Structure and Dynamics of Electrolyte Solutions in Ambient and Supercritical Water

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Molecular dynamics-free energy perturbation techniques are used to study solvation energies, entropies and free energies for several anions and cations in ambient and supercritical water (SCW). Strong electrostriction effects are found on thermodynamic properties of solvation of ions at infinite dilution in SCW. The results are analyzed and interpreted through an analogy to adsorption. Based on analysis of the molecular information obtained from the simulations, free energies of ion solvation in SCW are calculated with a semi-continuum model. Predictions of the model agree fairly well with full simulation results for a wide range of temperatures and densities in SCW.

To describe the dynamics of the system, reorientational times of the dipoles in the first shell of the ion are calculated and related to transport properties: diffusivity and conductivity of ions in SCW. Limiting ionic conductances, friction and diffusion coefficients are evaluated and compared to experimental results. The analysis yields a microscopic understanding of the effect of the solvent on the mechanisms of ion transport in SCW. The influence of electrostriction and dynamic effects on the diffusion coefficients is described. A critical discussion focuses on the value of the proposed theoretical model to guide an improved evaluation of transport properties in particular in the supercritical region.