Modelling the Influence of Solvation on the Electrochemical Double Layer and the Bulk Structure

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We present an extension to our previously published Continuum Transport Theory for Electrolytes. [1] This includes solvation interactions between the ions and solvent, which alter the structure of the electrochemical double layer (EDL). We combine a local solvation model with a full electrolyte model and investigate double layer structures for a wide range of electrolytes, especially including highly concentrated solutions. The solvation interaction is parametrised by two parameters per ion – the solvation shell size and solvent binding energy. We find that some of the parameters of our model significantly affect the solvent concentration at the electrode surface and thereby the rate of solvent decomposition. An increased salt concentration weakens the solvation shells and eases ion desolvation at the electrode surface. The strength of the solvent binding also shifts the potential required for desolvation. By extending our model to include multiple species in the solvation shell, we can also examine how temperature and the relative binding strength of the cation to the anion and to the solvent compete. Using these results, we can explain preferential formation of solvation shells including anions at higher temperatures. [2]

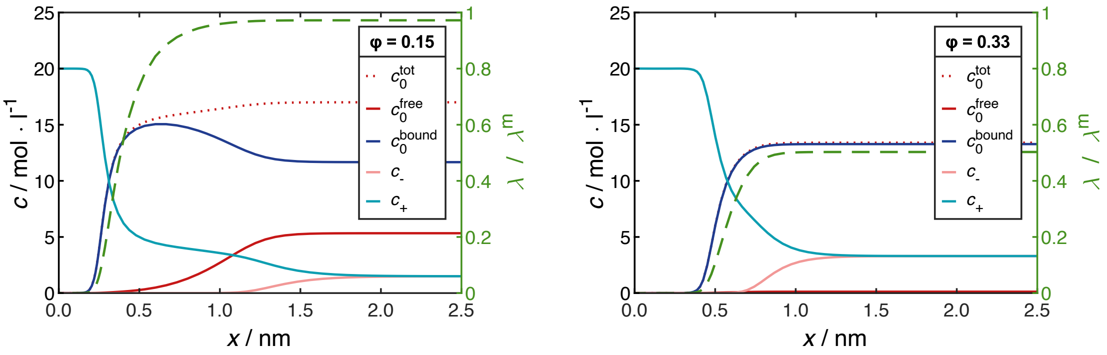

Figure 1: The concentration profiles in an EDL at two different salt concentrations. The left plot models a moderately dilute electrolyte, where the salt occupies 15% of the volume, whereas the right plot is of a concentrated electrolyte, where the salt makes up 33% of the total volume. The right axis shows the filling degree of the solvation shells around the cation, 1 representing full solvation shells (i.e. 4 solvent molecules), and 0 referring to a desolvated ion. It can be seen, that an intermediate region, in which the solvent is present in the cation solvation shells, but the anions have been displaced, is only present in the dilute case.

References

[1] Schammer, M. et al. Theory of Transport in Highly Concentrated Electrolytes. *Journal of the Electrochemical Society.* **21**, 026511 (2021), https://doi.org/10.1149/1945-7111/abdddf

[2] Lai, J. et al. Porous-electrode theory with battery applicationsLinking Solvation Equilibrium Thermodynamics to Electrolyte Transport Kinetics for Lithium Batteries. *Journal of the American Chemical Society.* **147**, 14348-14358 (2025), DOI: 10.1021/jacs.5c00106