ePC-SAFT advanced: A new thermodynamic model for electrolyte solutions
The importance of a concentration-dependent dielectric constant in electrolyte thermodynamic models.

Moreno Ascani, Mark Bülow, Christoph Held.

Non-aqueous electrolyte liquid systems become increasingly important for innovative technical processes. However, modeling such systems is very challenging, and still not all the physical effects are explicitly accounted for in advanced physics-based thermodynamic models. Thus, such models still rely on extensive parameter fitting over large experimental data sets. This does often not allow for extrapolation to other conditions as ion parameters that have been fitted to aqueous electrolyte solutions are not transferable to non-aqueous electrolyte solutions. In this work, a concentration-dependent dielectric constant was accounted for in the electrolyte theories of Born and Debye-Hückel, which were then combined with a classical equation of state, Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT). The new model, called ePC-SAFT advanced, allowed successfully predicting thermodynamic properties of alcohol+salt solutions. The highlight is that new model parameters were not required and existing ion parameters fitted to aqueous electrolyte solutions were transferred to the non-aqueous electrolyte solutions.

ePC-SAFT is a broadly applied electrolyte equation of state, which combines the classical PC-SAFT equation of state with the DebyeHückel theory in order to account for the electrostatic interactions among ions. However, ePC-SAFT considers the permittivity of any electrolyte solution as equal to that of the pure solvent, and electrostatic interactions between the ions and solvent are not accounted for explicitly. The drawback of this is that ePC-SAFT cannot be applied to predict physical properties of non-aqueous electrolyte solutions, which requires fitting a huge number of parameters to experimental data. However, the available data of non-aqueous electrolyte systems is rather scarce in the literature. Thus, a robust model is missing in the literature that is accurate for non-aqueous electrolyte solutions.

Within this work, the impact of a concentration-dependent dielectric constant $\varepsilon_r(x)$ was studied on ePC-SAFT modeling results of non-aqueous electrolyte solutions. $\varepsilon_r(x)$ was included in the theories from Debye-Hückel and Born, which was then included as contributions to the Helmholtz energy in ePC-SAFT. The Born energy a^{Born} describes the work required to discharge an ion from the vacuum and recharge it within a solvent of given dielectric constant (Eq. 1).

$$a^{Born} = -\frac{e^2}{4\pi\varepsilon_0 k_B T}\left(1 - \frac{1}{\varepsilon_r(x)}\right)\sum_i \frac{x_i z_i^2}{a_i} \qquad (1)$$

In Eq. (1) a_i, z_i and x_i denote the diameter, valence, and molar fraction of ion i, respectively. The free energy of solvation of ions changes dramatically between water and low-polar solvents as a^{Born} strongly depends on $\varepsilon_r(x)$. In this work, it was proven that predicting infinite dilution properties, such as the free energy of hydration of monovalent ions, is only possible by including a^{Born} in the modeling; in contrast, the original ePC-SAFT model fails (see Figure 1).
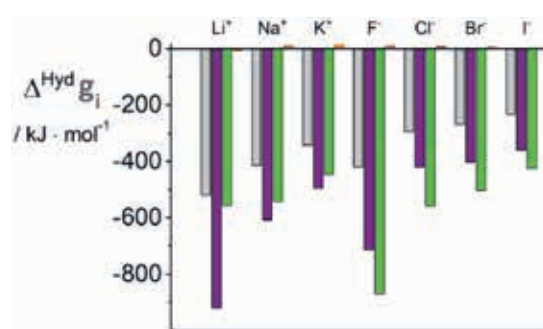

Figure 1: Gibbs energy of hydration at 298 K at infinite dilution. Original ePC-SAFT: orange; ePC-SAFT advanced: green; SAFT-VR: violet (Schreckenberg et al); Literature data: gray (Fawcett et al.). References: see publication.

The new model, called ePC-SAFT advanced, shows excellent accuracy towards predicting free energies of transfer of ions from aqueous to organic solvents (see publication) and towards predicting salt activity coefficients in alcohols, while other models fail (see Figure 2). Most importantly, none of the ion parameters of the original model were re-estimated.
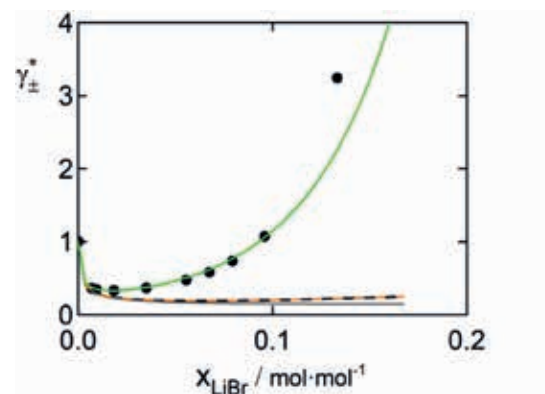

Figure 2: LiBr activity coefficient in ethanol at 298 K. Circles: experimental data (Zafarani-Moattar et al.). Black: original ePC-SAFT, orange: ePC-SAFT + a^{Born}, gray: ePC-SAFT + $\varepsilon_r(x)$ but without a^{Born}, green: ePC-SAFT advanced. References: see publication.

Contacts:
christoph.held@tu-dortmund.de
moreno.ascani@tu-dortmund.de