

# Modelling Solvation behaviour in highly concentrated Electrolytes

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Modelling of electrochemical systems supports designing improved chemistries for battery applications [1]. Electrolytes play an important role for the performance of batteries. As such, highly concentrated electrolytes constitute promising materials. However, due to their complexity, they are difficult to model. Here, we present a continuum transport theory for these materials, which incorporates solvation effects.

Dreyer et al. [2] presented an electrolyte model which includes solvation effects. Their approach is based on modified statistics, which leads to an excess chemical potential. However, their model is limited to dilute solutions and fixes the number of solvent molecules bound to each ion.

Our focus lies on the behaviour near electrified interfaces, i.e., the electrochemical double layer (EDL). To address this goal, we modify the transport theory for highly correlated electrolytes [3,4], which was recently proposed by our group. This description is based on modelling the free energy of the system. To incorporate solvation effects, we supplement it by an additional interaction energy which accounts for the correct mixing entropy due to modified statistics.

The theory is based on two novel parameters – the maximum number of solvent molecules binding to a single ion, and the binding energy. By using a local solvation parameter, we are able to model dissolution of the solvation shell in the EDL by an applied potential.

We supplement our analytic discussion by numerical double layer simulations of a ternary electrolyte. Our results capture the relationship of ion-solvent binding energy and the desolvation potential. The model is also able to give qualitative results down to a molecular scale, allowing us to predict coarse grained behaviour of MD-simulations. This shows that solvation effects have a significant influence on the EDL-structure.

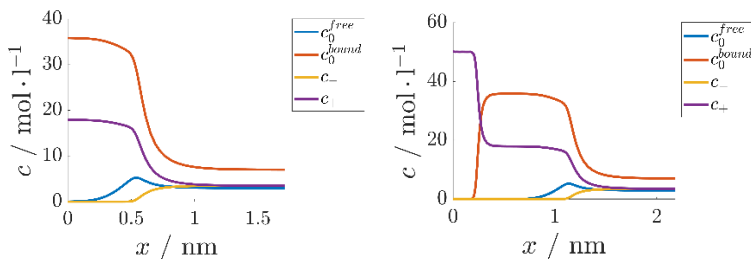


Figure: a ternary EDL at two different potentials, showing desolvation near the electrode surface at a higher potential (on the right)

## Literature

1. Armand, M.; Tarascon, J.-M. Nature 2008 451, 652.
2. Dreyer, W. et al Electrochem. Comm. 2014, 43, 75-78.
3. Schammer, M. et al J. Electrochem. Soc. 2021, 168, 026511.
4. Schammer, M. et al J. Phys. Chem. B 2022, 126, 14, 2761–2776