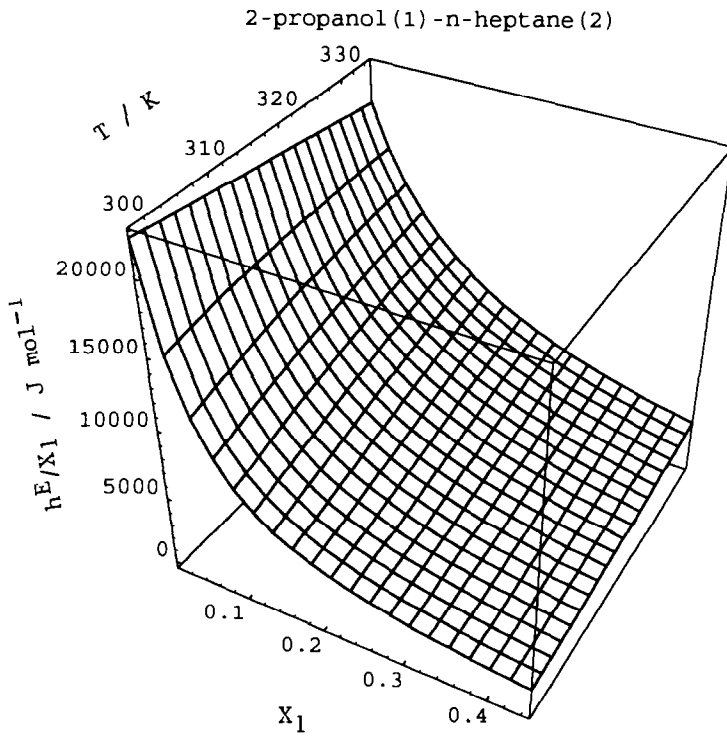


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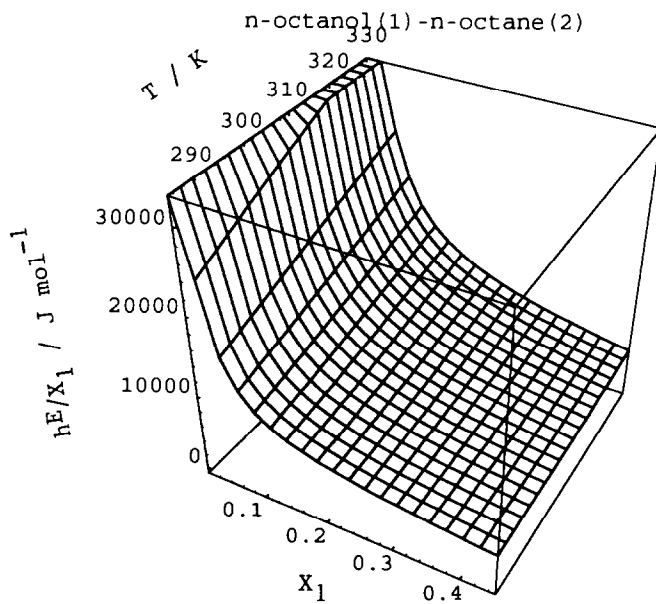
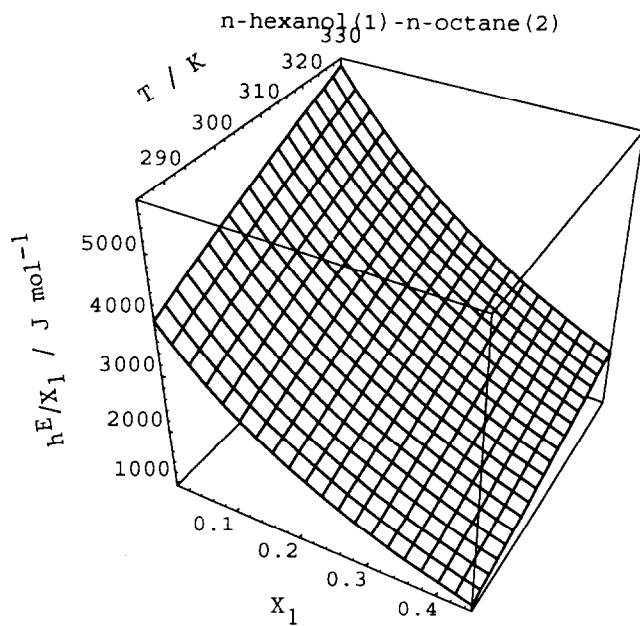


Fig. 2 (continued)

increase per unit amount of alkanol on dilution from pure alkanol to the x_1 value quoted. The shape of the curves of h^E/x_1 against x_1 is complex, with an inflection in the alkanol-dilute region which shifts towards higher alkanol concentration with temperature [21].

Fig. 3 shows the partial molar excess enthalpy of alkanol in the composition range 0.001–0.4. Except for the mixture *n*-hexanol–*n*-octane, and inflection at around 0.1 can be observed for all the mixtures studied within the experimental uncertainty.

Changes in alkanol–alkanol interactions with composition and temperature are shown in Fig. 4. As the composition of alkanol increases, the solute–solute interactions change steeply to about $x_1 = 0.1$ and thereupon remain almost constant. As the temperature increases, the inflection moves to higher alkanol compositions for all the mixtures.

The Kirkwood–Buff parameters (ρG_{ij}) are shown in Figs. 5 and 6 for the mixtures ethanol–cyclohexane and 2-propanol–*n*-heptane. The quantity ρG_{ij} for the alkanol–alkane mixtures shows a characteristic behavior. At low alkanol concentrations, it has a large negative value indicating a lower average concentration (deficiency) of alkanol molecules around a central molecule of the same species compared to the macroscopic

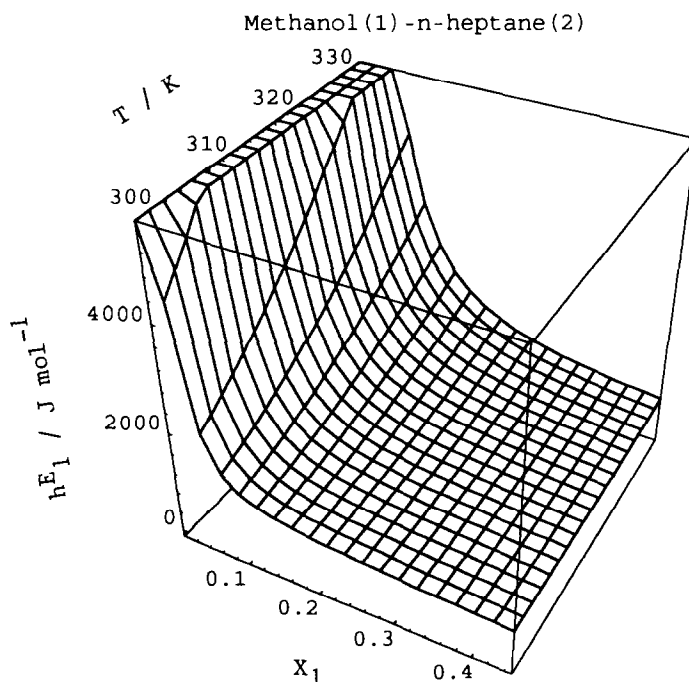


Fig. 3. Composition and temperature dependence of partial molar excess enthalpy h^E_1 . (a) Methanol(1)–*n*-heptane(2), 300.15–335.15 K. (b) Ethanol(1)–*n*-hexane(2), 280.15–320.15 K. (c) Ethanol(1)–cyclohexane(2), 275.15–335.15 K. (d) 2-Propanol(1)–*n*-heptane(2), 300.15–335.15 K. (e) *n*-Pentanol–*n*-hexane(2), 295.15–320.15 K. (f) *n*-Hexanol(1)–*n*-octane(2), 285.15–330.15 K. (g) *n*-Octanol(1)–*n*-octane(2), 285.15–330.15 K.

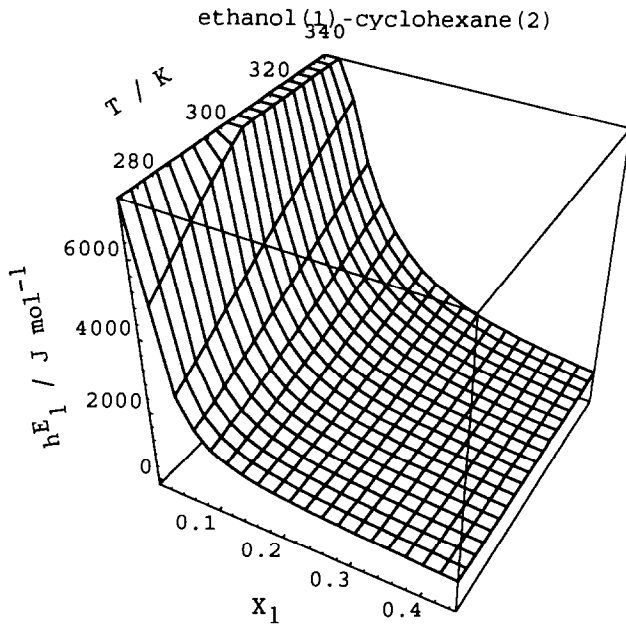
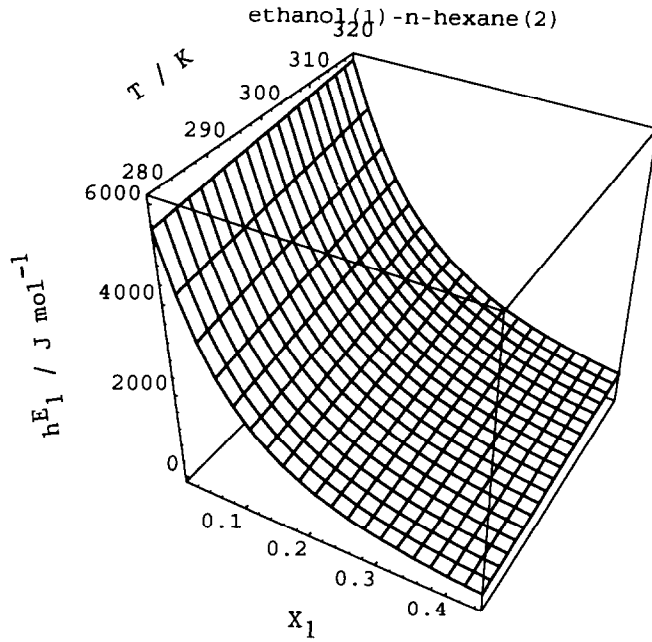


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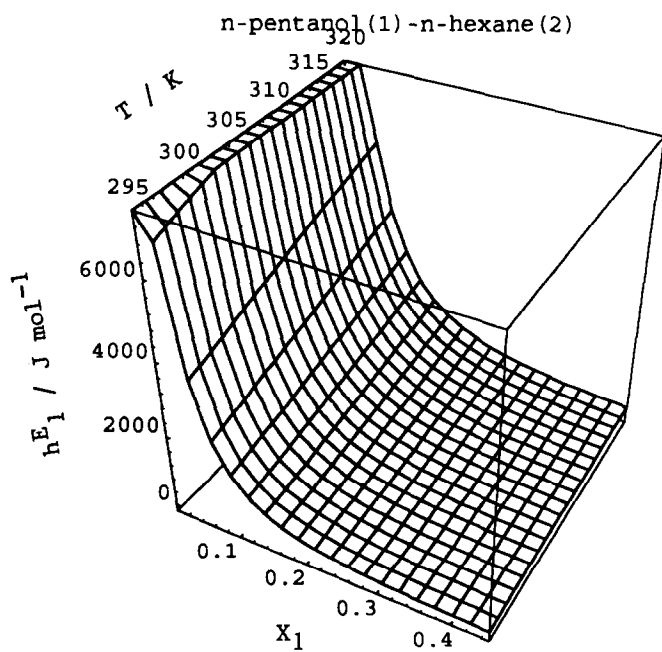
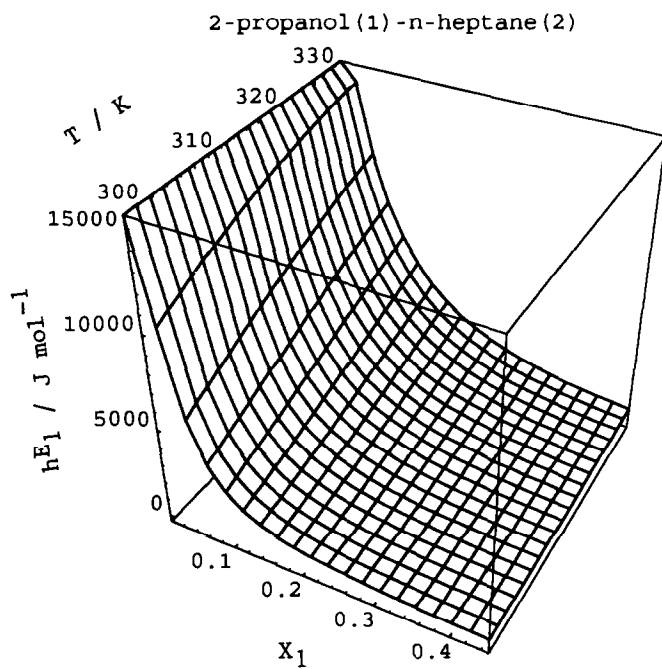


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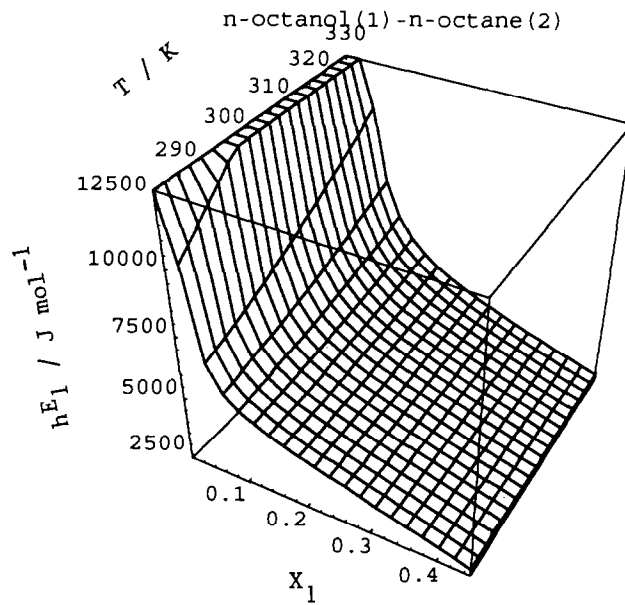
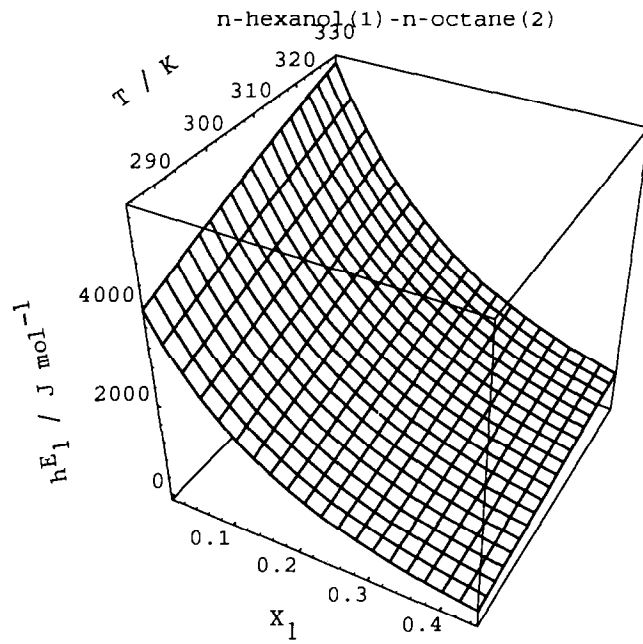


Fig. 3 (continued)

concentration. The interaction of the hydrophobic moiety of the alkanol with the alkane molecules is energetically favored leading to the dispersion of alkanol molecules in the mixture. The hydrogen bonds between the alkanol hydroxyl groups are absent at low concentrations, but their formations at higher concentrations lead to an increase in homocoordination and hence an increase in the value of ρG_{ij} .

Similar arguments can be applied to the quantities ρG_{11} and ρG_{22} . The alkane–alkane integral ρG_{22} shows a large negative value at low alkane concentration (large x_1) due to the absence of forces that can keep the alkane molecules together. The unlike integral ρG_{12} for the alkanol–alkane molecules is almost always positive, indicating heterocoordination due to the favorable interaction between the unlike molecules as discussed before. For the ethanol–cyclohexane mixture, the dilute alkanol region has an additional feature, namely a maximum in ρG_{11} and a minimum in ρG_{12} before the minimum in ρG_{11} and the maximum in ρG_{12} . This behavior indicates that the ethanol molecules tend to aggregate in this region, which could be due to the slightly weaker interactions between the ethanol–cyclohexane compared to the interactions between the 2-propanol and *n*-heptane molecules. The decrease of the pair integrals with temperature in ρG_{11} and ρG_{22} can be explained by the increased agitation at higher temperatures due to the increase in the kinetic energy of the molecules which brings the molecules slightly closer to randomness. However, the increase in ρG_{12} for ethanol–cyclohexane does not follow this trend.

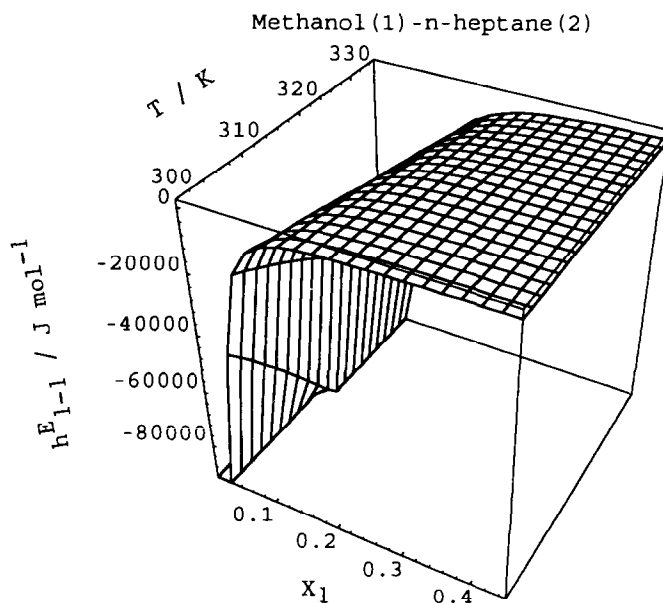


Fig. 4. Change of alkanol–alkanol interactions in terms of enthalpy h_{1-1}^E (a) Methanol(1)–*n*-heptane(2), 300.15–335.15 K. (b) Ethanol(1)–*n*-hexane(2), 280.15–320.15 K. (c) Ethanol(1)–cyclohexane(2), 275.15–335.15 K. (d) 2-Propanol(1)–*n*-heptane(2), 300.15–335.15 K. (e) *n*-Pentanol–*n*-hexane(2), 295.15–320.15 K. (f) *n*-Hexanol(1)–*n*-octane(2), 285.15–330.15 K. (g) *n*-Octanol(1)–*n*-octane(2), 285.15–330.15 K.

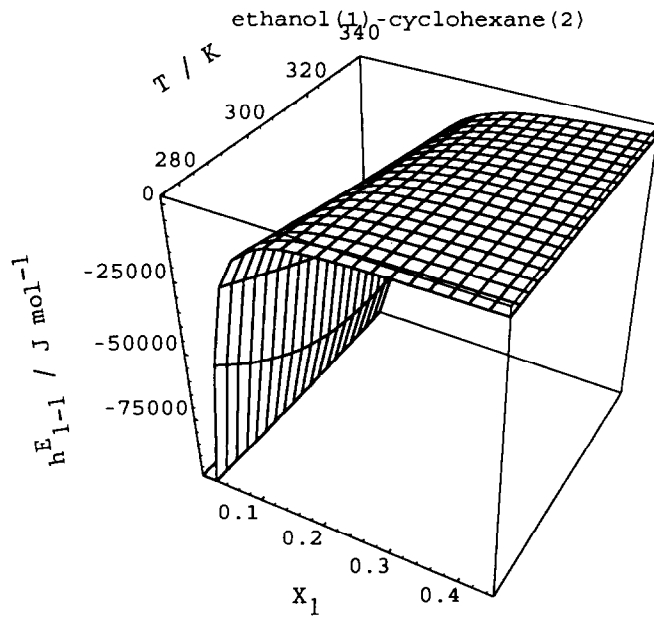
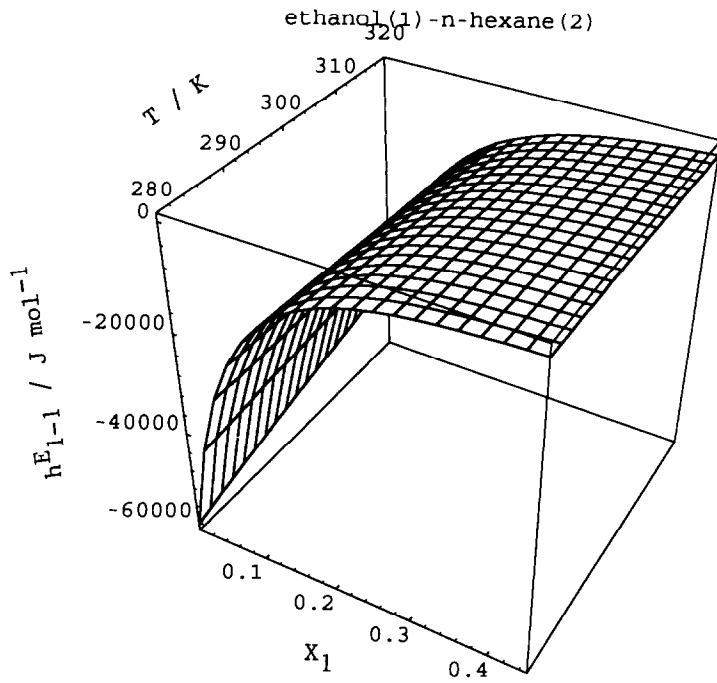


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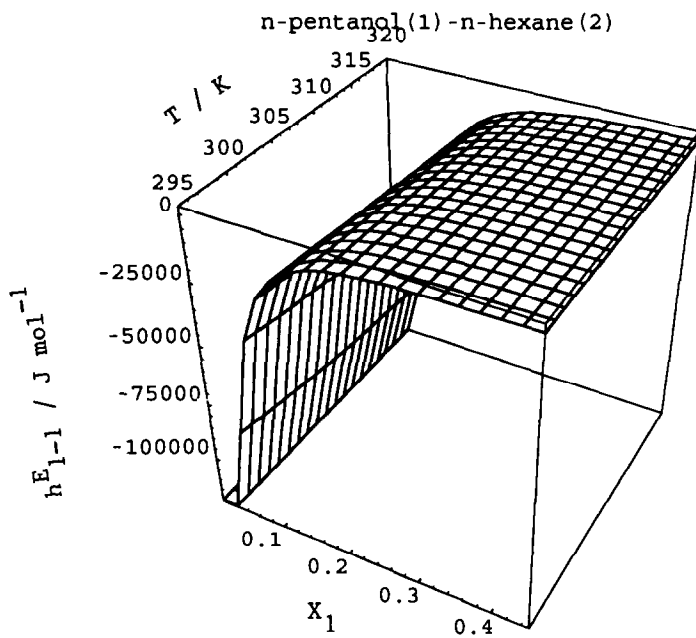
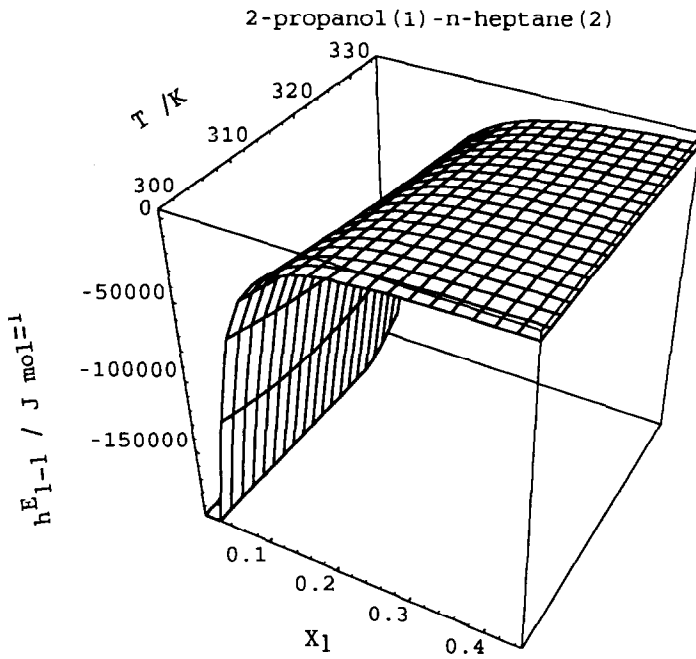


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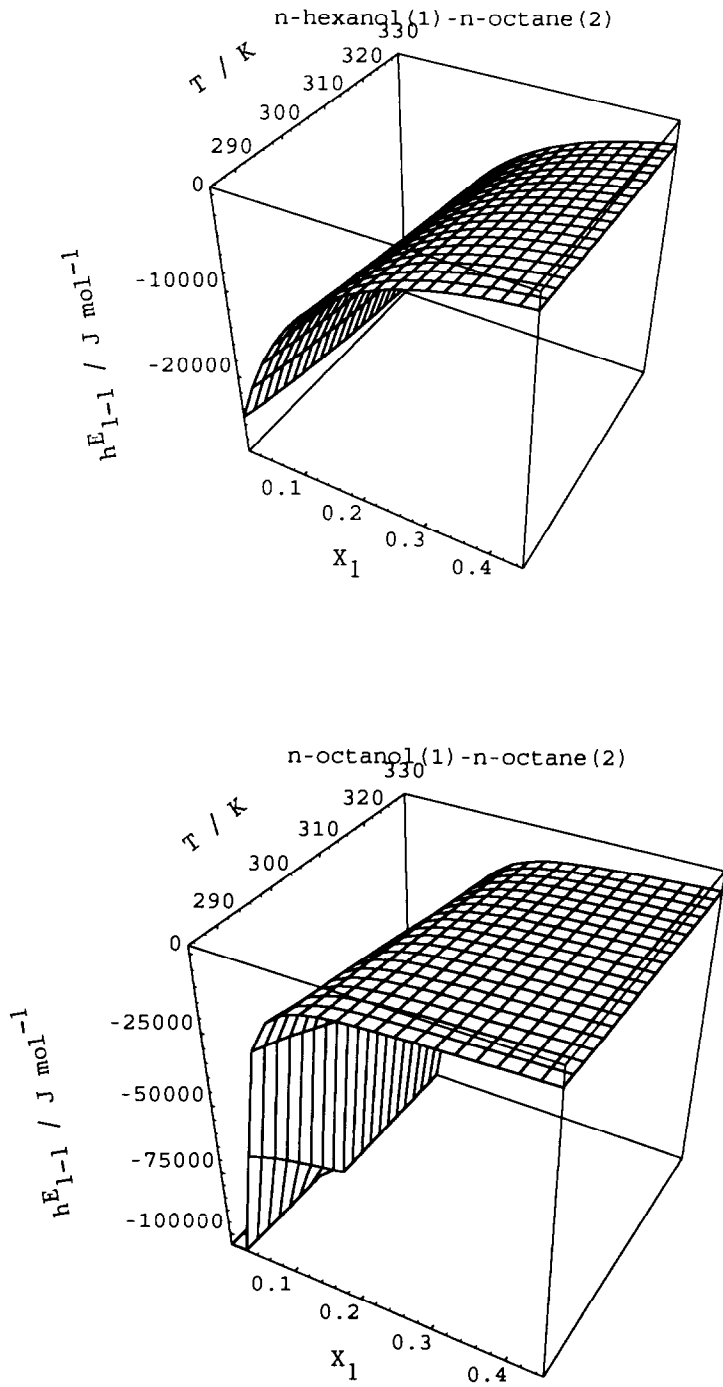


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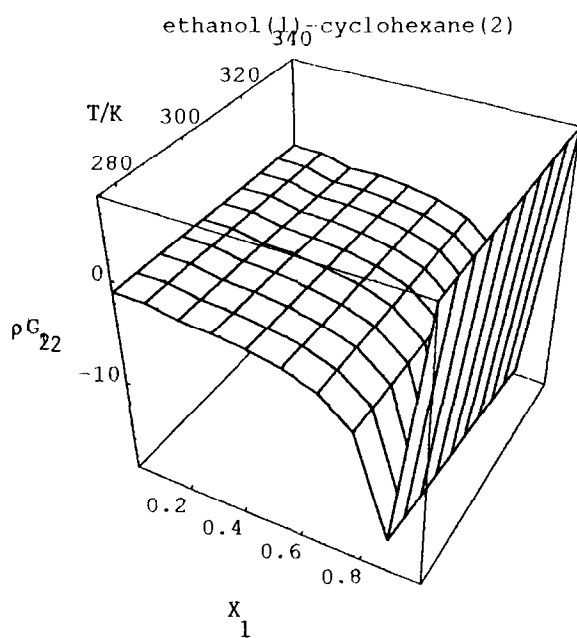
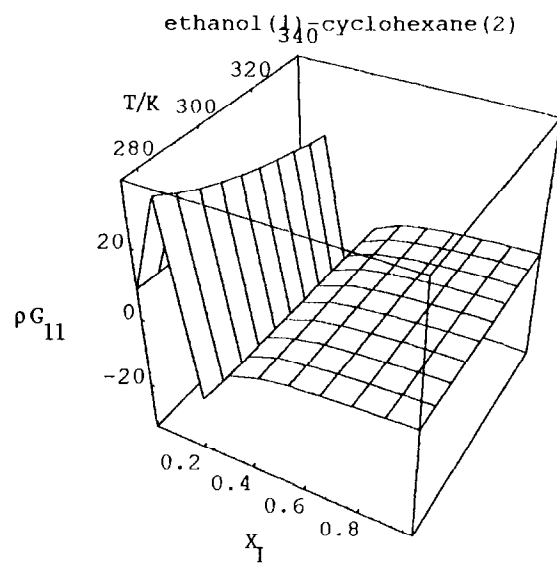


Fig. 5. Composition and temperature dependence of Kirkwood–Buff parameters for ethanol(1)–cyclohexane(2), 275.15–335.15 K: (a) ρG_{11} ; (b) ρG_{22} ; (c) ρG_{12} .

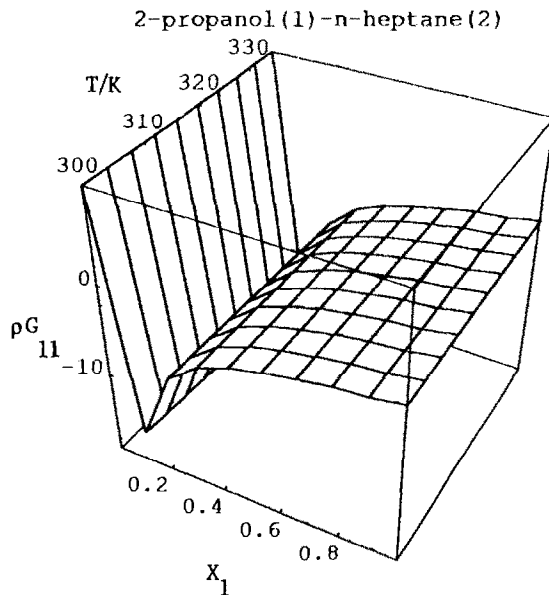
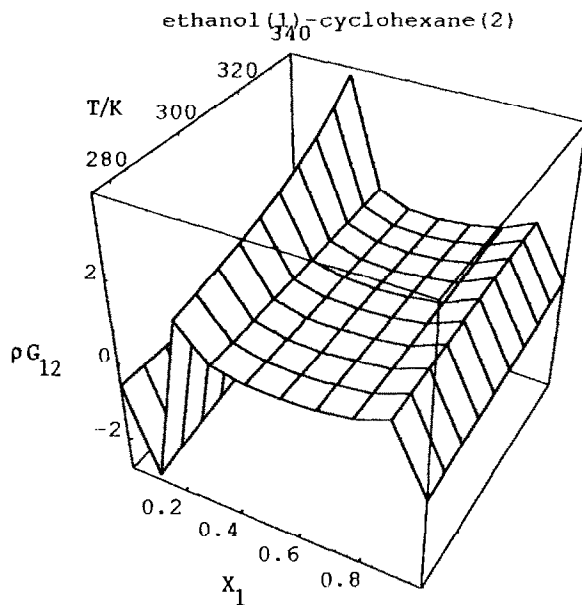


Fig. 6. Composition and temperature dependence of Kirkwood-Buff parameters for 2-propanol(1)-n-heptane(2), 300.15–335.15 K: (a) ρG_{11} ; (b) ρG_{22} ; (c) ρG_{12} .

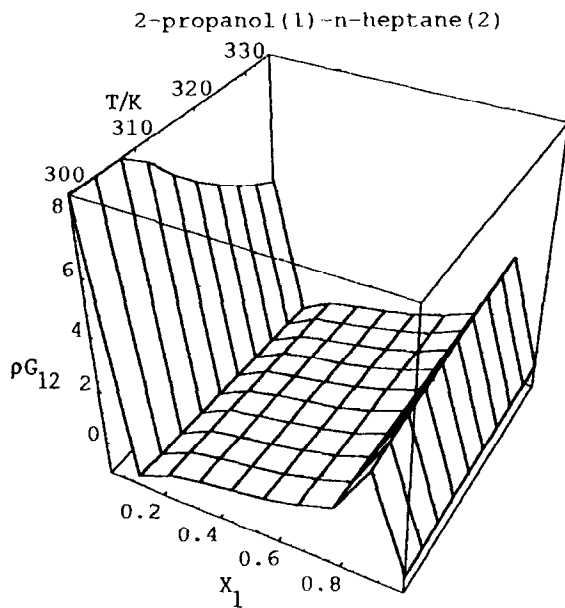
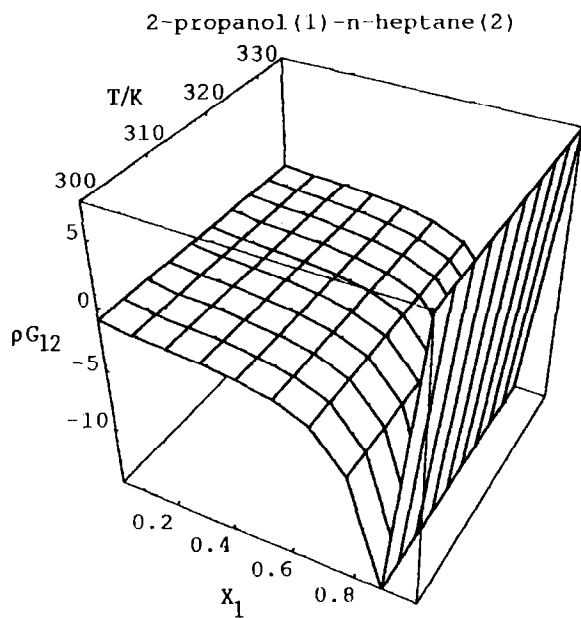


Fig. 6 (continued)

5. Conclusions

The enthalpy functions are sensitive to molecular complexation and provide a rigorous test of the limitations and applications of models. Therefore thermodynamic surfaces of such functions for alkanol–alkane mixtures have been calculated by the UNIQUAC model with temperature-dependent parameters. Kirkwood–Buff parameters were also calculated using the UNIQUAC model. The thermodynamic surfaces showing the concentration and temperature dependences are consistent with experimental data within the computational and experimental uncertainty. Such surfaces reveal the thermodynamic properties in a qualitative and quantitative manner, and thus help to understand the association of alkanol molecules and structural changes in the mixtures. The UNIQUAC model with temperature-dependent parameters is capable of representing satisfactorily the thermodynamic properties of alkanol–alkane mixtures at low pressures.

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