

Simulations of Mean Ionic Activity Coefficients and Solubilities in Aqueous Electrolyte Solutions

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We devised a method for obtaining mean ionic activity coefficients of aqueous electrolyte solutions from molecular dynamics simulations by gradually inserting ion pairs into the solution. The method is based on slow growth of the non-Coulombic part of the interactions first, followed by the Coulombic part. The infinite-dilution (reference) chemical potential of the salt is obtained by matching the simulation results at very low concentrations to the Debye-Hückel limiting law. Several common non-polarizable water and ion models were used to obtain the mean ionic activity coefficients of NaCl, KF, LiCl, LiBr, and CaCl₂ solutions at several concentrations at a temperature of 298.15 K and pressure of 1 bar. Gibbs-Duhem equation calculations of the thermodynamic activity of water were used to confirm thermodynamic consistency of the mean ionic activity coefficient calculations. We also tested the effect of the temperature on the mean ionic activity coefficient predictions. Deviations at high concentrations of the simulated mean ionic activity coefficients from experiment and the inaccuracies in solubility predictions necessitate the use of more sophisticated models. To this end, we are presently testing the accuracy of several polarizable ion and water models with respect to the solubility and activity coefficient predictions.