

A Molecular Dynamics study of the diffusion coefficients in water-tertbutyl alcohol mixtures: A comparison between All-Atoms and United-Atoms models.

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We report a Molecular Dynamics study of the equilibrium diffusion properties of mixtures of water and tert-butyl alcohol (TBA) performed at 298K and 1bar. Different compositions of the mixture were used covering the complete range between pure components.

The water was simulated using the SPC/E model [1]. Two models were used to describe the alcohol:

- A United-Atom (UA) model. According to this UA description, each methyl group is represented by a single interaction center.
- An All-Atoms (AA) model which contains the full atomistic description of the molecule.

The interactions between atoms were computed using Lennard-Jones potential while electrostatics were calculated between point charges. The UA parameters were taken from the Transferable Potentials for Phase Equilibria [2] while those of AA were taken from the Optimized Potentials for Liquids Simulation [3].

For each composition, 3 nanosecond long trajectories were generated by Molecular Dynamics in the canonical ensemble and the self-diffusion coefficient of water and alcohol were computed using Einstein's law. Preliminary calculations were carried out to reach the equilibrium density.

When the alcohol is modeled by united atoms, the calculated densities of the mixtures perfectly reproduce the experiments of Nakanishi *et al.* [4]. When the alcohol is modeled at an All-Atoms level, the discrepancy between calculations and experiments increases when the molar fraction of alcohol is increased, leading to a maximum overestimation of 5% for the pure alcohol density.

The self-diffusion coefficient of water is in qualitative agreement with the PFG-NMR experiments of Price *et al.* [5]. The shape of the curve reporting the variations of the self-diffusion coefficient of water is respected in both SPC/E(water)-TBA(UA) and SPC/E(water)-TBA(AA) mixtures. Quantitatively, the self-diffusion coefficient of water in SPC/E(water)-TBA(AA) mixtures is better than that of water in SPC/E(water)-TBA(UA) mixtures.

We report on figure 1 the comparison of our results dealing with the alcohol with Price *et al.* [5] and Mayele *et al.* [6] PFG-NMR measurements:

- The AA-TBA plot respects the shape of the experimental variations, and at high alcohol concentrations the variations are qualitatively reproduced.
- The UA-TBA results overestimate the self-diffusion, and the shape of the variations respect to composition is not reproduced.

We attribute the underestimation of the self-diffusion coefficient at high TBA molar fractions to the overestimated density for the AA model.

Finally, it should be noticed that even if the UA model yields an excellent description of a static property like mass density, it fails in reproducing the trends of a dynamic property like the self-diffusion coefficient for which the AA model is successful. This result is of general interest when the question of studying water-alcohol solvents by mean of the molecular simulation tools is addressed.

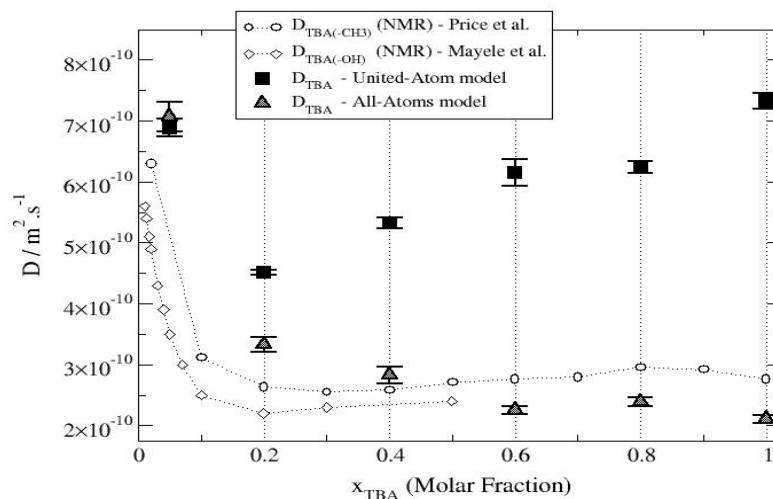


Figure 1 – Comparison between self-diffusion coefficient of TBA in TBA-water mixtures obtained by NMR experiments and MD simulation

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