

Introducing charge hydration asymmetry into continuum electrostatics framework

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ABSTRACT:

Charge hydration asymmetry (CHA) manifests itself in the experimentally observed strong dependence of free energy of ion hydration on the sign of the ion charge. The effect is present, to various degrees, in fully explicit solvent models such as TIPnP, as well as in "semi-explicit" approaches such as RIMS or semi-explicit assembly (SEA). The CHA effect is absent from the basis of the "standard" (PB, GB) continuum electrostatics framework; practical calculations partially account for it by adjusting atomic radii used to define the dielectric boundary. However, no universal, fully transferable radii set exists, errors relative to explicit solvent reference are common. We use basic statistical mechanics considerations to formulate a precise criterion for a water model to have charge hydration asymmetry, and to demonstrate how the CHA effects can be introduced into the conceptual framework of continuum electrostatics, at the Born equation level. In our approach, the issues of dielectric boundary placement and the CHA corrections are cleanly separated, leading to enhanced universality of the radii set developed within the new model. The model is generalized, tested on small molecules and amino acids; its accuracy approaches that of the semi-explicit assembly (SEA) treatment.