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Structure and dynamics of water in aqueous methanol

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Abstract

We have performed classical molecular dynamics simulations to investigate the structure and dynamics of water clusters in aqueous methanol across a range of solution compositions. Investigation of the effect of different model potentials and cluster membership criteria indicates that the qualitative trends in cluster size distributions are preserved. Characterization of the water molecules on the interior of such clusters using a tetrahedral order parameter previously used to study pure water suggests that they are over-structured compared to the pure liquid for a broad range of cluster sizes and at different compositions. Calculation of the hydrogen-bond dynamics indicates that the water–water hydrogen-bonds in the solution are longer lived than those in the pure liquid for all solutions studied and increase almost linearly as a function of methanol concentration.

1. Introduction

The long-held view of a low-entropy restructuring of water around hydrophobic solutes has in recent years been challenged by experimental [1] and computational [2–4] studies of aqueous alcohols. These structural investigations indicate that hydration of even the simplest of amphiphilic molecules exhibits subtle and surprising features. Despite their simplicity, aqueous alcohols are useful prototypes with which to probe a molecular-level understanding of the hydration of both polar and non-polar groups.

Previous work has established that the methanol–water system displays ‘micro-immiscibility’ across a wide concentration range [5] and has reported the effects of pressure and temperature on the cluster structures formed within the mixtures [6]. Very recently, a computational study has shown similar behaviour for aqueous ethanol [7]. This paper presents further investigations of the structure of the water clusters formed within aqueous methanol solutions and also reports the dynamics of the hydrogen-bonded network. Specifically, we

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investigate the sensitivity to technical aspects of the simulations, characterize the local structure of the water clusters and compute hydrogen-bond lifetimes for the components of the system.

2. Computational details and methodology

2.1. Simulation details

We present results and analysis from classical molecular dynamics (MD) simulations performed using the DLPOLY [8] and Mdmix [9] codes. Two different sets of interatomic potentials were used, in order to assess the sensitivity of the results to the potentials used. The first set comprised the commonly used united atom (UA) representation for methanol [10] (OPLS) and the SPC/E water [11] model. Henceforth, this combination is referred to in this paper as UA. The second set comprised fully flexible intermolecular potentials for both methanol [12] and water [13] that have been utilized in our previous work on this system [5, 4, 6] (and are henceforth denoted the FF set). Integration timesteps were set at 0.5 and 2 fs for the FF and UA potential sets, respectively. Simulations were equilibrated for 0.5 ns, then data collected for 2 ns, with trajectory sampling every 0.1 ps. For both potential sets, three different concentrations were analysed, $x_{\mathrm{m}} = 0.27, 0.54$ and 0.70, where x_{m} is the mole fraction of methanol. Cubic unit cells of approximately 30 Å were used, depending on the system density (with larger simulations with systems of cell edge approximately 60 Å to assess the dependence on system size). Simulations were performed at ambient conditions (298 K and 1 atm). The exact details are identical to those presented in [5] and are not presented here for brevity.

2.2. Cluster analysis

In our analysis of hydrogen-bonded clusters of water molecules, we use two different criteria to define cluster membership, which may be classified as loose and more stringent. For *criterion 1*, we judge two water molecules to be hydrogen bonded if the distance $R_{\mathrm{O_wO_w}}$ is less than a cut-off, determined from the position of the first minimum of the oxygen–oxygen radial distribution function at the composition and thermodynamic conditions of the simulation. *Criterion 2* [14] requires three conditions to be fulfilled: (1) the distance R_{OO} between water oxygens must be smaller than a cut-off, determined as above, (2) the distance R_{OH} between the *acceptor* oxygen of water and the hydrogen corresponding to the *donor* water must be smaller than R^{c}_{H}, and (3) the angle between the bonds in the conformation O–H · · · O must be smaller than $\varphi^{c} = 30°$.

In addition, we have further analysed the water clusters to partition constituent members to be on the *external surface* of the cluster (N_{e}) and those located on the *interior* of the cluster (N_i). The latter condition is satisfied for those cluster members having H-bonds exclusively with other water molecules; the former condition requires an H-bond with at least one solute molecule (determined using the same criteria as for the water molecules, with the relevant cut-offs). The fraction of water molecules on the surface of each cluster is then simply N_{e}/N, where N is the total number of elements in that cluster.

2.3. Internal structure of clusters

We have explored a possible relationship between the size of clusters and any particular local order of its constituent water molecules. To do this we compute a tetrahedral order parameter, q_i, for water molecules first proposed by Chau [15] and later used by Errington *et al* [16] to study the local structure of pure water.

$$q_i = 1 - \tfrac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}(\cos(\Psi_{jk}) + \tfrac{1}{3})^2 \tag{1}$$

where Ψ_{jk} is the angle formed by the lines joining the oxygen atom of a water molecule, in our case, with that of each of the nearest oxygen atoms of the neighbouring water molecules. Although the numerical value of this parameter ranges from -3 to 1, the steric repulsion of the particles in the first solvation shell ensures that q will effectively range from 0, for a random distribution of molecules (ideal gas), to 1, for a perfect tetrahedral arrangement.

Here, we compute this parameter only for water molecules on the interior of a given cluster (according to the previous definition). This is done in order to avoid the direct influence of the oxygens of the solute species (methanol, in this case) in the computation of the order parameter. The value of q_i for a cluster of a given size, q_{cl}, is given by

$$q_{\mathrm{cl}} = \frac{\sum_{i=1}^{N_i} q_i}{N_i} \tag{2}$$

and we obtain an average q_{cl} by considering all clusters of a particular size.

2.4. H-bond lifetimes

The study of the temporal evolution of the hydrogen-bonds between water and any other associating solute is not a straightforward issue. According to previous analysis on associating fluids we compute the survival probability by means of the autocorrelation function [17–19]

$$C_{\mathrm{HB}}(t;t^*) = \frac{\langle \eta_{ij}(t).\eta_{ij}(0)\rangle}{\langle \eta_{ij}(0)^2\rangle} \tag{3}$$

where the variable $\eta_{ij}(t)$ takes unit value depending on two conditions: (a) the hydrogen-bond between molecules i and j satisfies the criteria mentioned above at t and (b) in the period from 0 to t it has not been broken longer than t^*. $\eta_{ij}(t) = 0$ otherwise. We have in particular investigated the limiting case of $t^* = 0$ which corresponds to the so-called continuous H-bond survival probabilities, also employed in other previous analyses [17, 19, 20]. Physically, the case $t^* = 0$ measures the survival probability for H-bonds that have satisfied the HB criteria at all sample points in the time interval. The measure of the lifetimes τ^c_{HB} for $t^* = 0$ has been obtained from

$$C_{\mathrm{HB}}(t;t^*) \sim \exp\left\{\frac{-t}{\tau_{\mathrm{HB}}(t^*)}\right\} \tag{4}$$

as $t \to \infty$. $C_{\mathrm{HB}}(t;t^*)$ is indeed exponential at long times and thus the determination of the H-bond lifetimes from equation (4) is meaningful.

3. Results and discussion

3.1. Influence of interatomic potentials and simulation details

In this section we highlight the effect of different potential sets (figure 1) and criteria for determining cluster membership (figure 2) on the distribution of water cluster sizes for different compositions of aqueous methanol. The data in figure 1 illustrate that the influence of the choice of potential sets on the predicted cluster distribution is quite small. The UA potential set consistently predicts smaller clusters than the FF one; for example, at $x_{\mathrm{m}} = 0.54$ the sharp peak observed for clusters of about 250 molecules in the FF results has an equivalent

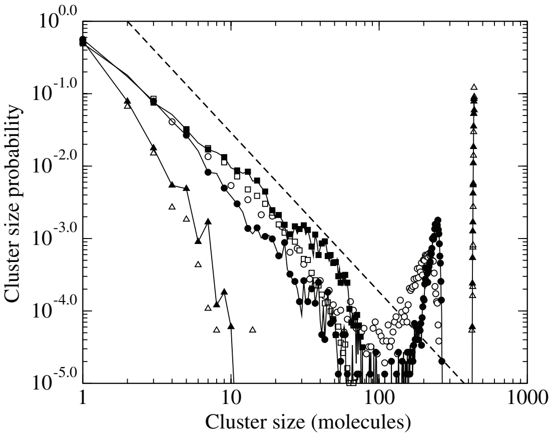

Figure 1. Cluster size probability of water clusters computed with the UA (open symbols) and FF potential sets (filled symbols) using hydrogen-bond criterion 1 and for different molar fractions of methanol $x_m = 0.27$ (△), $x_m = 0.54$ (○) and $x_m = 0.70$ (□). The dashed line shows the predicted cluster size distribution at the percolation threshold.

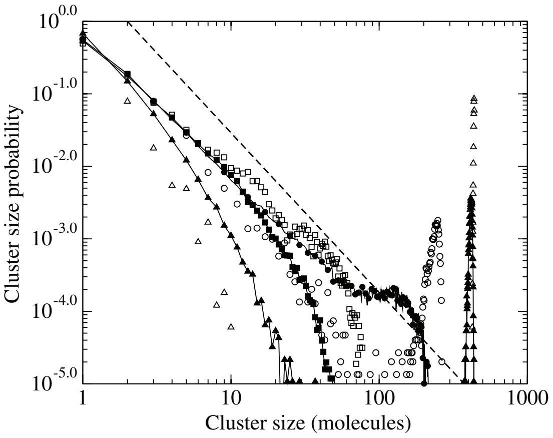

Figure 2. Cluster size probability of water clusters computed with the FF potential set with hydrogen bond criteria 1 (open symbols) and 2 (filled symbols) for different molar fractions of methanol $x_m = 0.27$ (△), $x_m = 0.54$ (○) and $x_m = 0.70$ (□). The dashed line shows the predicted cluster size distribution at the percolation threshold.

broader peak of approximately 215 molecules for the case of the UA potential set. These findings are consistent with the flexibility of the FF model leading to a greater adaptability of the conformation of molecules in different environments. This ability of the molecules in the system to adapt conformation means that more molecules are able to satisfy the H-bonding criteria, particularly at medium and methanol-rich compositions. A signature of this effect can be seen in the oxygen–oxygen radial distribution function of water molecules in the mixture. The second peak of this function is shifted to slightly larger r than in the case of pure water [5]. At the lowest methanol concentration, both models behave similarly because, in general, the system is a water-rich environment. We note that our previous conclusions regarding compositions which exhibit water clusters of sizes greater than the threshold for

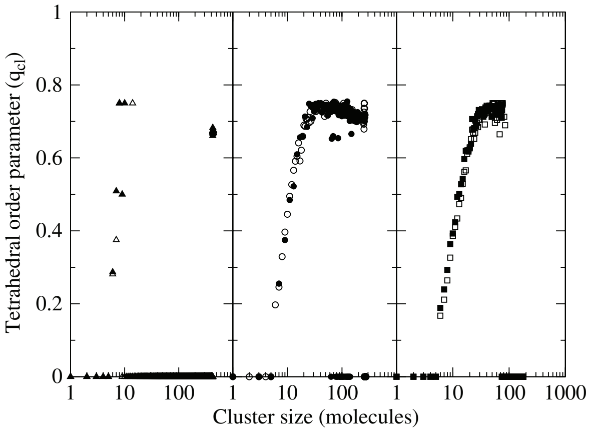

Figure 3. Variation of the tetrahedral order parameter $q_{\rm cl}$ with the size of water clusters computed with the UA (open symbols) and FF potential sets (filled symbols) using hydrogen-bond criterion 1 and for different molar fractions of methanol $x_{\rm m} = 0.27$ (△, figure at left), $x_{\rm m} = 0.54$ (○, centre) and $x_{\rm m} = 0.70$ (□, figure at right).

random percolation in 3D [5] (i.e. $x_{\rm m} = 0.27, 0.54$ but not $x_{\rm m} = 0.70$) are robust with respect to both sets of interatomic potentials used.

Figure 2 illustrates the effect of different H-bond criteria (as defined above) and here we see somewhat larger differences than in the choice of model potential. Unsurprisingly, the more stringent clustering criteria predict cluster distributions that are consistently shifted towards smaller cluster sizes, for all three compositions studied. Once again, it is interesting to notice that both criteria preserve the percolation of the water clusters at $x_{\rm m} = 0.27$ and $x_{\rm m} = 0.54$, but not $x_{\rm m} = 0.7$, independent of the criteria employed.

These tests lead us to conclude that the clustering features exhibited in these aqueous alcohols are not critically dependent on the specific technical details of the simulation. Similar tests for system size effects (not reported in detail here) confirm that the cluster distribution is relatively insensitive to such changes.

3.2. Structure of water clusters: tetrahedral order parameter

The variation of the mole fraction of methanol in the system has important consequences in the local structure of water. In this section we present the variation of the tetrahedral order parameter $q_{\rm cl}$ (computed using only molecules inside the clusters), with the size of water clusters using different models and different hydrogen-bond criteria. In figure 3 we report the variation of this order parameter with the size of water clusters and system composition, computed with the two models. The main feature observed is a significant fraction of cluster sizes for which the interior water molecules are more structured than pure water itself (with a maximum value of $q_{\rm cl} \approx 0.75$, compared to pure liquid values of $q_{\rm cl} = 0.625$ for the FF model and 0.622 for the UA). The variation of $q_{\rm cl}$ is rather independent of both $x_{\rm m}$ and the potential set used in the simulations. We note that the maximum value of $q_{\rm cl}$ occurs in clusters of several tens of water molecules. In the $x_{\rm m} = 0.27$ solution, the variation in $q_{\rm cl}$ is limited by the fact at this composition the water tends to form a small number of very large clusters (figure 1) and the value of $q_{\rm cl}$ approaches that of pure water. At $x_{\rm m} = 0.7$, the distribution of cluster sizes is towards smaller clusters, leading to a rather compressed distribution of $q_{\rm cl}$ as a

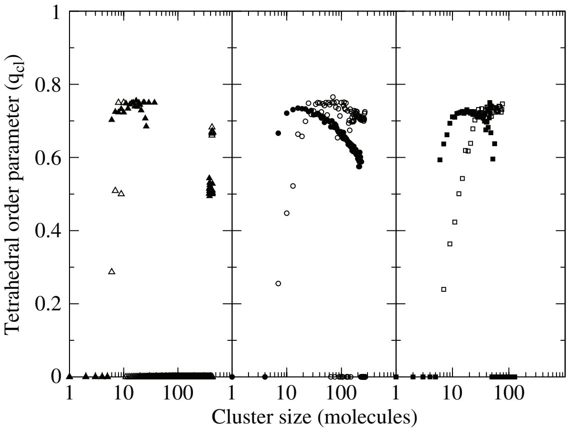

Figure 4. Variation of the tetrahedral order parameter q_{cl} with the size of water clusters computed with the FF potential set using hydrogen-bond criteria 1 (open symbols) and 2 (filled symbols) for different molar fractions of methanol, $x_{\mathrm{m}} = 0.27$ (△, left), $x_{\mathrm{m}} = 0.54$ (○, centre) and $x_{\mathrm{m}} = 0.70$ (□, right).

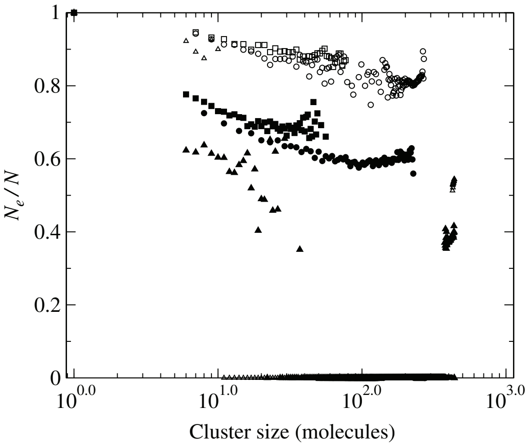

Figure 5. Variation of the ratio of external water molecules on the surface of a cluster (N_e) to total number of molecules in the same cluster (N), computed with the FF potential set using hydrogen-bond criteria 1 (open symbols) and 2 (filled symbols) for different molar fractions of methanol, $x_{\mathrm{m}} = 0.27$ (△), $x_{\mathrm{m}} = 0.54$ (○) and $x_{\mathrm{m}} = 0.70$ (□).

function of cluster size. For the intermediate concentration, $x_{\mathrm{m}} = 0.54$, q_{cl} is greater than 0.7 for cluster sizes ranging from approximately 30 to the maximum cluster size of 250.

In figure 4 we explore the influence of different clustering criteria on the predicted variation in q_{cl} as a function of cluster size for the FF model. Both criteria predict an over-structuring of the interior water molecules for a range of cluster sizes, at all the compositions investigated. However, using criterion 2 the maximum value of q_{cl} (which is once again found to be approximately 0.75) is shifted to clusters of lower sizes. This difference is due in part to the fact that criterion 2 predicts small cluster sizes, but (see figure 2) an additional effect is evinced in figure 5, which shows that the more stringent clustering criteria predict a consistently larger fraction of water molecules in the interior of the cluster (smaller N_e/N) than that found

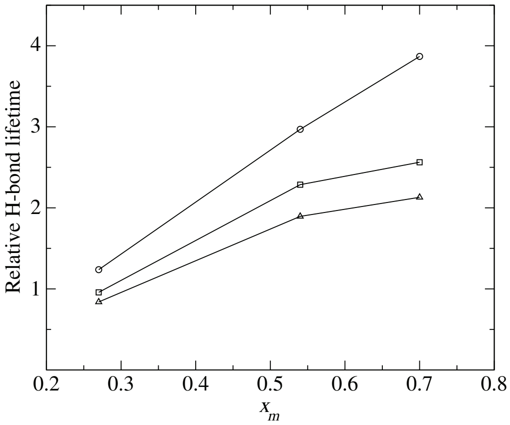

Figure 6. Variation of continuous hydrogen bond lifetimes for water–water (○) water–methanol (□) and methanol–methanol (△) relative to that for pure water, as a function of the mole fraction of methanol. Values were computed with the FF potential set using hydrogen bond criterion 1 and the lines are intended as a guide to the eye.

with criterion 1. Thus, calculation of q_cl using criterion 2 to determine cluster membership will result, on average, in smaller cluster sizes, but a greater fraction on the interior, hence contributing to the value of q_{cl}. Disentangling any systematic effects may not be possible: instead, we view the different clustering criteria as complementary. By far the most important feature is reproduced irrespective of the criteria, and that is that they predict qualitatively the same trend and approximately the same maximum value of q_{cl} (albeit shifted to a different cluster size). The molecules at the very core of the water clusters (irrespective of the criteria utilized to define the entire cluster) have the same local structure. In addition, the results presented in figure 5 confirm those previously obtained from an empirical potential structure refinement (EPSR) analysis of neutron diffraction experimental data [5]. Consideration of the topology of clusters as a function of size is currently underway and this will hopefully provide insight into the variation of q_{cl} as a function of cluster size presented here.

3.3. Dynamics of H-bond network

The impact of the presence of the methanol molecules on the local structure of the water clusters must have its counterpart in the dynamics of the water molecules. In this section, we present results of an analysis of the dynamics of the H-bonded network in the solution, in terms of the continuous H-bond lifetime, τ^c_{HB}, for the three types of hydrogen-bond in the system (water–water, water–methanol and methanol–methanol). In figure 6 we report values of these H-bond lifetimes as a function of solution composition, with the data expressed relative to the H-bond lifetime for pure water, determined in the same manner with the same model potential ($\tau^c_{\mathrm{WW}} = 2.11$ ps).

We observe a relatively uniform increase in the H-bond lifetime with increasing methanol concentration for all the three types of H-bonds in the system. This fact was also observed in other aqueous solutions of associating fluids [21]. Other works attribute this behaviour to be the origin of the increase of the shear viscosity of the mixture through a rigidization of the molecules, forming chain-like structures [22], though no direct calculation is provided in [22] to support this argument. However, the value of the self-diffusion coefficient of the two molecules in the system is indeed affected by changes in the composition. From the $x_{\mathrm{m}} = 0.7$

simulations, the calculated diffusion coefficients of the water and methanol species in the mixture are 1.5×10^{-9} m^2 s^{-1} and 1.9×10^{-9} m^2 s^{-1}, respectively. These are both smaller than the corresponding values for the pure components (2.4×10^{-9} m^2 s^{-1} and 2.6×10^{-9} m^2 s^{-1}).

At all compositions studied the H-bond lifetimes for water–water bonds are greater than unity, i.e. greater than that found using the same simulation details for the pure liquid. The m–m value in pure methanol is 3.76 ps, less than the absolute value for m–m in the mixture at $x_{\mathrm{m}} = 0.7$ and 0.54 but greater than that at $x_{\mathrm{m}} = 0.27$.

4. Conclusions

Classical MD simulations of aqueous methanol have been performed and analysed to study the structural characteristics of the water clusters that form across a range of solution compositions and the dynamics of the H-bonds in the system. We find that the trends in cluster size distributions at different compositions are relatively insensitive to the potential models used and the cluster membership criteria employed. Analysis of the structure of the interior of the water clusters via calculation of a tetrahedral oder parameter indicates that the interior water is over-structured compared to the pure liquid for a range of cluster sizes at the three compositions studied. A further investigation of the relationship between cluster structure and topology is underway and will be presented elsewhere. An investigation of the H-bond dynamics suggests that the lifetime of H-bonds between water molecules increases as a function of methanol mole fraction and is greater than the lifetime calculated in pure water, suggesting that the addition of methanol rigidizes the system. Further calculations to investigate this are underway.

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