

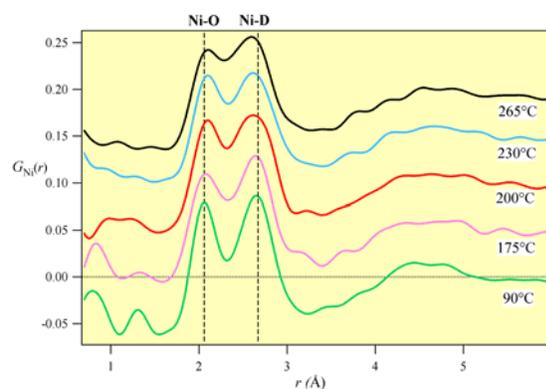
Changes in Solvation of Metal Ions with Temperature: Atomic-level Interactions between Solvent and Solute

Basic Aqueous Chemistry to High Temperatures and Pressures

Interactions of ions in solution with the solvent, and with each other, determine the solubility of compounds and their reactions in solution. For example, the dissolution of corrosion products such as metal oxides strongly affects the extent of corrosion of metals, and the possible precipitation of sludge or scale in steam generators. In the natural environment, the transport and deposition of valuable materials or contaminants is driven by small differences in interactions between solutes, water, and solid surfaces such as rocks or soil. We have determined hydration structures and the extent of hydration for nickel chloride in aqueous solution over a wide temperature range, addressing the effects of changing solvent properties on the interactions between metal ions and water. The results indicate that hydration structures persist with increasing temperature, but become less well defined as the thermal energy of the system increases.

By measuring wide-angle neutron scattering in a matched pair of NiCl_2 solutions differing only in the isotopic composition of the Ni^{2+} ion, we have shown that the metal ion is less-strongly hydrated as the temperature increases [

J. Chem. Phys. 119, 4413, 2003]. The first peak in the radial distribution function around Ni^{2+} , corresponding to the distance between nickel and oxygen in the hydration shell around the metal ion, moves to longer distances and indicates lower hydration numbers with increasing temperature. These results, obtained from the GLAD diffractometer at the Intense Pulsed Neutron Source (Argonne National Laboratory) using a scattering cell designed for high temperatures and pressures, are the first systematic investigation of the subtle changes of hydration in Ni^{2+} with increasing temperature.



The curves of $G_{\text{Ni}}(r)$ can be further resolved through molecular-level modeling of these solutions. Our molecular-dynamics simulation of this system at the concentration of the experimental solutions [*Mol. Phys.* 100, 2307, 2002] indicates that there should be a contribution to the second peak (near 2.6 Å) from an ion-pairing interaction of nickel and chloride, and that the contribution should be nearly constant at temperatures to 200°C. We cannot fully match the simulation and experimental results under these conditions. Additional experimental measurements are being planned to address the predictions of the model, and to provide a firm experimental basis for an improved theoretical description of the system.

This research was performed by J. Michael Simonson, D. A. Palmer, M. Gruszkiewicz, A. A. Chialvo, and P. T. Cummings, Chemical Sciences Division, Oak Ridge National Laboratory.