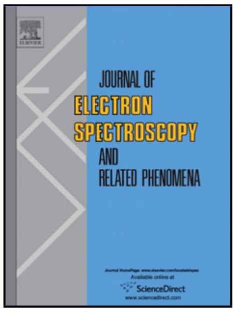

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Contact ion-pair structure in concentrated cesium chloride aqueous solutions: an extended X-ray absorption fine structure study

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Highlights

- Corefinement of multiple EXAFS spectra is used to evaluate a set of different aqueous CsCl solutions.
- The hydration structure of fully hydrated Cl- in aqueous solution is determined.
- The ion-pair structure of Cs-Cl at moderate and nearly-saturated concentrations is reported.
- There is a higher degree of ion pairing for Cs-Cl than for Rb-Cl that is not expected from the Collin's law of matching water affinities.

Abstract

The hydration and ion pair structure of Cl^- ion in aqueous cesium chloride solutions at 0.5, 6 and 11 mol/kg (H_2O) has been studied using Extended X-ray Absorption Fine Structure (EXAFS) at the Cl K-edge. The co-refinement of multiple EXAFS datasets shows the hydration structure of the free Cl^- ion is consistent with previously reported studies. In concentrated solution the Cl^- ion is strongly associated with the cation forming contact ion pairs with 1.6 and 2.8 Cs ions in 6 and 11 mol/kg aqueous CsCl, respectively. Together with ion-pairing structure of RbCl and RbBr, reported in our previous work, these results for the Cs-Cl ion-pair structure provide a more general view of ion-pairing in concentrated aqueous alkali halide solutions. The reported Cs-Cl ion-pair structure provides a basis for the development and testing of improved interaction potentials leading to more realistic structures from molecular dynamics (MD) simulations.

Keywords: contact ion-pair, Cs-Cl ion pair, EXAFS, differential EXAFS, Cl^- hydration structure