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Deriving formation constants for aqueous metal complexes from XANES spectra: Zn^{2+} and Fe^{2+} chloride complexes in hypersaline solutions

Weihua Liu,[1,2,*] Barbara Etschmann,[1] Garry Foran,[3] Michael Shelley,[4] and Joël Brugger[2,5]

[1]CSIRO Exploration and Mining, School of Geosciences, Monash University, Clayton, Victoria 3800, Australia
[2]South Australian Museum, North Terrace, Adelaide, South Australia 5000, Australia
[3]Australian National Beamline Facility, Photon Factory, KEK, Oho 1-1, Tsukuba-shi, Ibaraki-ken 305-0801, Japan
[4]Research School of Earth Science, Australian National University, ACT 0200, Australia
[5]School of Earth and Environmental Sciences, University of Adelaide, Adelaide, South Australia 5005, Australia

Abstract

The development of numerical modeling of reactive transport relies on the availability of thermodynamic properties for the solid, surface, aqueous, and vapor species stable at the conditions of interest. The lack of experimental studies and comprehensive activity-composition models severely limits the predictive capabilities of these models in systems involving highly saline fluids or low-density volatile-rich fluids. X-ray absorption near-edge structure spectroscopy (XANES) is a powerful technique to study the speciation of transition metals in aqueous fluids: it is element specific; sensitive to the oxidation state of the metal, the ligand field and the coordination geometry of the complex; and it is suitable for measuring trace amounts of metals (<1 wt%) in solutions over a wide pressure and temperature range.

Formation constants for the aqueous complexes of transition metals can be determined from a series of XANES spectra obtained on solutions containing a constant amount of the metal of interest and variable concentrations of a ligand. The method relies on a non-linear, least-squares-fitting approach, with full distribution of species calculations based on a complete thermodynamic model for the experimental system under consideration. The technique is particularly suitable for following octahedral to tetrahedral transitions among weak chloride complexes of transition metals. The log *K* for the reaction $Zn^{2+}_{(octahedral)} + 4Cl^- = ZnCl_4^{2-}{}_{(tetrahedral)}$ at 25 °C is retrieved to be 0.1(6), within error of the accepted literature value. The same method applied to Fe^{2+}-chloride complexes shows that the log *K* for the reaction $Fe^{2+}_{(octahedral)} + 4Cl^- = FeCl_4^{2-}{}_{(tetrahedral)}$ increases from –6.2(6) at 25 °C to –2.9(3) at 150 °C. This study confirms that tetrahedral chloride complexes play an important role in Fe transport in hypersaline brines especially at elevated temperatures, and shows that XANES is well suited to study systems that may be difficult to study with other techniques.

Keywords: Fe and Zn chloride complexes, XAS, XANES, stability constants, thermodynamics, hydrothermal solutions