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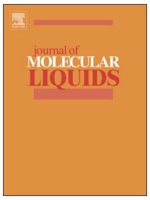

Molecular dynamics study of the local structure and diffusivity of partially miscible water/*n*-alcohols binary mixtures

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In this work, we look at partially miscible water/*n*-alcohol mixtures that have been studied extensively by experiment and, in some cases, by classical simulation methods. As a reference point, we chose Su et al.'s [*J. Chem. Phys.* 132 (2010), 044506] experimental study of the diffusion of water in its binary mixtures with *n*-alcohols and *n*-alkanes. Their measurements showed that diffusivity of water in *n*-alcohols is substantially lower than in *n*-alkanes of similar size whereas its decrease with increasing *n*-alcohol viscosity violates Stokes–Einstein relation, a result attributed by them to the hydrogen bonded water molecules spending most of their time near the *n*-alcohol hydroxyls. To explore their hypothesis that that is the main determinant of water's dynamic behaviour in those mixtures, we employed the molecular dynamics method to simulate the organic phase of binary mixtures of water and *n*-alcohols (butan-1-ol, pentan-1-ol, and hexan-1-ol) at ambient conditions. The chosen force fields (SPC/E and TraPPE) were shown to predict accurately the systems' volumetric properties. Also, self-diffusion coefficients of water compared very well with experimental measurements and previous simulations. As the local structure and dynamics of the mixtures are not fully understood so far, special attention was paid to the interaction sites taking part in hydrogen bonding, their pair distribution functions and the local structure in their vicinity. Our results, expressed in terms of specific quantitative descriptors, provide a clear picture of hydrogen-bonding connectivity between *n*-alcohol molecules, water molecules and each other. In particular, it is shown that water and *n*-alcohol molecules take part in complex extended structures with a rather stable topology, thus confirming, and at the same time, enriching Su et al.'s initial hypothesis. Both species occupy places in these structures in proportions depending on the mixtures' composition — and that is the main cause of their particular diffusive behaviour.

1. Introduction

In a previous work by some of the authors of the present article [1,2], the microscopic mechanisms underlying the diffusive motion of small molecules through heavier species was studied with the aid of molecular dynamics (MD) simulations; a new method of identifying and describing in a quantitative manner the diffusive jumps of the penetrants was particularly useful. The systems studied in that work comprised linear alkane-like non-polar non-associating molecules. This way, it was possible to place the emphasis on the role of differences in molecular weight and draw conclusions that could apply in liquid systems characterised mainly by the size of their molecules, e.g. amorphous polymeric materials.

In those systems, the high molecular weight of the surrounding material was the main factor controlling the rate of diffusion of the light species. However, diffusion can also be checked by other factors depending on the nature or chemical composition of the interacting compounds rather than molecular size alone. Such is the case, for instance, of associating species capable of forming hydrogen bonds. Therefore, to extend our study in a systematic fashion we now focus on partially miscible water/*n*-alcohol systems where molecular weight is of less importance than in polymer/gas systems but hydrogen bonding is present, thus forming another factor possibly playing a substantial role in checking diffusion of the light species (water).

Apart from offering an opportunity to conduct simulation studies on the factors affecting transport properties, alcohols and water/alcohol systems are also interesting for more practical reasons. Partition coefficients of other substances in reference systems of water and alcohols, especially octanol, have long been used as a means to study intermolecular interactions between biomolecules and other small organic compounds [3]; such interactions are of great interest because they govern the partitioning of drugs in biological systems (the importance of water/*n*-alcohol mixtures as model systems stems from the ability of alcohols to act as both donors and acceptors in hydrogen bonding; while our work is confined to water in alcohols, it could serve as a reference

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point for studies of more complex systems, like enzymes and biological membranes, where the presence of many –NH and –OH groups determines their behaviour). Also, it is important to mention that a large number of measured partition coefficients exist already for the water/octanol system, concerning a wide range of functional groups. Based on these data, well correlated values were obtained for partition coefficients between the reference system and other solvent systems. In a similar fashion, water/octanol is useful in the study of the distribution of anthropogenic organic contaminants, serving as a means to measure their tendency to migrate from water to sediment organic matter and living species in aquatic environments. This tendency is quite similar to the one in the particular alcohol/water system, hence its choice as a convenient surrogate for natural and biological organic components — with the additional advantage of avoiding tests on living organisms [4–6].

As the above studies suggest, understanding molecular interactions in water/alcohol systems may offer useful insights with application in pharmacokinetics, drug design, pesticide chemistry, studies in ecotoxicity of man-made compounds and the environmental fate of contaminants — not to mention applications in the study of the phase behaviour of industrial amphiphilic compounds, like detergents. Molecular simulation allows one to look at the very microscopic mechanisms controlling the system's behaviour; at the outset, a study of the binary water/alcohol mixtures themselves would serve as a convenient starting point. In the present work, we chose to begin with Su et al.'s [7] experimental work and the systems investigated therein as a reference point. Su et al.' s work is especially interesting for comparing water/*n*-alcohol mixtures with water/*n*-alkane systems in which the alkanes are of similar molecular weight as the alcohols studied — a novel “droplet dissolution” experimental technique had to be introduced to overcome difficulties due to the extremely low solubility of water in alkanes. In particular, their method was based on monitoring the dissolution and gradual shrinking of water microdroplets suspended in an excess of alcohol or alkane at the end of a micropipette. In that setup, diffusive mass transfer takes place at the droplet's boundary where the composition is assumed to equal the saturation concentration. The Epstein–Plesset equation [8] related the rate of decrease in a droplet's radius with the diffusion coefficient. This way, comparisons between associating and non-associating systems were possible and conclusions about the role of hydrogen bonding could be drawn.

Su et al.'s purpose was to measure the decrease in diffusivity of water through bigger molecules when going from non-associating (alkane) to associating (alcohol) systems, and offer possible explanations for such a behaviour. Su et al. chose a number of partially miscible water/*n*-alcohol systems; they also included in their study previous diffusivity measurements in fully miscible systems of water and light *n*-alcohols [9]; and they conducted measurements for water/*n*-alkane systems using their novel experimental technique. The alcohols studied by Su et al. were $n\text{-C}_\nu\text{H}_{2\nu+1}\text{OH-1}$, $\nu = 4, 5, 6, 7$ and 8; the alkanes were $n\text{-C}_\nu\text{H}_{2\nu+2}$, $\nu = 6, 7, 8, 10, 11, 14$ and 16. The measurements by Lusis and Ratcliff concerned *n*-alcohols for $\nu = 1, 2, 3$ and 4. The measurements showed that water diffusivity in a particular alcohol would be about 20 times lower, on the average, than the one through the alkane with a molecular weight closest to the alcohol. The same observation, of a consistent decrease in diffusivities, held when comparing diffusion of water in alcohols with the one in alkanes of similar viscosity. On the other hand, in both kinds of systems, diffusive behaviour exhibited a power law, clearly deviating from Stokes–Einstein equation.

The latter observation was in line with the multiply reported fact that small solutes moving through a solvent with larger molecules, do not obey Stokes–Einstein relation: their diffusion coefficient is inversely proportional, not to viscosity but a fraction power thereof — and that formed a key aspect of Su et al.'s interpretation. In a nutshell, Su et al.'s argument goes as follows: Decrease of water diffusivity through an alcohol with respect to the measurements in water/*n*-alkane systems is similar to the one observed for the larger, but not hydrogen-bonding, molecule of organotin. This finding seems to imply a larger effective hydrodynamic radius of water due to its association with alcohol molecules. However, if that were assumption true, measured diffusivities and viscosities would obey the Stokes–Einstein relation, which is not the case. Therefore, Su et al. conclude that it is more reasonable to assume that water diffusive motion is decelerated because of water molecules spending more time near alcohol hydroxyl groups, due to the formation of hydrogen bonds.

Studying the diffusive behaviour of water/*n*-alcohol mixtures, understanding the underlying microscopic mechanisms and checking the validity of Su et al.'s conclusions constituted the focus of our work. In this article we present results of predicted volumetric and mass transport properties of certain partially miscible water/alcohol systems analogous to the ones studied by Su et al. We also report on the local structure in relation to the hydrogen-bond network; a more detailed analysis of the latter will also be given in a separate forthcoming publication. In the next section, we briefly review the simulation literature related to the microstructure and diffusive behaviour of water/*n*-alcohol systems and then, present the details of our simulations. The post-processing methods and simulation results are presented in Section 3, along with a discussion on their analysis. The main conclusions are summarised in Section 4.

2. Simulations

2.1. Brief review of previous simulation studies

As mentioned in the Introduction section, we carried out MD simulations of a number of water/*n*-alcohol systems closely resembling the ones investigated by Su et al., to assess the validity of their conclusions and understand the microscopic mechanisms affecting diffusion of water, especially with regard to hydrogen-bonding. In the following paragraphs, some interesting previous simulation studies of water/alcohol-1 systems are briefly mentioned. Among these systems, the success of *n*-octanol/water mixtures in emulating the competing hydrophilicity and lipophilicity in natural organic and biological matter drew the attention of the molecular simulation community.

Modelling studies of *n*-octanol/water systems included both MD and Monte Carlo (MC) simulations aimed at predicting partition coefficients for various compounds [10–14]. Other researchers looked also at the microstructure of such systems and the role of hydrogen bonding. According to Jedlovszky et al. [15], hydrogen bonding underlies a two-stage process of *n*-octanol adsorption at free water surfaces with formation of a layer of strongly bound octanol molecules until saturation, followed by condensation and thickening of the layer. Chen and Siepmann [16] showed that hydrogen-bonded aggregates of various sizes, shapes and architectures can be formed in dry octanol and wet octanol. Linear aggregates dominate in dry octanol whereas water-centred micelles are equally frequent in wet octanol.

A fair share of water/alcohol simulation studies belongs to water/*n*-hexanol binary systems and the study of their interfacial properties. Gao and Jorgensen [17] conducted MC simulations to study monolayer, bilayer and double bilayer water/*n*-hexanol systems with alcohol hydroxyls forming an interface between the alkyl tails and the aquatic phase. Analysis of hydrogen bonds, based on geometric and energetic criteria, showed that water molecules formed 3.5 hydrogen bonds on the average; near the interfaces, about half of them would involve hexanol molecules.

An interesting approach, reminiscent of Su et al.'s alkane-alcohol comparisons, was taken by Wang et al. [18] who carried out MD simulations of liquid–liquid interfaces in water/*n*-hexane and water/*n*-hexanol systems. Density profiles showed the water/hexane liquid–liquid interface to be sharp, as expected for an immiscible system. On the other hand, the partially miscible water/hexanol system displayed an ordered and at the same time spatially extended interfacial configuration with the alcohol –OH groups in contact with the water phase and

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