



Cluster formation and percolation in ethanol-water mixtures



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ABSTRACT

Results of systematic molecular dynamics studies of ethanol-water mixtures, over the entire concentration range, were reported previously that agree with experimental X-ray diffraction data. These simulated systems are analyzed in this work to examine cluster formation and percolation, using four different hydrogen bond definitions. Percolation analyses revealed that each mixture (even the one containing 80 mol% ethanol) is above the 3D percolation threshold, with fractal dimensions, d_f , between 2.6 and 2.9, depending on concentration. Monotype water cluster formation was also studied in the mixtures: 3D water percolation can be found in systems with less than 40 mol% ethanol, with fractal dimensions between 2.53 and 2.84. These observations can be put in parallel with experimental data on some thermodynamic quantities, such as the excess partial molar enthalpy and entropy.

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1. Introduction

The structure of alcohol-water solutions has been studied widely by both experimental [1–5] and theoretical [6–8] methods. The emerging picture is still somewhat confusing and contradictory. Detailed discussions concerning these preliminaries have been provided in the introductory parts of our very recent publications [9–11], so these are not repeated here. In these recent works, H-bond connectivities [9], ring formation and statistics [10], and the ‘lacunarity’ [11] have been analyzed. To complete our extensive investigations on water-ethanol mixtures, here characteristics of cluster formation (clusters being defined here as assemblies of molecules interconnected by hydrogen bonds) and percolation observable in these systems are presented. To the best of our knowledge, such properties have not been considered before for aqueous ethanol solutions.

Similarly to the aforementioned recent studies of water-ethanol mixtures [9,10,11], the basis of the present analyses is our preceding extensive molecular dynamics (MD) investigation [12]. There, a series of MD simulations for ethanol-water mixtures with 20–80 mol% ethanol contents, for pure ethanol and water was performed with one ethanol and three different water force fields. The primary aim of that work was to find the potential models that provide the best agreement with experimental X-ray diffraction

data. In each mixture the OPLS-AA [13] potential was used for ethanol, in combination with three different water force fields, the rigid SPC/E [14] and TIP4P-2005 [15], as well the rigid polarizable SWM4-DP [16] ones. No single water force field could be identified that would provide the best agreement with experimental data over the entire concentration range: for higher ethanol contents the SWM-DP, whereas at lower ethanol concentrations the TIP4P-2005 potential provided the closest match.

In this work, detailed analyses of the hydrogen-bonded network are provided for the most successful simulations at each concentration, in terms of hydrogen bonded assemblies (clusters) of molecules. The number and size of the clusters strongly depend on the number of hydrogen bonds (HB) which, in turn, is determined by some (somewhat arbitrary) definitions of hydrogen bonds. As discussed (for instance) in our previous paper [9], there is not an exact rule for the definition, and several different approaches can be found in the literature. We have opted for purely geometric definitions: the intermolecular O···H and O···O distances should fall into a certain distance range, and sometimes there is an additional constraint on the O–H···O angle, as well (‘O–H’ refers to the intramolecular O–H bond, whereas ‘H···O’ denotes the closest intermolecular, i.e., hydrogen bonding, distance). A collection of such definitions are introduced and analyzed in Ref. [9]. Concerning earlier studies on ethanol-water mixtures, Noskov [17] applied an (intermolecular) O···H cutoff of 2.4 Å and O–H···O angle >150° for defining H-bonds. Our criteria are comparable to these choices (see Ref. [9]). In our MD simulation investigation [12] the LOOSE condition for hydrogen bonding was based solely on distance

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ranges: the upper limiting values were defined by the first minima of the O—O, and by the second (i.e., first intermolecular) minima of the O—H PRDFs. On average, the “H-bonding” ranges were set to be between 2.4 and 3.6 Å for O—O and 1.4–2.7 Å for O—H pairs (see the Supporting Information Tables 1 and 2 in the preceding work for details [12]). A STRICT condition with the distance ranges of the LOOSE condition and with an additional angular restriction of $O-H\cdots O > 120^\circ$ was also applied; the 120° value was based on the definition of Chen et al. [18] and on our other previous work [19].

In the present paper, similarly to the immediate predecessor [9], four different H-bond definitions were applied, in order to explore how cluster formation might depend on the choice of the cutoff conditions. Apart from the LOOSE (L), and STRICT120 (S120) conditions (STRICT120 being the same as STRICT in the previous paper [12]), STRICT140 (S140) with $O-H\cdots O > 140^\circ$ and STRICT150 (S150) with $O-H\cdots O > 150^\circ$ are also applied here for each simulation result.

Percolation theory is frequently and successfully applied for explaining some of the unusual macroscopic features of hydrogen-bonded systems like water [20–23], methanol [24] and aqueous solutions [25,26]. Liquid water can be described by bond-percolation theory as a gel-like network with bent (and to some extent, broken) hydrogen bonds, well above the percolation threshold [20]. Dividing oxygen atoms into categories based on the number of their intact hydrogen bonds can be considered as a polychromatic correlated site percolation problem. The infinite hydrogen-bonded network in simulated water was found to contain patches of four-bonded water molecules with structures less ramified than that could be expected from their random distribution. This way, the anomalous behavior of, for example, the isothermal compressibility, constant-pressure and constant-volume specific heat and thermal expansion could be predicted and to some extent, explained [21]. The local density in the vicinity of these spatially correlated four-bonded patches was found to be lower than the global density [22].

According to random site percolation theory, infinite open clusters (here: assemblies of H-bonded molecules) are true fractals at the percolation threshold with fractal dimensions $f_d = 2.53$ for the 3 D, and $f_d \cong 1.896$ for the 2D case [27]. Based on the fractal dimension, a different percolation behavior was detected in tetrahydrofuran–water mixtures by Oleinikova et al. [24]. The predicted immiscibility gap was in good agreement with the concentration interval where both water and the solute were above their respective 3D percolation threshold. This suggested that totally miscible solutions can only exist if not both (and not only one) of the two compounds percolate in 3D [24]. Here, we wished to establish the percolation behavior of ethanol–water mixtures, so that later similar analyses may be conducted.

This paper is organized as follows: Section 2 briefly describes the computational methods used, while in Section 3, results on the cluster distributions and percolation properties are given in detail. Finally, Section 4 summarizes our findings.

2. Methods

2.1. Molecular dynamics simulations

Details of the MD simulations were provided in our previous paper [12] and therefore here only a brief description is appropriate. All MD simulations were performed by the GROMACS 4.0 simulation package [28], in the NVT ensemble at $T = 293$ K. The length of the ‘production phase’ of the simulations (i.e., having reached thermal equilibrium) was 2000 ps in each case. Particle configurations in the production phase were collected 20 ps apart and in the

end, 76 configurations were used for calculating average cluster sizes, connectivities and morphologies.

Calculations reported here are identified by their ethanol content and by the first letter of the water force field applied (see Table 1); for example, ‘Et60S’ refers to the mixture containing 60 mol% ethanol where the MD simulation was performed by using the SWM4-DP water force field (Table 1).

2.2. Cluster analyses

Analyses of the hydrogen-bonded clusters/network was performed by our own C++ computer code, specifically developed for this purpose, using a depth-first search algorithm for identifying clusters (see also Refs. [9–11]). The term ‘cluster’ is applied only for molecules connected by hydrogen bonds (i.e., lone molecules are not considered as clusters). Sometimes the distinction is made between cluster (no percolation) and network (percolation is present), but generally the term ‘cluster’ is used to describe assemblies of hydrogen bonded molecules, regardless of their percolation properties. (Also note that the term ‘cluster’ here does not refer to well defined, fixed units.) During HB determination the simulation box was treated as an isolated system, as in the work of Geiger et al. [20], namely that only one instant of the periodic box – and consequently, each hydrogen bond – was used, even though hydrogen bonds were determined by using the minimum image convention.

Cycle perception was performed by the same software; detailed results can be found in Ref. [10].

2.3. Percolation

Percolation properties of each system have also been analyzed by the computer code mentioned above. For each cluster of each configuration of every system, it was determined whether the cluster in question was infinite (i.e., if the interconnected assemblies of H-bonded molecules reached from ‘wall-to-wall’ in the simulation boxes; this is the way one may state that the cluster is larger than the box); if it was then in how many dimensions. In general, a cluster is said to percolate if there is an infinite open cluster in at least one dimension. In this work the term ‘network’ is applied to a 3D percolating infinite cluster. Fractal dimensions have been calculated using the box-counting method, by the same software.

3. Results and discussion

Having located the H-bonds, clusters (molecules connected by HB-s) were identified; some of their statistical descriptors, as a function of the actual H-bond definition, have already been discussed in detail in Ref. [9].

3.1. Number of clusters

The average number of clusters for all the systems were calculated, and are shown in Fig. 1. Results for cluster sizes and distributions for the less strict HB conditions are shown, as well, in order to see the extent the choice affects the results.

For the same simulation with different HB conditions, the number of clusters increases with the increasing angular cutoff, as expected, similarly to the number of lone molecules. (The observation that the ‘L’ condition brings about results that are nearly identical with those based on the ‘S120’ condition is consistent with previous findings in Ref. [9].) Regarding these values for the same HB condition for different concentrations, the number of clusters generally increases monotonically with increasing ethanol concentration. (Note that the maximum around the Et40–Et60 region for

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