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LETTER

Concentration Fluctuations In Hydrogen-Bonded Fluid Mixtures

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The concentration fluctuations, $S_{cc}(0)$, of three hydrogen-bonded binary mixtures, $H_2O - X$ ($X = Ar, H_e, H_2$) have been calculated using a Thermodynamic Perturbation Theory based on polarizable dipolar hard spheres, at a temperature T and several values of the pressure P .

Given the choice of equal hard sphere diameters for the component of the three mixtures, and that the second component, X , does not possess a dipolar moment, this study probes directly the polarization contribution to $S_{cc}(0)$, which is shown to produce non-negligible effects.

KEY WORDS: Polarization, Gibbs free energy.

Over the last few years two of the authors and their co-workers, have developed a thermodynamic perturbation theory (TPT) which has been successfully applied to study the phase equilibria of a number of polar liquid mixtures¹⁻⁷. The latter work has involved H_2O as one of the components^{6,7}, and it is on these systems we shall be concerned in this note.

The TPT is applied to a polarizable hard-sphere dipole model, such that the reduced Helmholtz free energy is written as

$$F^* = F_0^* + F_\mu^* + F_{\alpha,\mu}^* ; \quad F^* = \beta F/N \quad (1)$$

where the rhs of Eq. (1) includes the hard-spheres F_0^* , dipolar F_μ^* and polarization $F_{\alpha,\mu}^*$ contributions. The last two terms of Eq. (1) are evaluated using Pade approximants, whereas for F_0^* the Carnahan-Starling⁸ form was used.

In a separate development the first author, and one of his co-workers, has studied the behaviour of the Bhatia-Thornton concentration-concentration partial structure

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factor — in its long wavelength limit — $S_{cc}(0)$, for a model binary mixture of dipolar and quadrupolar molecules.⁹ The results of this work have been used as the basis for the understanding of the behaviour of liquid mixtures of organic molecules, particularly those whose excess heat capacity C_p^E exhibits a 'W-shape' as a function of concentration, namely two regions of positive curvature separated by one of negative curvature.¹⁰

Many polar organic molecules, as well as colloidal particles, are also polarizable and it is therefore of interest to study the interplay of the different contributions, particularly those arising from the polarization term, in deciding the behavior of $S_{cc}(0)$. A detailed study of this behavior for a large number of cases of model liquid mixtures of polarizable molecules is under way.

We recall that⁹

$$S_{cc}(0) = Nk_B T [\partial^2 G / \partial c^2]_{P,T}^{-1} = [\partial^2 G^* / \partial c^2]_{P,T}^{-1} \quad (2)$$

where,

$$G^* = \beta G / N$$

denotes the reduced Gibbs free energy. β is the inverse of the Boltzmann's constant k_B times the temperature T .

The number concentration $c = c_{H_2O}$, such that,

$$c = c_{H_2O} + c_X = 1$$

G^* , in our case, is obtained from Eq. (1) using the thermodynamic relations

$$G = F + PV$$

and

$$P = -(\partial F / \partial V)_{T,N}$$

All contributions to $\partial^2 G^* / \partial c^2$ are obtained without recourse to numerical derivatives thus minimizing errors in the calculations.

In this note we report the results of $S_{cc}(0)$ for $H_2O - X$ ($X = Ar, He, H_2$) at constant temperature but at different pressures. Since in these systems the second component, X , does not have a dipolar moment (we also ignore the quadrupolar contribution in H_2) the contribution from F_μ^* vanishes. Moreover, given our choice of equal size diameters, the hard spheres contribution is $S_{cc}^0(0) = c(1 - c)$, namely the ideal case of random fluctuations in concentration. Hence departures from the ideal behavior in $S_{cc}(0)$ for these systems — within the TPT used herein — are either due to the polarization term $F_{\alpha,\mu}^*$ or, else, are caused by the onset of phase transitions. Actually our choice of pressures P and temperatures T have been dictated, in each case, so that we present results for which, in the calculated phase diagram, the binary mixture is miscible over the whole range of concentrations.

The results obtained are shown in Figures 1–3. The value of the hard sphere diameter chosen in the three mixtures is $\sigma = 2.78 \text{ \AA}^6$. The values of the polarizabilities are: $\alpha_{\text{H}_2\text{O}} = 1.44 \text{ \AA}^{11}$, $\alpha_{\text{Ar}} = 1.64 \text{ \AA}^{12}$, $\alpha_{\text{He}} = 0.21 \text{ \AA}^{12}$, and $\alpha_{\text{H}_2} = 0.79 \text{ \AA}^{13}$. In all our calculations $c = c_{\text{H}_2\text{O}}$. The polarization contribution appears to produce two effects; first the mixture has preferred homo coordination, $\text{Scc}(0) > \text{S}^{\text{idcc}}(0)$, which is more pronounced as the ratio of the polarizabilities $\alpha_{\text{H}_2\text{O}}/\alpha_X$ increases; second, it tends to shift the maximum value of $\text{Scc}(0)$ towards the water rich concentrations.

In the three cases studied in this work we are concerned with pressure induced phase transitions, and the results show clearly the effects of approaching a phase change or the critical line. In Figure 1, the blip at the water rich end the $\text{H}_2\text{O} - \text{Ar}$ mixture signals the approach to a critical point, which can be reached by increasing further the pressure at constant temperature and concentration. In Figure 2 the large increase in $\text{Scc}(0)$ for the $\text{H}_2\text{O} - \text{He}$ mixture signals the onset of a gas–liquid phase transition, which is more pronounced with increasing pressure. Finally the two large, narrow peaks in $\text{Scc}(0)$ for the $\text{H}_2\text{O} - \text{H}_2$ mixture, shown in Figure 3, are related to a gas–liquid transition at $c = 0.928$ with a maximum value $\text{Scc}(0) = 33.01$, and the approach to a critical point at $c = 0.949$ with $\text{Scc}(0) = 8.94$.

The results of this work point to a non negligible contribution of the polarization. Although by itself it will not lead to ‘W-shaped’ specific heats, this term cannot be ignored in calculations aimed at a correct modeling of polar binary mixtures.

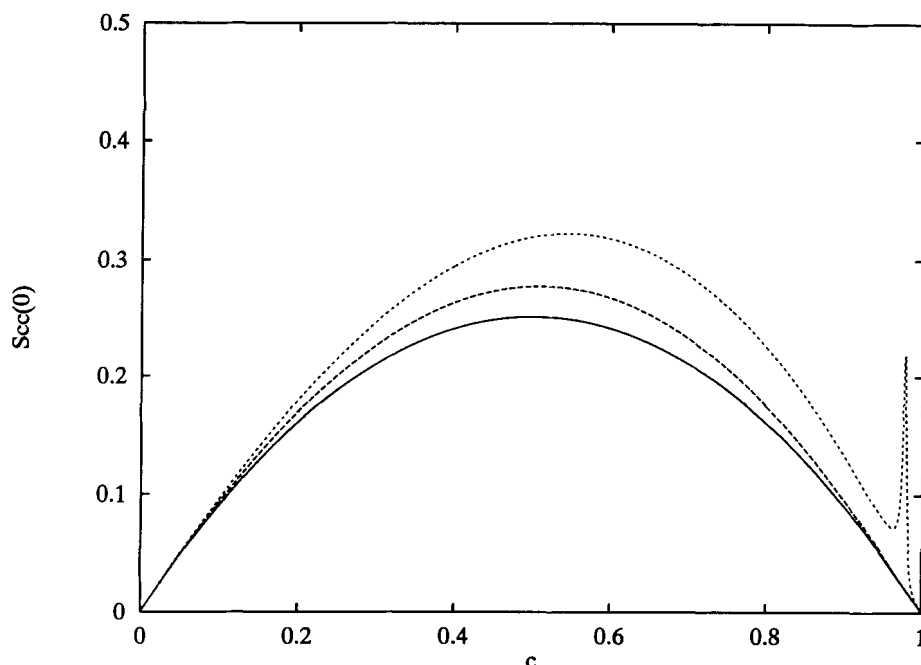


Figure 1 Concentration fluctuations, $\text{Scc}(0)$, for the $\text{H}_2\text{O} - \text{Ar}$ fluid mixture at $T = 647.23 \text{ K}$, and different pressures P . Solid line: $P = 0.6 \text{ MPa}$; broken line: $P = 12 \text{ MPa}$; dotted line: $P = 24 \text{ MPa}$.

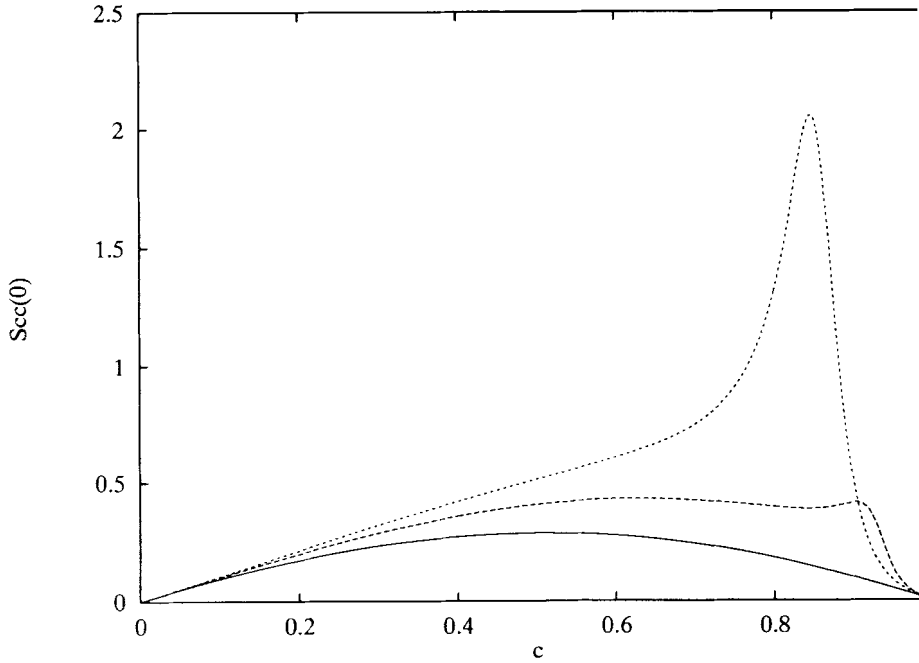


Figure 2 Concentration fluctuations, $S_{cc}(0)$, for the H_2O -He fluid mixture at $T = 668.0$ K, and different pressures P . Solid line: $P = 6.27$ MPa; broken line: $P = 37$ MPa; dotted line: $P = 50$ MPa.

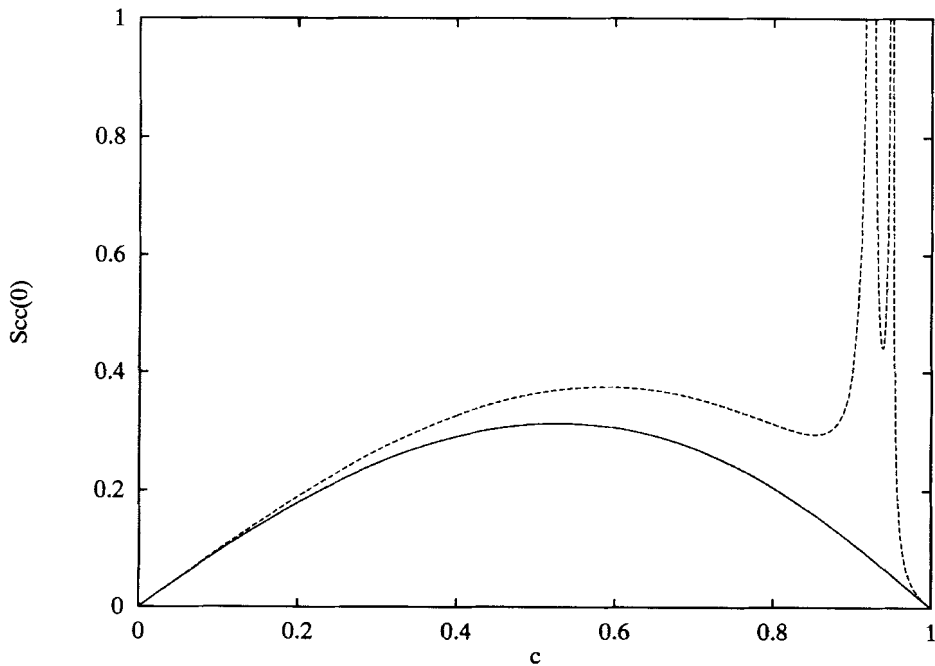


Figure 3 Concentration fluctuations, $S_{cc}(0)$, for the H_2O - H_2 fluid mixture at $T = 648.0$ K, and different pressures P . Solid line: $P = 20$ MPa; dotted line: $P = 30$ MPa.

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