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Technical Report No. 1

Structure and Hydrogen Bond Dynamics of Water-Dimethyl Sulfoxide Mixtures by Computer Simulations

by

A. Luzar and D. Chandler

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Department of Chemistry
University of California, Berkeley
Berkeley, CA 94720

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Abstract

We have used two different force field models to study concentrated dimethyl sulfoxide (DMSO)-water solutions by molecular dynamics. The results of these simulations are shown to compare well with recent neutron diffraction experiments using H/D isotope substitution [A.K. Soper and A. Luzar, J. Chem. Phys. 97, 1320 (1992)]. Even for the highly concentrated 1DMSO : $2H_2O$ solution, the water hydrogen-hydrogen radial distribution function, $g_{HH}(r)$, exhibits the characteristic tetrahedral ordering of water-water hydrogen bonds. Structural information is further obtained from various partial atom-atom distribution functions, not accessible experimentally. The behavior of water radial distribution functions, $g_{OO}(r)$ and $g_{OH}(r)$ indicate that the nearest neighbor correlations among remaining water molecules in the mixture increase with increasing DMSO concentration. No preferential association of methyl groups on DMSO is detected. The pattern of hydrogen bonding and the distribution of hydrogen bond lifetimes in the simulated mixtures is further investigated. Molecular dynamics results show that DMSO typically forms two hydrogen bonds with water molecules. Hydrogen bonds between DMSO and water molecules are longer lived than water-water hydrogen bonds. The hydrogen bond lifetimes determined by reactive flux correlation function approach are about 5 ps and 3 ps for water-DMSO and water-water pairs, respectively, in 1DMSO: $2H_2O$ mixture. In contrast, for pure water, the hydrogen bond lifetime is about 1 ps. We discuss these times in light of experimentally determined rotational relaxation times. The relative values of the hydrogen bond lifetimes are consistent with a statistical (i.e., transition state theory) interpretation.