Computer simulation of structural properties of dilute aqueous solutions of argon at supercritical conditions.

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Abstract

Computer simulation studies of aqueous solutions of argon are performed from ambient to supercritical conditions by using a recent polarizable potential model (BSV) and the non polarizable simple point charge extended (SPC/E) model. At $T = 673$ K we compare the water-solute pair correlation functions of the argon-water mixture with recent experimental results obtained from neutron scattering experiments. The comparison shows that the introduction of the polarizable effects decreases the solute-water repulsion and improves the agreement with the experiment at supercritical conditions. In particular we find that the water-solute structure predicted by the polarizable model is in good agreement with the experiment.

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I. INTRODUCTION

The problem of solubility of non polar solutes in water has become of large interest for the applications in many chemical processes in industrial technology and biochemistry. At ambient conditions the solubility of non polar gases in water is some order of magnitude lower than in other solvent like liquid hydrocarbons, for this reason they are usually considered as hydrophobic solutes. The solubility however increases steeply above the water critical point, $T_c = 647.13$ K and $P_c = 220.55$ bar. Most applications involve the use of water at supercritical conditions, where it becomes a good solvent for several non polar materials.

In fact the curve of solubility of non polar gases at increasing temperatures shows a very peculiar behaviour, starting from room temperature it decreases and reaches a minimum, then it sharply increases toward water supercritical temperature, where complete miscibility is reached for some system. It is also been observed that the solubility of rare gases is larger for larger size of the solute. The behaviour is determined by the interplay between energetic and entropic contributions to the free energy of solvation. According to the simulation work done by Guillot and Guissani with the simple point charge extended (SPC/E) model for water the energetic term favors the solubility of larger solutes while the entropic term depresses the solubility at increasing size.

The size of the solute seems also to be connected to the different behaviour of the mixtures of water and noble gases at high pressure at the gas-gas critical point.

Structural and computer simulation studies on aqueous solutions of rare gases indicate that at ambient conditions strong modifications of the water structure are induced by the solutes with the formation of hydration cages around the gas atom. Guillot and Guissani found that at increasing temperature the solute tends to disrupt the cage. The entropic contribution is dominated by the reorientation of the water molecules in the first shell of hydration, where only the repulsive part of the water-solute interaction plays a role.

In this respect the change in the structural properties of water approaching the supercritical state with the modification of the hydrogen bond network could be very relevant in determining the strong increase of the solubility of apolar gases with temperature. Recent neutron diffraction studies performed at supercritical conditions in mixtures of rare gases at low concentration in water found that the structure of water is modified and compressed by the presence of the apolar solutes.

Simple pair potential used in computer simulation of water based on parameters fitted to the properties at ambient conditions like TIP4P and SPC/E do not agree with the experimental results of neutron diffraction studies performed at supercritical conditions. Due to the interest in supercritical water several polarizable potentials have been recently developed with the aim of reproducing the properties of water around and above the critical point. According to a recent detailed analysis performed by comparing the simulation with the more recent neutron diffraction data, the polarizable models give pair correlation functions which agree with the experimental data in the supercritical region much better than the nonpolarizable models. On the other hand the nonpolarizable models reproduce better the temperature dependence of some thermodynamical quantities and the SPC/E potential for instance predicts a critical point for water in agreement with the experiments, while some polarizable models do not reproduce well the coexistence curve. Polarizable models however are generally more accurate in describing the modifications of the structure of water at increasing temperature and pressure above the critical point.

In this paper we present a comparison of the pair correlation functions of mixtures of argon and water at supercritical conditions obtained from computer simulation with the recent experimental data quoted above. In the numerical calculations water is simulated with the SPC/E potential and the polarizable potential model.
II. COMPUTER SIMULATION OF AQUEOUS SOLUTIONS

We performed the computer simulations of a mixture of 256 water molecules and rare gas atoms at the concentration of one atom for 40 molecules of solvent, the same used in the neutron diffraction experiment quoted above. The interaction of the water molecules has been described by the polarizable BSV model and, for comparison, by the SPC/E model. In both the cases the simulations have been performed in the microcanonical ensemble with the minimum image convention and a cut-off of the interactions at half of the box length. The reaction field has been used to take into account the long range part of the electrostatic interactions. The system with the SPC/E water has been simulated with the DLPoly package in the version 2.10, see reference (33) for further details.

The BSV potential has the same geometry as the TIP4P potential with a polarizable dipole moment placed on the center of mass of the molecule. The two positive charges, the parameters of the Lennard-Jones potential on the oxygen and the position of the negative charge are adjusted to reproduce some of the properties of water at ambient conditions (see model 4 in ref. (33)). The induced dipole moment $p_i = \alpha E_i$ is calculated from the local electric field $E_i$ with an iterative procedure by assuming an isotropic polarizability fixed to the value for water molecules $\alpha = 1.44 \text{Å}^3$. The long range part of the electrostatic interactions were taken into account by the reaction field method. Details of the extension of the reaction field method to include polarization effects can be found in references (29, 32).

We used a time step of $10^{-15}$ s and the structural quantities have been calculated by averaging over $2 \cdot 10^6$ configurations. We carried out the simulations for mixtures of water with Ar and Ne. Here we focus mostly on the results of the simulation of water with argon atoms, for which we can compare with recent experiments. The interaction of the water with the noble gas atoms has been modeled with a Lennard-Jones potential between the oxygen of the water molecules and the solute. The parameters of the Lennard-Jones potential of argon are assumed as $\epsilon_{Ar}/k_B = 125$ K, $\sigma_{Ar} = 3.415$ Å and for neon $\epsilon_{Ne}/k_B = 18.56$ K and $\sigma_{Ne} = 3.035$ Å. The parameters of the oxygen-solute potential have been derived from the Lorentz-Berthelot rules.

We explored a range of temperature and density from ambient conditions to the values in the supercritical region where the experiment has been performed, as indicated in Table I. The calculations were performed below $T = 673$ K at the points which correspond to the liquid branch of the coexistence curve of the SPC/E model. The point at $T = 673$ K corresponds to the conditions of temperature and density ($\approx 0.499$ g/cm$^3$) of the experiment.

III. SOLUTE-SOLVENT STRUCTURE

In Fig. 1 we report the pair correlation functions argon-water $g_{OAr}(r)$ at the different thermodynamical points indicated in Table I obtained by the BSV and the SPC/E models. At ambient conditions in both the models the $g_{OAr}(r)$ show well defined first peak slightly different in the position due to the different value of the Lennard-Jones parameter. The argon-hydrogen pair correlation functions $g_{HAr}(r)$ (Fig. 2) show a first peak at the same position as $g_{OAr}(r)$ indicating that the solute is located interstitially in the hydrogen bond network equidistant on the average from the oxygens and hydrogens.

The shoulder around 3.8 Å in the $g_{HAr}(r)$ indicates however that some of the O-H bonds point radially toward the second shell. Comparing the positions of the second peak of the $g_{OAr}(r)$ with the one of the $g_{HAr}(r)$ it is evident that the in the second shell the water molecules are preferentially oriented with the oxygen atoms towards the solute and the hydrogen atoms towards the bulk. Similar trends were already found by Guillot and Guisani on rare gases in SPC/E water and explained in terms of the formation of an hydration cage around the solute (see ref. (34) for more details). We can conclude that the same effect is predicted by the polarizable BSV model at ambient conditions.

On increasing temperature the first and second peak of the $g_{OAr}(r)$ decrease and the second hydration shell tends to disappear. In the $g_{HAr}(r)$ only the shoulder remains at the supercritical conditions indicating that the solute tends to expel the water molecules which are in its solvation shell. As it appears from Fig. 1 and 2 the BSV model confirms the prediction of the SPC/E model.

| $T$ (K) | $\rho$ (g/cm$^3$) |
|--------|-----------------|
| 300    | 0.998           |
| 373    | 0.949           |
| 473    | 0.841           |
| 673    | 0.499           |

TABLE I: Thermodynamical points where the computer simulations have been performed. The point at $T = 673$ K corresponds to temperature and density of the experiment.
and the microscopic scenario described in ref. 5, but it shows a more drastic reduction of the peaks in going from ambient temperature to the point at $T = 373$ K.

In the supercritical state at $T = 673$ K the BSV potential, which is more attractive with respect to the SPC/E model, predicts a more structured $g_{OAr}(r)$. We can infer that in the process of expelling the solvent the depth of the solute-solvent potential well plays an important role in agreement with the conclusions of computer simulations 5 and previous theoretical predictions 33,34 on the relevance of the solute-solvent interaction as compared with the solvent-solvent.

In Fig. 3 the argon-water radial distribution functions obtained from our simulation are compared with the experimental results 14. In both $g_{OAr}(r)$ and $g_{HAr}(r)$ the use of BSV model improves substantially the agreement with the experiment. The solute-solvent effective interaction results to be more attractive in the polarizable model with respect to SPC/E as evident from the comparison of the height of the first peak of the radial distribution functions.

This trend is confirmed by calculations of the coordination numbers of the water molecules around the argon atoms. The deficit of water molecules around the solute can be estimated by calculating the quantity

$$h_w(r) = \left| \frac{n_{OAr}(r)}{n_u(r)} \right| - 1$$

where

$$n_{OAr}(r) = 4\pi \rho \int_0^r g_{OAr}(r') r'^2 dr'$$

(1)

and the coordination number for a homogeneous fluid is given by

$$n_u(r) = \frac{4}{3} \pi \rho \left( r^3 - \sigma^3 \right)$$

(2)

$\rho$ is the water density and $\sigma$ is the minimum approach distance between argon and oxygen. The results are shown in Fig. 5 compared with the quantity $h_w(r)$ obtained from
FIG. 4: Hydrogen-argon pair correlation function: comparison between the BSV model (solid line), the SPC/E model (long dashed line) and the experimental results (crosses) at the thermodynamical conditions of the experiment (\(T = 673\) K) as indicated in Table I.

FIG. 5: Deficit of water molecules around the solute, as defined in the text (see Eq. 1), obtained in the BSV (solid line) and in the SPC/E (long dashed line) models compared with the same quantity calculated from the experimental points (crosses).

FIG. 6: Radial distribution functions of the mixtures at the supercritical conditions of the experiment at \(T = 673\) K (see Table I): \(g_{OO}(r)\) solid line, \(g_{OAr}(r)\) long dashed line, \(g_{HAr}(r)\) point line. On the left results from the BSV model, on the right results from the experiment in the inset results from the SPC/E model.

FIG. 7: Radial distribution functions of the mixtures from the BSV model at \(T = 673\) K: \(g_{OO}(r)\) (long dashed line), \(g_{OAr}(r)\) (solid line), \(g_{ONe}(r)\) (point line). \(g_{OO}(r)\) is extracted from the Ar-water simulation and it is shown as representative of the position of the first O-O shell.

the experiments. The negative values indicate a repulsive behaviour of the solute, but the repulsion is overestimated by the SPC/E model particularly in the region of the first peak of the \(g_{OAr}(r)\).

In Fig. 5 we report together the radial distribution functions \(g_{OO}(r)\), \(g_{OAr}(r)\) and \(g_{HAr}(r)\) for the water-argon mixture. On the right side there are the results of the BSV, on the left the experimental findings and the inset shows the SPC/E results. Both the models reproduce correctly how the solute penetrates the shells of the water molecules. The \(g_{OAr}(r)\) does not penetrate beyond the second shell, while the minimum approach distance in the \(g_{HAr}(r)\) is shorter than that observed in the \(g_{OO}(r)\).

In Fig. 6 we show the solute-oxygen radial distribution functions of the water-argon and water-neon mixtures.
FIG. 8: Radial distribution functions of the mixtures from the BSV model at $T = 673$ K: $g_{OO}(r)$ (long dashed line), $g_{HAr}(r)$ (solid line), $g_{HNNe}(r)$ (point line). $g_{OO}(r)$ is extracted from the Ar-water simulation and it is shown as representative of the position of the first O-O shell.

Together with the $g_{OO}(r)$ of the argon-water mixture as obtained from the BSV model. The calculations for the water-neon mixture were performed at the same density and concentration of the water-argon mixture, which correspond, as stated above, to the experimental conditions. The $g_{OO}(r)$ of the two mixtures are very similar and any of them could be chosen for the comparison. It is evident the role of the size of the apolar solute. The Ne atoms almost penetrate the first shell of water molecules. The distance of minimum approach of Ne shifts to a lower value and roughly coincides with the minimum approach distance of the $g_{OO}(r)$. The maximum of the $g_{ONe}(r)$ is at the same position of the maximum of the $g_{OO}(r)$. In Fig. 8 it is shown that the $g_{HS}(r)$ of each solute have a minimum approach shorter than that of the $g_{OS}(r)$. Our trend with the size of the solute is in agreement with the one found in the experiment.

IV. CONCLUSIONS

We performed a computer simulation of a solution of argon atoms in water at the same conditions of a recent neutron diffraction experiment. We compared the results obtained by using the SPC/E model and the BSV polarizable potential. For both the models we determined the solute-solvent radial distribution functions from ambient to supercritical conditions. The local structure of the solvent is perturbed by the presence of the solute with the formation of a cage of hydration around the non polar atoms. At increasing temperatures the solute tends to expel the water which resides in the solvation shell. Both the models reproduce this trend, at supercritical conditions however the BSV potential predicts a more structured $g_{OA}(r)$ with respect to SPC/E as a consequence of a more attractive solute-solvent interaction. The argon-water radial distribution functions are well reproduced at the experimental conditions by the polarizable model. The SPC/E model overestimating the solute-solvent repulsion gives the effect of collapsing the argon-water structure. The polarizable model predicts much better the solvent-solute correlation at supercritical conditions. This supports the idea that the BSV model works quite well at high temperatures.

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