Influence of Solvation on the Structure of the Electrochemical Double Layer: a Continuum Approach for Ionic Liquids

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Here, we present a holistic framework for the description of IL based electrolytes, which couples nonequilibrium thermodynamics with mechanics and electromagnetic theory. Our continuum approach applies both to the bulk phase and to charged regions near electrified interfaces, thus spanning a wide range of length-scales from cell-level (micrometers) to microscopic interactions (nanometers).

For bulk electrolytes, e.g. in battery applications, our description comprises all transport mechanisms (diffusion, migration, convection), and predicts the evolution of the electrolyte species. In a series of publications, we validated this theory with experimental results [1,2].

To describe the electrochemical double layer (EDL), we supplemented our bulk description by non-local ion interactions. For pure ILs, our theory predicts that the structure of the EDL is governed by three energies scales related to short-ranged ion-correlations, thermal energy, and electrostatic energy of Coulombic interactions [3] (in particular, dominant correlations lead to nanostructuring). We validated this approach with AFM experiments [4].

Recently, we extended our EDL model to also account for solvation effects. Analysing the differential capacitance, our approach reproduces known effects, as the shift from "camel"-shape to "bell"-shape for larger salt concentrations. As novel features, it describes the effect of ion asymmetry on the capacitance minimum, and predicts the emergence of additional peaks in the differential capacitance resulting from stripping of the solvation shell in the EDL.
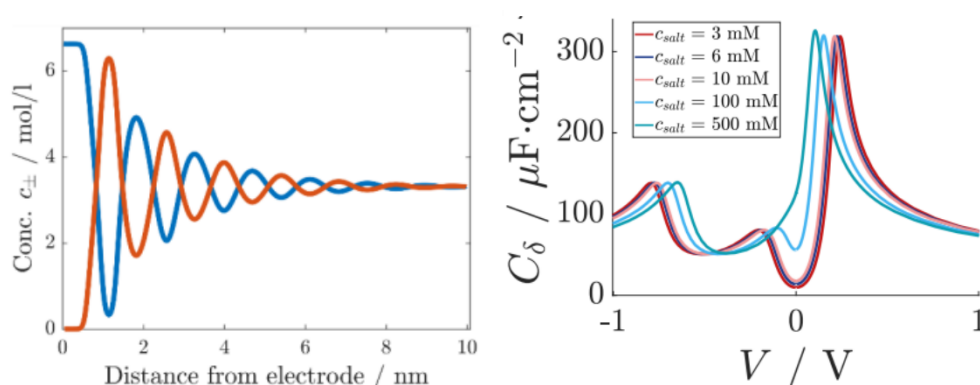

Fig. 1 Left: Charge oscillations in the EDL for a pure ILs. Right: Differential capacitance curve.

REFERENCES
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