Alkali Halide aqueous solutions under temperature gradients: A non equilibrium molecular dynamic study

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We study the response of alkali halide aqueous solutions to a thermal gradient using non equilibrium molecular dynamics simulations. Using an atomistic approach we examine the microscopic mechanisms defining heat transpot and the thermal diffusion of the solution in terms of salt concentration and composition, in an attempt to correlate transport with the solvation structure.

Aqueous solutions play an important role in nearly every aspect of our life. The properties and behaviour are a focus of intense study by researchers in physics, chemistry, biology or engineering. The response of an aqueous solution to a thermal gradient is relevant to understand heat- and mass transport (the Ludwig-Soret effect [1, 2]) in a wide range of practical applications, e.g., in customized refrigerant fluids for industrial processes. Lithium bromide solutions are for example often used in simple absorption refrigeration systems which are common in large commercial plants [5]. Unfortunately there is not yet available a full microscopic interpretation of the Ludwig-Soret effect [3]. Recent work has also illustrated that water is not a passive solvent, and that can feature a sizable polarization as a reponse to strong thermal gradients, which are achievable at micro and nanometer scales[6]. We have also recently observed the possibility of orienting non polar molecular fluids with temperature gradients and established a link with the Soret effect. Hence, a systematic study on solvent orientation effects is of particular interest on ionic solutions given the competition between orientation and ion solvation.

To study aqueous solutions under a thermal gradient we utilized boundary driven non equilibrium molecular dynamics (NEMD) simulations. The motion of a predefined set of water molecules located at different regions in the simulation cell are restrained by a harmonic potential and thermalized to predefined hot and cold temperatures, to induce a temperature gradient and heat flux. The water is modelled via the rigid SPC/E model, whereas for the ions we use a combination of Lennard-Jones (LJ) and Coulombic potential with parameters optimized to model electrolyte solutions [7, 8].

With this simulation set up we study the dependence of the Soret coefficient on concentration, thermal gradient and the solution composition (charge, size, strength of dispersion interaction of the ions). The contribution of the ions to the heat transport is analyzed at a microscopic level. The alignment of the water molecules in the direction of the thermal gradient and the coupling of this thermopolarization with the Soret effect is also analyzed.

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