

HEAT CAPACITIES AND TRANSPORT PROPERTIES OF AQUEOUS NONPOLAR SOLUTE MIXTURES

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EXTENDED ABSTRACT

Heat capacity, diffusion coefficients, and velocity autocorrelation functions for water mixtures with different nonpolar solutes (methane and noble gases) have been studied using molecular dynamics at constant volume and temperature. A combined SPCE + Lennard-Jones potential was chosen for these systems with Lorentz-Berthelot combining rules. The use of such a potential for water-solute and solute-solute interactions allows us to study the system in a single phase region over the wide pressure-temperature range and solute molar fractions up to 15%. The heat capacities were calculated using the formalism developed in works of Lustig [1] for NVT ensemble. Comparison with experimental data for pure water [2] in the temperature range 298 - 650 K has been done. Simulations show good agreement of bulk water C_v with experimental data in the high temperature region, and slight overestimation at ambient temperatures.

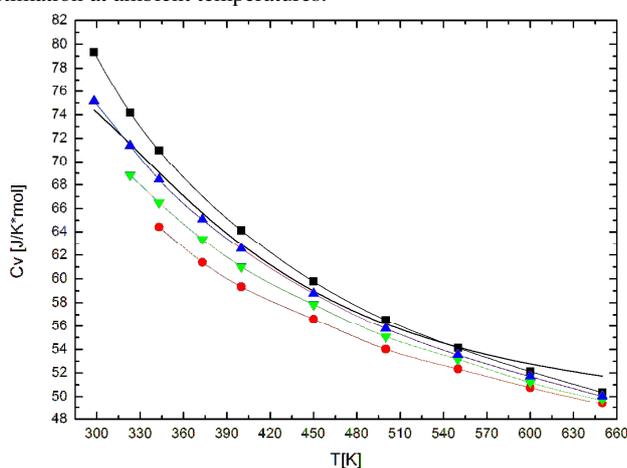


FIG. 1. Isochoric heat capacity as a function of temperature at 0.998 g/cm^3 : water + 0% CH_4 (black ■), water + 6% CH_4 (blue ▲), water + 10% CH_4 (red ●), water + 15% CH_4 (green ▼), and IAPWS-95 reference data[2] for water (—). The lines through the data points are given only for guidance.

The first MD simulations of heat capacity changes in water induced by the solvation of nonpolar solutes (methane, krypton) at solute molar fractions up to 15% are reported (see Fig. 1). Heat capacities of aqueous nonpolar solute mixtures are smaller than that of pure water, and proportional to the solute concentration. This is in agreement with the previous results for very dilute aqueous nonpolar solute mixtures [3] and aqueous solutions of alcohols in wide concentration range [4]. Difference between heat capacities of pure water and water-solute mixtures gradually decreases with temperature, completely converging at critical temperature.

Self-diffusion constants of water are in fairly good agreement with experimental data almost up to the boiling temperature. Diffusion coefficients of the given aqueous nonpolar solute mixtures decrease with solute concentration and show the following temperature-mass dependence $D \propto T / \mu^\beta$. Self-diffusion coefficients of water molecules in the mixture are smaller than that of pure water. Degree to which D of water in the mixture is smaller than in the pure water appears to be proportional to the solute concentration.

Solvation of nonpolar groups in water is accompanied by specific changes in structure and transport properties which appear to be proportional to particles mass and size, and are very different from the changes in water structure induced by solvation of polar and ionic groups.

REFERENCES

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