The Mean Countershell Approximation (MCSA) theory for the excess chemical potential of electrolytes: comparison to Monte Carlo simulations

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A new theory of the excess chemical potential (or, equivalently, the activity coefficients) for homogeneous electrolytes modeled with the primitive model has been derived [1]. We focus on the electrostatic screening component of the excess chemical potential that is defined as the difference of the excess term and the hard sphere term. In the primitive model, ions are modeled as charged hard spheres immersed in a dielectric continuum (representing the solvent). The new Mean Countershell Approximation (MCSA) is an analytic theory of the electrostatic screening correlations derived from physical arguments with no adjustable parameters. Comparisons to Monte Carlo (MC) simulations show the MCSA to be highly accurate. It makes qualitative improvements over the original Mean Spherical Approximation (MSA) [1-3], and its formulas are simpler.

The new theory is based on the idea that the ion cloud around a central ion with charge $z_i e$ is a shell of charge with the radius like that described by the MSA's second-order direct correlation function. The new contribution to the excess chemical potential is the MCSA shell-shell term that is the interactions of the two clouds of screening ions around two distinct ions. This provides a significant contribution to the energetics of an electrolyte, especially at high concentrations, high ion size asymmetries, and low dielectrics. All of these conditions are seen in ionic liquids. The screening cloud interactions produce a minimum in the screening component of the excess chemical potential as seen in Fig 1 that, to our knowledge, had not been explained before.

Here, we show results for the screening component of the excess chemical potentials in comparison with the original MSA theory and MC simulations of charged hard spheres of varying diameter and valence at varying concentrations. We also show results for the II+IW model of the activity coefficient of electrolytes, where the ion-ion (II) term is computed with the MCSA, MS, and MC methods, while the ion-water (IW) term is estimated by the Born theory [5]. The II+IW theory is based on a concentration dependent dielectric constant of the electrolyte solution. We show results for 2:1 and 3:1 electrolytes as functions of concentration [6,7].

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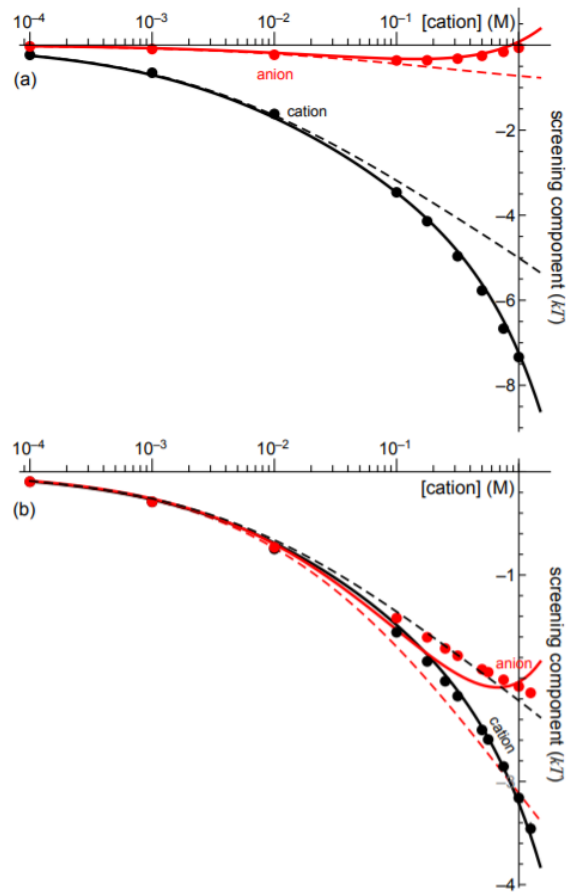[7]   M. Valiskó, D. Boda. Mol. Phys. 115, 1245 (2017)

Figure 1: Comparison of the screening component of the excess chemical potential as a function of the cation concentration from MC (symbols), MSA (dashed lines), and MCSA (solid lines) for cations (black) and anions (red). (a) $z_+=3 =$, $z_-= 1$ and (b) $z_+=2 =$, $z_-= 2$. In both cases, , $\sigma_+= 0.9$ nm, $\sigma_- =0.3$ nm, $\varepsilon = 78.45$, and T = 298.15 K.