Bhatia-Young Model Calculations of the Thermodynamic Properties of TKEBS-Based Binary Liquid Mixtures

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Z. Naturforsch. **44a**, 793–800 (1989); received February 24, 1989

The simplified random phase approximation Bhatia-Young model has been used to evaluate the properties of mixing and the concentration fluctuations of the binary liquid mixtures of TKEBS with cyclohexane, carbon tetrachloride and benzene. At this level of description the details of the potentials are not important; only the values of the long-wavelength limit of the average effective ordering pair potential and its temperature derivative are required. In the three mixtures the constituent molecules are assumed to be globular in shape.

1. Introduction

The thermodynamic excess functions of organic liquid mixtures depend on the chemical nature, size and shape of the constituent molecules. The complexity of these molecules, however, rules out the application of the most successful theories of molecular liquids, such as the interaction site models [1]. In the long run, we hope that ab-initio theories which appeal to potentials of the Kihara type could be used for these systems [2]. For the time being, we have to appeal to semiphenomenological models, such as the group contribution theories [3]. This work is no exception. However, our approach is casted in a way which allows contact to be made with the limiting behaviour of both the correlation functions and the approximate sphericalized pair form of a linear combination of the intermolecular potentials, the ordering potential.

This approach was extensively used by Bhatia and coworkers [4] in the study of liquid binary alloys, to relate the limiting behaviour of the Bhatia-Thornton partial structure factors to the thermodynamic properties of the system. Of these we shall only be concerned here with the limiting behaviour of the concentration-concentration partial structure factor, $S_{cc}(0)$. More recently, the work of Bhatia and Young [5, 6] has provided the rationale which links the asymptotic behaviour of the ordering potential to the interchange energy parameters which makes its appearance in the semiphenomenological theories of the thermodynamic properties of mixtures [7].

We believe to have been the first who have extended the ideas of Bhatia and coworkers to insulators [8–10]. Here we present the results of calculations of the thermodynamic properties (entropies ΔS, enthalpies ΔH, and Gibbs free energies ΔG) and $S_{cc}(0)$ for three tetrakis-(2-ethylbutoxy)-silane(TKEBS)-based binary mixtures. This is not a fortuitous choice for, in these systems, the volume ratio between the TKEBS molecules, and the molecules of the other components in the mixtures – cyclohexane (C_6H_{12}), carbon tetrachloride (CCl_4), and benzene (C_6H_6) respectively – is approximately five to one in all three cases. This large size difference poses a severe test for any theory of liquid mixtures. There is an other advantage in studying these systems. In the large TKEBS molecules the hydrocarbon chains surrounding the Si–O bonds are highly branched, making the molecule globular in shape. We shall also assume, though with less justification, that the smaller molecules making up the binary mixtures are also spherical in shape. This assumption considerably simplifies our formalism. Actually we are also assuming that the constituent molecules of the mixtures are rigid, thus neglecting any contribution which may arise from their intramolecular behaviour, or from any possible coupling between intra- and

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inter-molecular forces, to the thermodynamic properties studied in this work. We believe these assumptions to be reasonable, and the results presented in Section 3 appear to confirm this to be the case.

The layout of the paper is as follows. In the next section we discuss briefly the Bhatia-Young model, and we introduce all the basic formalism needed for this work. In Sect. 3 we present the results of our calculations and compare them with the experimental data reported by Tomlins and coworkers [11–13]. We complete the paper with a brief discussion of our results.

2. Theory

Bhatia and Young [5] have recently proposed a simple model for the free energy of mixing, using: i) hard sphere mixtures as a reference system; and ii) a tail interaction between unlike molecules. The former embodies the assumption of a mixture of globular, rigid, molecules. The latter entails a subtle approximation on the ordering potential, $v=\Phi_{11}+\Phi_{22}-2\Phi_{12}$, where the Φ_{ij} denote the intermolecular potentials in the mixture (for a careful discussion, see reference [6]). Briefly, we have for the Helmholtz free energy of the mixture per molecule

$$F\simeq F_{\mathrm{HS}}+n c_1 c_2 \omega\,, \tag{1}$$

where F_{HS} denotes the corresponding hard-spheres free energy, n the number density, and $c_1\equiv c$, $c_2=1-c_1$, the mole fractions. Moreover

$$\omega\simeq\tilde{v}(0)\equiv\frac{1}{4\pi}\iint v(\boldsymbol{r},\Omega)\,\mathrm{d}\boldsymbol{r}\,\mathrm{d}\Omega\,, \tag{2}$$

where the integration is over the volume of the system and relative orientations between the constituent molecules.

The approximation involved in (2) implies that, in principle (as with all effective pair potentials [14]) ω is a function of the thermodynamic state, namely $\omega=\omega(n,c,T)$. In this work we neglect the dependence of ω on the density and focus our attention on its temperature dependence; there appears to be no dependence of ω on concentration. Actually, the need to consider its temperature dependence was originally raised on experimental grounds [15]. As stated by (1), the Bhatia-Young model is based on a van der Waals-like equation where the correlations are treated within a simplified form of the random phase approximation (RPA).

From (1) the entropy of the mixture reads

$$S=-\left(\frac{\partial F}{\partial T}\right)_{N,V}=S_{\mathrm{HS}}-nc_1c_2\frac{\partial\omega}{\partial T}\,. \tag{3}$$

Defining the Helmholtz free energy of mixing as $\Delta F=F-c_1F_1-c_2F_2$, where F_1 and F_2 refer to the free energies of the unmixed components, and using similar expressions for ΔS and ΔE (the entropy and internal energy of mixing, respectively) we have

$$\Delta F=-T\Delta S_{\mathrm{HS}}+nc_1c_2\omega\,. \tag{4}$$

Bearing in mind the thermodynamic relation

$$\Delta F=-T\Delta S+\Delta E \tag{5}$$

and (3), one obtains

$$\Delta E=nc_1c_2(\omega-T(\partial\omega/\partial T))\,. \tag{6}$$

In this work we regard both ω and $(\partial\omega/\partial T)$ as adjustable parameters.

Actually, (4) is very much like the expression of the free energy in Flory's semiphenomenological theory of mixtures [16], in which case ω can be identified to the interchange energy. Moreover, as the experiments of Tomlins and coworkers were conducted under normal pressure conditions, we are assuming throughout this work that the Gibbs free energy of mixing $\Delta G\simeq\Delta F$, and that the enthalpy of mixing $\Delta H\simeq\Delta E$.

We now turn to the relation between the asymptotic behaviour of the correlation of fluctuations and the thermodynamic properties of binary mixtures. As noted by Landau and Lifshitz [17], there are at least two ways of looking at the fluctuations in a binary mixture. Either we consider the fluctuations in the number of molecules N_1, $N_2(N_1+N_2=N)$ of each component, and their cross fluctuations $\langle\Delta N_i\Delta N_j\rangle$ $(i,j=1,2)$; or we study the fluctuations in the number of molecules, regardless of the components, $\langle\Delta N^2\rangle$, the fluctuations in mole fraction $\langle\Delta c^2\rangle$, and the cross fluctuations. In all cases $\langle\ \rangle$ denotes an ensemble average, in the grand canonical ensemble.

Kirkwood and Buff [18] adopted the first of these approaches in relating the long-wavelength limit of the correlation of fluctuations to the thermodynamic properties of the system. In particular, if

$$S_{ij}(k)=\delta_{ij}+4\pi n(c_ic_j)^{1/2}\int\limits_0^\infty[g_{ij}(r)-1]\cdot\frac{\sin kr}{kr}r^2\,\mathrm{d}r\,(i,j=1,2) \tag{7}$$

defines the partial structure factors $S_{ij}(k)$ in terms of the pair distribution functions $g_{ij}(r)$, then, in the long-wavelength limit,

$$n k_B T k_T = \frac{S_{11}(0)\, S_{22}(0) - S_{12}^2(0)}{c_2 S_{11}(0) + c_1 S_{22}(0) - 2(c_1 c_2)^{1/2} S_{12}(0)}, \tag{8}$$

where k_B denotes Boltzmann's constant, k_T the isothermal compressibility, and $S_{ij}(0) = \lim_{k \to 0} S_{ij}(k)$.

The recent paper by Rubio et al. [19] illustrates very clearly how the formalism of Kirkwood and Buff is used to analyse and interpret experimental results on liquid mixtures.

The second approach was originally explored by Pearson and Rushbrooke [20] and further developed by Bhatia and Thornton [21]. The so-called Bhatia-Thornton partial structure factors $S_{NN}(k)$, $S_{Nc}(k)$ and $S_{cc}(k)$ may be written as linear combinations of the $S_{ij}(k)$ defined above [4]. Here, we are only concerned with the long-wavelength limit of the mole fraction-mole fraction partial structure factor $S_{cc}(0)$, which is related to the thermodynamic properties through the relation

$$\begin{aligned} S_{cc}(0) &= N \langle \Delta c^2 \rangle \\ &= k_B T [\partial^2 G / \partial c^2]^{-1}_{T,P,N} . \end{aligned} \tag{9}$$

Although we shall not make use of them, we write below the long-wavelength limits of the number-number $S_{NN}(0)$, and number-mole fraction $S_{Nc}(0)$ partial structure factors.

$$S_{NN}(0) = \frac{\langle \Delta N^2 \rangle}{N} = n k_B T k_T + \delta^2 S_{cc}(0) \tag{10}$$

and

$$S_{Nc}(0) = \langle \Delta N \Delta c \rangle = -\delta\, S_{cc}(0) , \tag{11}$$

where δ is a dilatation factor defined by

$$\delta = \frac{1}{V} \left(\frac{\delta V}{\delta c} \right)_{T,P,N} . \tag{12}$$

3. Results of Calculations

We have calculated the entropy, enthalpy and Gibbs free energy of mixing, as well as $S_{cc}(0)$, for three TKEBS-based mixtures: TKEBS-C_6H_{12}, TKEBS-C_6H_6 and TKEBS-CCl_4 at 308 K. We discuss below the details of the parametrization used in our calculations.

To evaluate the effective hard-spheres diameters of the constituent molecules of the three mixtures we have followed the prescription of Snider and Herrington [22], namely fitting to the experimental particle densities n_i and heats of vaporization $L_{v,i}$ of the pure components, which are approximately related by

$$\frac{L_{v,i}}{N k_B T} = \frac{1 + \eta_i + \eta_i^2}{(1 - \eta_i)^3} + 1 , \tag{13}$$

where $\eta_i = \frac{1}{6} \pi n_i \sigma_i^3$ denote the packing fractions of the pure components. The densities were taken from the work of Tomlins [13]. The heats of vaporization were calculated as follows. For C_6H_{12}, C_6H_6 and CCl_4 we applied Watson equation [23], using the available heats of vaporization at $T = 298$ K [24]. In the case of TKEBS we also applied Watson equation, but using the experimental boiling point data [11] and the heats of vaporization at this temperature calculated from the Fishtine equation [23].

The values of the effective hard sphere diameters, in Ångstrom, are:

$$\sigma(\text{TKEBS}) = 9.904, \qquad \sigma(CCl_4) = 5.277,$$
$$\sigma(C_6H_{12}) = 5.491, \qquad \sigma(C_6H_6) = 5.168.$$

Henceforth we assume that these values do not change on mixing.

The values of ω and $\partial \omega / \partial T$ were deduced from the best fitting to the experimental ΔG and ΔH using the non-linear optimum-seeking procedure of Marquardt [25]. Actually, we have evaluated $W = \omega / N k_B T V_2$ and $W' = (\omega - T \partial \omega / \partial T) / N k_B T V_2$, where V_2 is the volume per molecule of component 2 which, in our case, is always TKEBS. Table 1 lists the optimal values of W and W', as well as the standard deviations (in parenthesis).

The HS entropy of mixing may be written as [26, 27]

$$\Delta S_{\text{HS}} = \Delta S_{\text{F}} + k_B \ln(V/V_0) + \Delta S_\eta + S_\sigma . \tag{14}$$

ΔS_{F} denotes the entropy of mixing in Flory's theory:

$$\Delta S_{\text{F}} = -k_B (c_1 \ln \Phi_1 + c_2 \ln \Phi_2) , \tag{15}$$

Table 1. Optimal values of the parameters W and W' (see text). Values in brackets denote standard deviations.

System	W	W'
TKEBS-C_6H_{12}	−0.055 (12)	0.142 (1.8)
TKEBS-CCl_4	−0.188 (12)	−0.202 (21)
TKEBS-C_6H_6	0.288 (8.0)	0.505 (6.9)

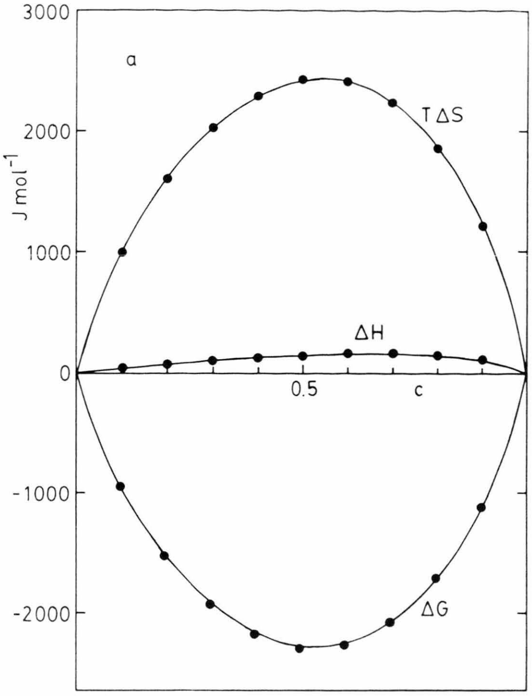
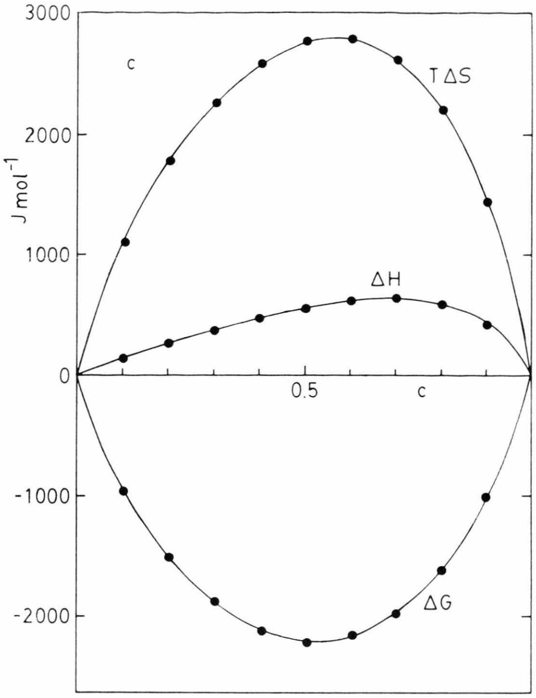


Fig. 1 a



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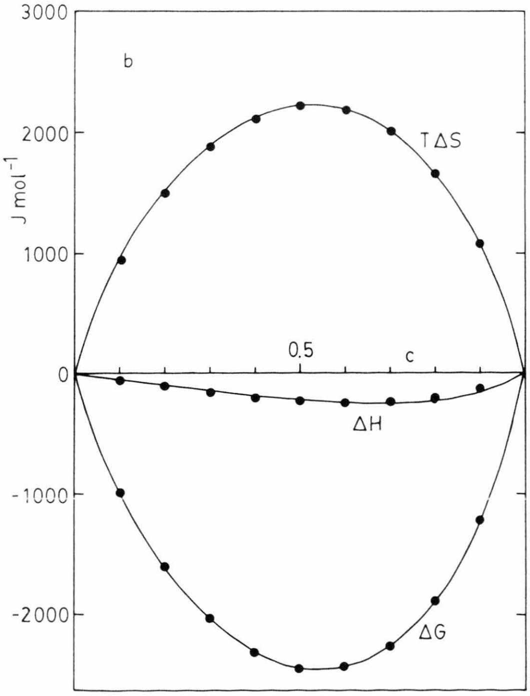

Fig. 1 b

where $\Phi_i = c_i V_i / V_0$ denotes the concentration by volume of component i, and $V_0 = c_1 V_1 + c_2 V_2$. It is clear that ΔS_{HS} incorporates, and improves upon, the Flory entropy. Moreover, as noted by Hoshino [26], the contributions beyond ΔS_{F} can sometimes be significant.

For ΔS_η and S_σ we write [6, 28]

$$\frac{\Delta S_\eta}{k_B} = 3 - \frac{2}{(1-\eta)} - \frac{1}{(1-\eta)^2} - c_1 \cdot \left[3 - \frac{2}{(1-\eta_1)} - \frac{1}{(1-\eta_1)^2}\right] - c_2 \left[3 - \frac{2}{(1-\eta_2)} - \frac{1}{(1-\eta_2)^2}\right], \qquad (16)$$

Fig. 1. Entropies $T\Delta S$, enthalpies ΔH, and Gibbs free energies of mixing ΔG of three TKEBS-based liquid mixtures at 308 K. Full line: theory, this work; dots: experimental results of Tomlins and coworkers [11–13]. (a) TKEBS-C_6H_{12}; (b) TKEBS-CCl_4; (c) TKEBS-C_6H_6.

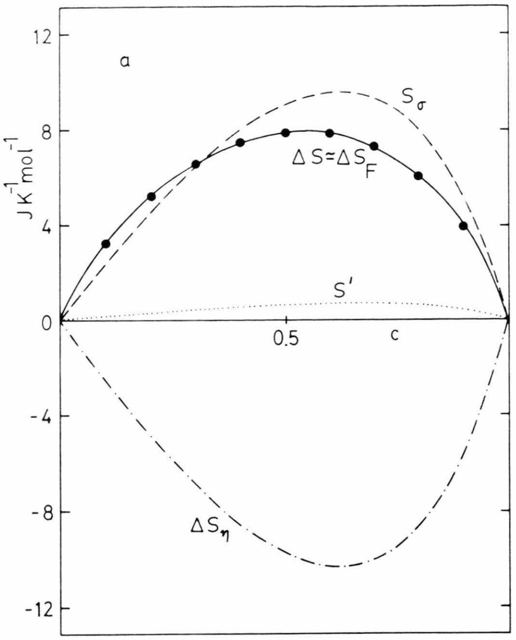

Fig. 2 a

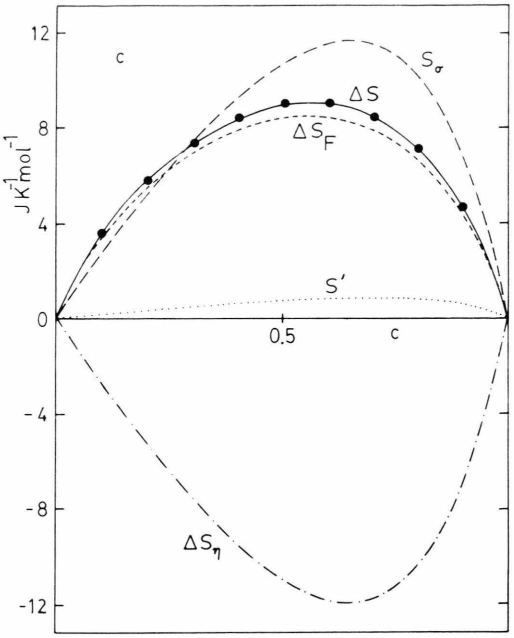

Fig. 2 c

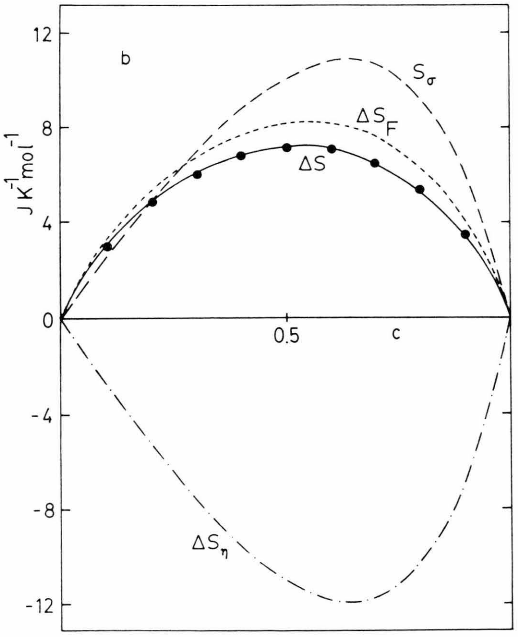

Fig. 2 b

where the total packing fraction $\eta = \frac{1}{6}\pi n(c_1\sigma_1^3 + c_2\sigma_2^3)$, and

$$\frac{S_\sigma}{k_B} = A\, c_1 c_2 (\sigma_1 - \sigma_2)^2 , \tag{17}$$

where

$$A \equiv \left[\frac{\eta}{(1-\eta)^2} + \ln(1-\eta)\right](Y_1 + Y_2) + \frac{3\eta}{(1-\eta)}\, Y_1 \tag{18}$$

with

$$Y_1 = (\sigma_1 + \sigma_2)/(c_1\sigma_1^3 + c_2\sigma_2^3);$$

and

$$Y_2 = \sigma_1\sigma_2(c_1\sigma_1^2 + c_2\sigma_2^2)/c_1\sigma_1^3 + c_2\sigma_2^3)^2 . \tag{19}$$

←

Fig. 2. Separate contributions to the total entropies of mixing: Flory entropy ΔS_F; packing contribution ΔS_η; mismatch contribution S_σ; contribution due to the temperature dependence of the interchange energy, S'. The contributions due to the excess volumes of mixing are not shown as these are too small to show up in the figure (see text). Full line: total entropy of mixing; dots: experimental results. (a) TKEBS-C_6H_{12}; (b) TKEBS-CCl_4; (c) TKEBS-C_6H_6.

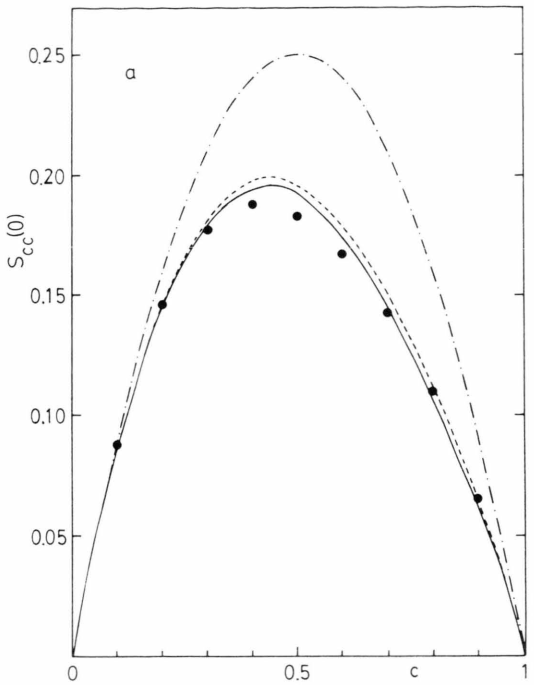

Fig. 3a

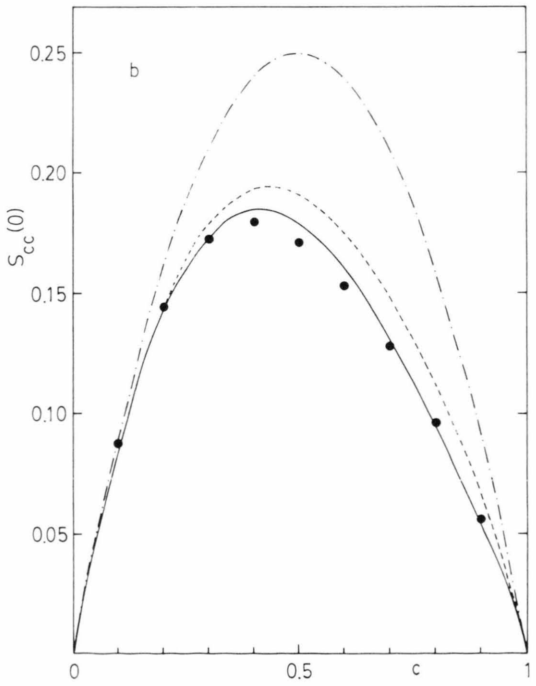

Fig. 3b

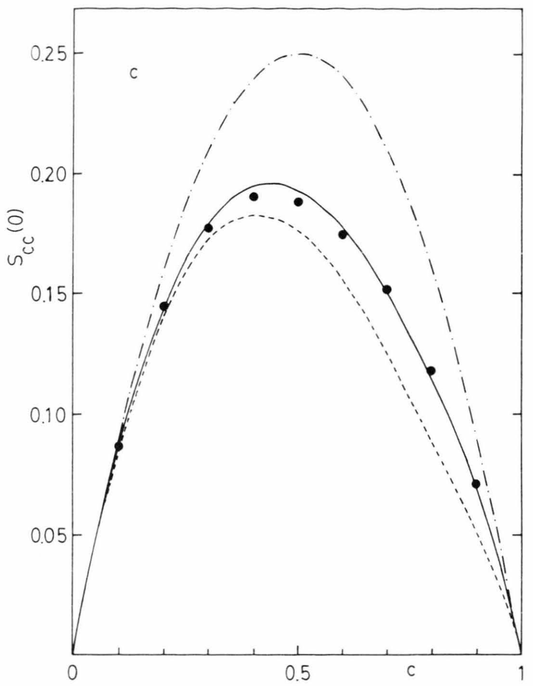

Fig. 3c

Finally, for the concentration fluctuations we appeal to the RPA side of the Bhatia-Young model, to write

$$S_{cc}^{-1}(0) = S_{cc}^{\mathrm{HS}-1}(0) + S_{cc}^{\omega-1}(0)\,. \qquad (20)$$

For the first term on the *rhs* of (20) we use a form consistent with the above expression for ΔS_{HS}; we evaluate $S_{cc}^{\omega}(0)$ from the second term of (4).

The results of our calculations are presented in Figs. 1 to 3. Figure 1 shows the results for ΔG, ΔH and $T\Delta S$: (a) TKEBS-C_6H_{12}; (b) TKEBS-CCl_4; and (c) TKEBS-C_6H_6. The experimental results of Tomlins and coworkers are indicated by dots. The experimental $T\Delta S$ was deduced from $T\Delta S = \Delta H - \Delta G$. It is clear that the Bhatia-Young model provides an excellent description of the thermodynamic properties of mixing of the three systems studied in this work. The

Fig. 3. Long wavelength limit of the concentration-concentration partial structure factor, $S_{cc}(0)$: -·-·-·- ideal solution value, $S_{cc}(0) = c_1 c_2$; - - - - hard spheres contribution, $S_{cc}^{\mathrm{HS}}(0)$. Full line: theory, this work; dots: experimental results deduced from the activity data of Tomlins [13]. (a) TKEBS-C_6H_{12}; (b) TKEBS-CCl_4; (c) TKEBS-C_6H_6.

assumption of globular shape behaviour is justified by our results, although the need to introduce the temperature dependence of ω indicates that the averaging of some aspect of the interaction is required. The fact that ω does not depend on concentration suggests that no chemical short range order (CSRO) is present in these systems, and this is also reflected in the fairly simple behaviour of the thermodynamic properties of these mixtures.

Figure 2 shows how the different contributions to the entropy of mixing add up to give the overall $T\Delta S$. In the figure, S' denotes the contribution due to the temperature dependence of ω. In all cases the excess volume contribution – second term in (14) – is too small to be shown in the figure; this is a consequence of the very small excess volumes of mixing in these systems. On the other hand, the large contribution of S_σ reflects the size difference between the constituent molecules in the three mixtures. We note that only in the case of the TKEBS-C_6H_{12} mixture ΔS is approximately equal to the Flory entropy ΔS_F. This is only due to the approximate cancellation between the packing, ΔS_η, and mismatch, S_σ, contributions. Bearing in mind the smallness of the S' contribution, the excellent agreement between the experimental and theoretical results confirms the view that, in systems with no CSRO, the entropy of mixing is largely determined and, in turn, reflects the packing (or excluded volume) properties of these systems.

Finally in Fig. 3 we present the results of the $S_{cc}(0)$ calculations for the same three mixtures at $T=308$ K. The experimental results were deduced from the activity data of Tomlins [13], which is related to $S_{cc}(0)$ through the equivalent equation to (9),

$$S_{cc}(0)=c_2(\partial \ln a_1/\partial c_1)^{-1}_{T,P,N}\,. \tag{21}$$

The theoretical results have been calculated using (20). Our simple theoretical model characterizes very well the experimental situation. The three systems exhibit a tendency of preferred heterocoordination as, in all cases, the actual results are below the ideal solution value, $S_{cc}(0)=c_1c_2$. In our calculations this tendency to heterocoordination is dominated by the hard-core contributions; the large size difference favours such a topological arrangement. The potential tail or, more precisely, the sign and magnitude of the interchange energy, is enough to perform the necessary fine tuning leading to such a good agreement between theory and experiment.

4. Conclusions

We have shown that the simple Bhatia-Young model provides a good description of the thermodynamic properties of mixing of the three TKEBS-based liquid mixtures studied in this work. At this level of description it appears that the details of the potentials are not important. This places the theory of the thermodynamic properties of this class of liquid organic mixture on a par with that of simple liquid mixtures.

With hindsight the assumption of globular shape molecules has been justified. However, the fact that we had to appeal to the temperature dependence of the interchange energy implies that we have made use of an effective, averaged, pair ordering potential.

Within the framework of the Bhatia-Young model no further insights are possible. While we acknowledge the limitations of our approach, we surmise that its simplicity may allow for a systematic characterization of the thermodynamic properties of liquid organic mixtures.

Acknowledgements

One of us (LJG) is grateful to the Xunta de Galicia of Spain for the provision of a Research Fellowship to visit the University of East Anglia where this work was completed.

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