On the structure of highly concentrated aqueous lithium chloride solutions from a combination of RMC and MD techniques and 29 interatomic potential models

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In spite of the huge effort spent on the determination of the structure of aqueous lithium chloride solutions, several open questions still remain. The structural reordering of water molecules, the extent of ion-pairing and the hydration number of the chloride and lithium ions are crucial problems. The complete description of the structure at the two-particle correlation level would require the combination of ten independent experimental data sets, but the number of the available data sets is significantly lower. The low partial weight of the ion-related partials in the measured data (especially in dilute solutions) can be another problem.

Classical molecular dynamics (MD) and reverse Monte Carlo (RMC) simulations were performed to describe the structure of highly concentrated aqueous lithium chloride solutions. The structural predictions of 29 ion-water interaction models (force fields, FF) were compared at four salt concentrations. The contributions of different structural motifs to the partial pair correlation functions (PPCF) were determined. Particle configurations obtained from MD simulations were further refined using the RMC method to get better agreement with experimental X-ray and neutron diffraction data. The MD models were validated according to the quality of the fits. It was found that those FFs, which have lower ion pairing tendency show better agreement with the experiments. Although none of the tested FFs can describe the structure perfectly at the highest investigated concentration, their comparison made it possible to determine the main structural properties of that solution as well.

Four nearest neighbors (oxygen and Cl^- ions together) are around the Li^+ ions at each investigated concentration, while in the environment of the Cl^- ion two hydrogen atoms are replaced by one Li^+ ion as the concentration increases. While in pure liquid water four water molecules can be found around a central water molecule, near the solubility limit nearly all water molecules are connected to two Cl^- ions (via their hydrogen atoms) and one Li^+ ion (by their oxygen atoms).

See also:

I. Pethes, *J. Mol. Liq.* **242** (2017) 845

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