

ESRF	Experiment title: Structure and temperature dependence of concentrated aqueous LiCl	Experiment number: HE-3308
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Shifts: 18	Local contact(s): Dr. Simo Huotari	
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Report:

Monitoring and understanding the hydration structures in salt solutions are of fundamental importance in many applications [1]. Salt solutions as multicomponent systems exhibit many relatively poorly understood phenomena at the atomic scale. The interesting phenomena relate to the structure and dynamics of the coordination shells, which can be strongly affected by temperature and solute concentration, e.g. through enhanced ion pairing. Few traditional experimental techniques are able to probe the structure truly at the atomic scale. The predicted structures by *ab initio* molecular dynamics (MD) methods need to be carefully corroborated due to their inherent limitations. The coordination shell structure (of cations, anions and solvent molecules) is generally a much studied and debated subject. The hydration structures obtained from classical MD simulations tend to depend strongly on the force field chosen [2]. For hydrated Li^+ both 4- and 6-fold coordination numbers, for example, are found depending on the force field ([3] and references therein). *Ab initio* MD simulations (for LiCl performed by Petit *et al.* [4]) have limitations due to short time scales and small simulation cells. This emphasizes the need for novel studies where the theoretical suggestions are verified by experimental methods sensitive to the detailed atomic-scale structures.

To clarify the issues outlined above for LiCl, we have performed a systematic high-resolution XRS study on the effect of concentration on the O *K*-edge spectrum of water. The samples were prepared by mixing ultrapure water with LiCl powder and circulated in a peristaltic-pump-based flow setup, which produced a 2-mm diameter vertical liquid jet from a stainless steel nozzle. Spectra were gathered at room temperature for nine concentrations ranging from 0 to 17 mol/l.

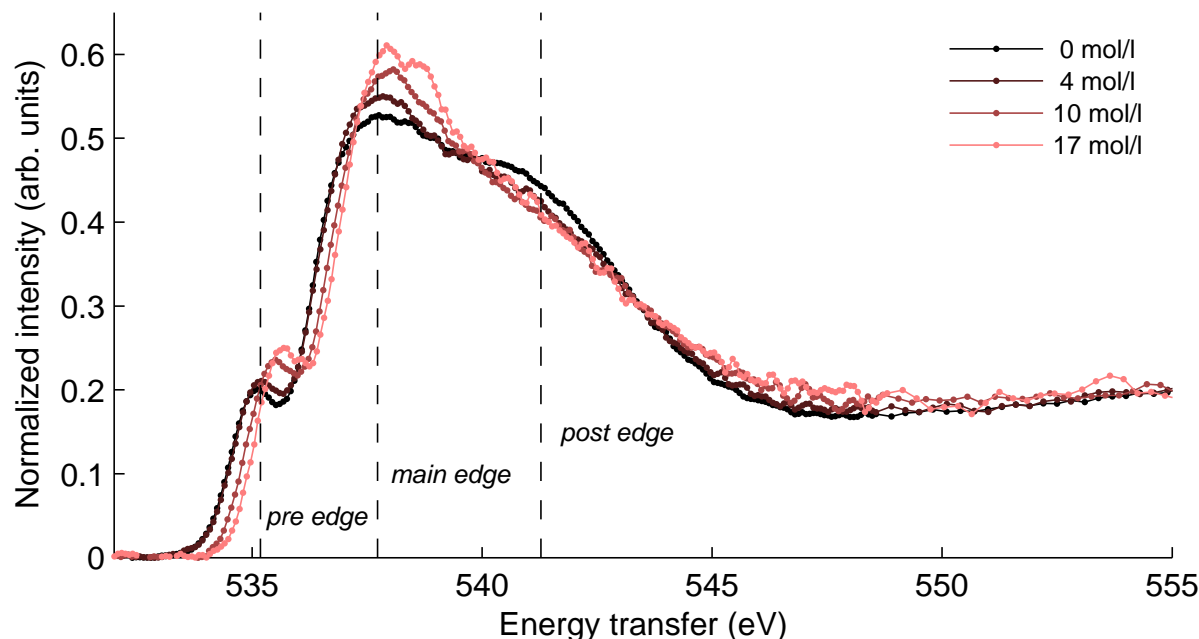


Figure 1. The O *K*-edge XANES of aqueous solution of LiCl at selected concentrations. Dashed lines mark approximate pre-edge, main-edge, and post-edge positions of neat water.

The incoming radiation was monochromatized with a double-crystal Si(111) monochromator followed by a Si(440) channelcut. The beam was focused into a 130(H)×50(V) μm^2 spot by a Rh-coated toroidal mirror. The measurements were performed utilizing a multianalyzer spectrometer, in which the scattered radiation is focused on the 2D photon-counting Maxipix2 detector by 9 spherically bent Si(110) crystal analyzers. Spectra were gathered scanning the incident energy while analyzing the scattered radiation using the Si(660) reflection near backscattering, giving an elastic energy $E_0 = 9.68$ keV and energy resolution of $\Delta E = 0.5$ eV (FWHM). Spectra were measured at an average scattering angle of $2\theta = 36^\circ$, corresponding to a momentum transfer $q = 1.7$ a.u.

Preliminary results are shown in Figure 1. The spectra are of high quality even at the largest concentrations. It is worth noting that we have accessed much higher concentrations than have been studied previously (maximum concentrations were 4 mol/l or 4 mol/kg in Refs. 5–7), allowing us to observe the full range of behavior from dilute to nearly saturated. A detailed study of the various effects contributing to the O *K*-edge is underway.

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