Thermodynamic properties of electrolyte solutions from the SAFT-VR+DE equation of state

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Recently, the statistical associating fluid theory for potentials of variable range[1] (SAFT-VR) equation of state (EoS) was extended to include the explicit consideration of dipolar and electrostatic interactions and used to describe the thermodynamics of electrolyte solutions. In the resulting SAFT-VR+DE EoS,[2] long-range ion-ion, ion-dipole, and dipole-dipole interactions were introduced through the incorporation of integral equation theory into the SAFT-VR framework. Specifically, the mean spherical approximation for the non-primitive model of electrolytes, in which the ions are described in an explicit dipolar solvent, was implemented and the theoretical predictions compared with computer simulations of electrolyte solutions at different ion concentrations and different ratios of the cation, anion, and solvent segment diameters. The theory was shown to accurately predict the phase behavior of model electrolyte solutions and, through these comparisons to the commonly used Debye-Hückel theory and primitive model, illustrated the need to accurately account for the size of the ions and the dielectric constant.

Here we extend the SAFT-VR+DE approach to describe 1:1 aqueous electrolyte solutions. Both fully dissociated and partially dissociated models for the electrolytes are considered to capture ion association at high salt concentrations. Salt specific binary interaction parameters between the cations and solvent are obtained by fitting to experimental mean ionic activity coefficient data, with the anion-solvent interactions captured purely through the electrostatic terms. The approach is found to predict thermodynamic properties such as osmotic coefficient, water activity coefficient, solution density, Gibbs free energy of hydration and dielectric constant across different salt concentrations and temperatures in good agreement with experiment. At higher salt concentrations near the saturation limit ion-association is considered through the inclusion of an association energy parameter, which is obtained by fitting to experimental mean ionic activity coefficient data. Mixed solvent electrolyte systems have also been studied for which the SAFT-VR_DE equation is particularly suited as experimental data on the dielectric constant is not required.

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2. Zhao, H. G.; dos Ramos, M. C.; McCabe, C., Development of an equation of state for electrolyte solutions by combining the statistical associating fluid theory and the mean spherical approximation for the nonprimitive model. *J Chem Phys* **2007,** *126* (24).