Ion Specific Effects with the Continuum Solvent Model

Timothy T. Duignan and Drew F. Parsons

Applied Mathematics Department, Australia National University, Canberra, 2602, Australia, tim@duignan.net

Explaining the behaviour of ions in water is both incredibly important and incredibly challenging. [1] Essentially, the task is to calculate the interaction energies of ions with molecules and surfaces found in the blood, ocean, and industrial applications. Before these can be calculated the ion-water interaction must first be fully understood. We present a continuum model, which accurately reproduces the solvation energy of ions, explaining key puzzles about these properties. In particular, it explains the difference in solvation energies for some ions of the same size. It also semi-quantitatively reproduces partial molar volumes, and entropies of solvation. These are two properties against which solvation models are often tested. All the expressions are physically derived with good external justification for the values of the parameters. This model therefore addresses some common criticisms of continuum solvent models [2], that they depend on ad hoc correction terms, which are only accurate when compared with the data against which they are fitted. The new model meets the criteria for a predictive, quantitative model of solvation. It therefore casts doubt on the argument that effects due to the position and orientation of individual water molecules are critical in explaining ion specificity.

Using this model as a foundation, we have calculated ion-ion interactions and ion-surface (air-water) interactions. Tentative comparison of these potentials with experimental properties gives promising results, qualitatively explaining ion-specific trends as well as some puzzling properties of electrolyte solutions. Examples include the excess of iodide ions at the air-water interface and the affinity of like-sized ions for each other in water. This approach alleviates the need for problematic corrections such as Gurney potentials and hydrated ionic radii, which involve using parameters fitted individually for each ion to reproduce ion specific behaviour. However, some troubling puzzles remain such as a large overestimation of the magnitude of the ion-ion interaction energies. This could possibly be due to the continuum model's neglect of some entropic contributions.

References.
[1] Ninham, B. W.; Lo Nostro, P. Molecular Forces and Self Assembly; Cambridge University Press: Cambridge, 2010
[2] Hunenberger, P.; Reif, M. Single-Ion Solvation: Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities; The Royal Society of Chemistry, 2011

Corresponding Author: T. T Duignan
Australia National University, Canberra, 2602, Australia, Phone: +61 (2) 61257590
Email: *tim@duignan.net*