

## STRUCTURAL AND POLARIZATION PROPERTIES OF AQUEOUS NONPOLAR SOLUTE MIXTURES

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### EXTENDED ABSTRACT

The microscopic structure and polarization properties of aqueous solutions of Ne, Ar, CH<sub>4</sub>, Kr, and Xe over the wide range of state points have been investigated via molecular dynamic simulation. The use of a polarizable MCYna potential [1, 2] for water and Lennard-Jones potential for water-solute and solute-solute interactions allows us to study the system over the temperature range 278-750 K and solute molar fractions up to 30%. A combined MCYna + LJ potential was chosen for these systems with Lorentz-Berthelot combining rules. The MCYna + LJ model reproduces the experimentally observed homogeneous phase region of both water-methane and water-noble gas systems more accurately than the SPC/E + LJ model.

The effect of the solute size and concentration on solubility of system, shell structure, hydrogen bonding, static dielectric constant and dipole moment has been investigated. It is found that even at low concentrations and high temperature solute particles affect structure of water, resulting in the compression of oxygen-oxygen (O-O) and oxygen-hydrogen (O-H) radial distribution functions [3,4]. Coordination numbers of aqueous solutions of nonpolar solutes appear to be proportional to the size of solute particles. Our study shows that at the solute molar fractions  $x_s \leq 30\%$  some strengthening of vicinal water structure has been observed. It manifests mainly in increasing of the number of water molecules in the 1st solvation shell around central solute particle and consequent increase in O-O and O-H coordination numbers. At the same time at solute concentration  $x_s > 30\%$  nonpolar solute plays clearly destructive role on tetrahedral water structure and the formation of hydrogen bonds (H-bonds).

The dielectric constant  $\epsilon_r$  and average dipole moment  $\mu_m$  of water-nonpolar solute systems have been calculated. The calculations confirmed the gradual decrease of dielectric constant and average dipole moment with temperature and solute concentration. At high temperatures, this trend is caused by the reduction of polarizability of the system, which in turn is caused by the collapse of the H-bond network and resulting thermal fluctuations that oppose dipole alignment by an electrostatic field. In case of high solute concentration, the trend is caused by the "negative" influence of solute particles on cooperative response of water molecules on the external field. Dielectric constants  $\epsilon_r$  calculated in the given MD simulation are in good agreement with the analytical approach of calculating  $\epsilon_r$  of aqueous solutions at small solute concentrations  $x_s$  and temperatures up to the boiling temperature of water. At higher temperatures and solute concentrations, analytical calculations underestimate  $\epsilon_r$  compared to MD results.  $\epsilon_r$  and  $\mu_m$  do not show any clear dependence from solute particles size.

### REFERENCES

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