Multistate Model of Ion Hydration

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Short range ion-solvent interaction energies are typically strong on a thermal energy scale and can rival covalent bonds in strengths, whereas the long-range interactions usually represent a collection of uncorrelated, energetically weak contributions that admit a Gaussian distribution. In developing thermodynamic models of aqueous electrolytes, one has to acknowledge these disparate scales of energy. Here we use the quasichemical organization of the potential distribution theorem to parse the short-range and long-range phenomena. The short-range contributions are recast in terms of the energetics of forming ion-water clusters within the first hydration shell and the long-range contribution is obtained using a Gaussian model of interaction energies. We use this framework to study ion hydration at infinite dilution. Using simulations based on classical (empirical) potentials, we show that for the monovalent ions studied here, only a small subset of water molecules populating the inner shell sense the chemical type of the ion. These core-water molecules also tend to attenuate the interaction of the ion with the rest of the medium, and thus the higher coordination states of the ion more sensitively reflect density fluctuations of the solvent medium at the size scale of the observation volume. This observation is used to rationalize the success and limitation of models of ion hydration that combine gas-phase modeling of ion-water clusters with approximate models of the bulk solvent. The relevance of the multistate approach in rationalizing model constants entering the semiempirical, unified theory of electrolyte solutions, a continuum-scale approach, and in informing the development of models of electrolytes based on the statistically associating fluid theory (SAFT), a meso-scale approach, is indicated.