Bridging Molecular and Macroscopic Models of Solution Thermodynamics

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The equilibrium behavior of natural aqueous solutions can be predicted using chemical thermodynamic models of solvent and solute activities. However, existing thermodynamic models of electrolyte solutions are semi-empirical: (i) the values of parameters in the model equations are fitted to experimental measurements; (ii) key molecular level processes controlling the behavior of aqueous electrolyte solutions (hydration and association of ions) are not treated explicitly. Major advances in the ability of these models to predict the properties of complex aqueous solutions, over wide ranges of solution conditions, are only likely when the molecular-level processes affecting solutes and solvent are explicitly described in the model.

In this work we propose a strategy to reparametrize thermodynamic models using atomistic calculations: it uses information on the structure and dynamics of water molecules from ab initio molecular dynamics simulations of electrolyte solutions in numerical expressions which can subsequently calculate solute and solvent activities at a wide range of concentrations. For example, we will show that the effective hydration number parameter h in Zavitsas' model can be obtained from the analysis of the hydrogen-bonding autocorrelation function of the water molecules surrounding the ions. The performance of various reparametrized thermodynamic models using this approach is compared to experimental activity coefficients. Our approach represents a unique upscaling tool to bridge molecular simulations and macroscopic models of electrolyte solutions.