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Z. Zhang, P. Fenter, S.D. Kelly, J.G. Catalano, A. Bandura, J.D. Kubicki, J. Sofo, D.J. Wesolowski, M.L. Machesky, N.C. Sturchio, and M.J. Bedzyk, "Structure of Hydrated Zn²⁺ at the Rutile TiO₂ (110)-Aqueous Solution Interface: Comparison of X-Ray Standing Wave, X-ray Absorption Spectroscopy and Density Functional Theory Results," *Geochim. et Cosmochim. Acta*, **70**, 4039-4056 (2006).

FUNDING

U.S. Department of Energy; Materials Simulation Center; a Penn State MRSEC facility; U.S. NSF/DOE Environmental Molecular Sciences Institute, Center for Environmental Kinetics Analysis (CEKA)

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Structure of Hydrated Zn²⁺ at the Rutile TiO₂ (110) – Aqueous Solution Interface: Comparison of X-Ray Standing Wave, X-ray Absorption Spectroscopy and Density Functional Theory Results

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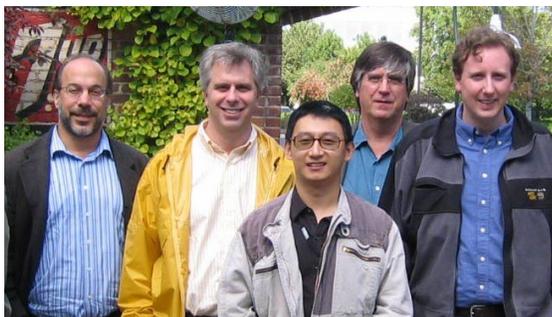
Adsorption of Zn²⁺ at the rutile TiO₂ (110)-aqueous interface was studied with x-ray standing waves, surface x-ray absorption spectroscopy, and density functional theory calculations to understand the interrelated issues of adsorption site, occupancy, ion coordination geometry, and hydrolysis. At pH 8, Zn²⁺ was found to adsorb as an inner-sphere complex at two different sites. A 4- or 5-fold first shell coordination environment was observed for adsorbed Zn²⁺ instead of the 6-fold coordination found for aqueous species at this pH. DFT calculations confirmed the energetic stability of a lower coordination environment and revealed that such change is correlated with the hydrolysis of adsorbed Zn²⁺. In addition, the derived adsorption locations and the occupancy factors of both sites from three methods agree well.

Ion adsorption and electrical double layer (EDL) formation at the oxide-aqueous solution interface are fundamental to a number of processes, including contaminant transport in the subsurface, mineral dissolution and precipitation rates and mechanisms, bioavailability of trace metals, incorporation of trace metals into growing crystals, and heterogeneous catalysis. While there have been extensive studies of EDL phenomena over the past decades, the connection between molecular-scale processes and their macroscopic manifestations remains elusive. Recent experimental and computational studies led to new insights concerning the adsorption of various mono- di- and tri-valent cations at the rutile (*α*-TiO₂) (110)-aqueous interface with excellent consistency between studies ranging from macroscopic observations to microscopic structures and processes. While these previous studies clearly demonstrated that the Zn²⁺ adsorbs

in a manner that was distinct from other cations, discrepancies between the predicted and observed behavior of Zn²⁺ suggested that its interaction at the rutile-water interface was poorly understood. To resolve this gap, we used a combination of Bragg-reflection x-ray standing waves (XSW), surface x-ray absorption spectroscopy and density functional theory (DFT) to understand the adsorption of Zn²⁺ at the rutile (*α*-TiO₂) (110)-aqueous interface.

In the current study, we first

confirmed with XSW imaging that Zn²⁺ ions adsorbed at two distinct surface sites at pH 8, i.e., monodentate above the bridging oxygen (BO) site, and bidentate between two terminal oxygen (TO) sites (**Figure 1**), with however, a coverage and partitioning of Zn²⁺ ions between the two sites that was found to be sensitive to solution pH. Polarization-dependent surface extended x-ray absorption fine structure (EXAFS) spectroscopy results revealed a reduced (i.e., 4- or 5-fold) first shell coordination environment for adsorbed Zn²⁺ with respect to the 6-fold coordination found for aqueous species at pH 8. Octahedral to tetrahedral coordination geometry changes have previously been observed for adsorbed Zn²⁺ ions, although this was not well understood. It could, for instance, be due to the interfacial charge distribution and reduced interfacial dielectric constant, which might be significant enough to overcome the



Authors (from left to right), Neil Sturchio, Paul Fenter, Zhan Zhang, Michael Bedzyk, and Jeffrey Catalano.

relatively small energy differences between the ion's two coordination environments. DFT calculations revealed that this transformation was favored energetically and was directly coupled to surface induced hydrolysis of the hydrated Zn^{2+} cation. Very good agreement between all experimental and computational results is achieved when comparing the predicted and observed Zn^{2+} adsorption structures and coverage. Ball-and-stick models for the two adsorption geometries based

on the DFT results are shown in **Figure 2**.

These results demonstrated that a multi-technique approach, including structural and spectroscopic measurements and high-level DFT theory, allow for a complete characterization of the adsorption of ions at the oxide-water interface, even when the actual structure involves numerous complexities, including multiple adsorption sites, changes in the ion hydration shell

structure, as well as hydrolysis of the adsorbed species. Comparison of such results with macroscopic pH-titration/adsorption studies of powder suspensions and large-scale molecular dynamics simulations leads to definitive information on the molecular structure of sorbed species at the oxide-water interface, as well as realistic models to rationalize and accurately predict the macroscopic manifestations of ion adsorption phenomena.

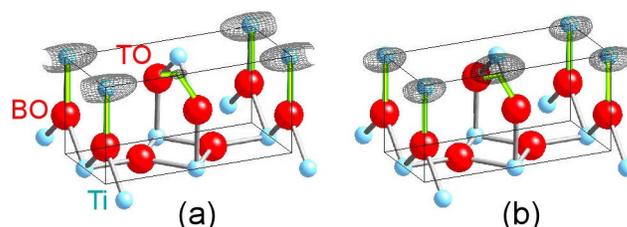


Figure 1. XSW generated 3D iso-density contour surfaces for Zn^{2+} cations at (a) pH 8, and (b) pH 6. The iso-density contour surfaces at 65% of the peak element density are plotted overlapping with the reference ball-and-stick model of a half rutile surface unit cell terminated at the Ti-O basal plane.

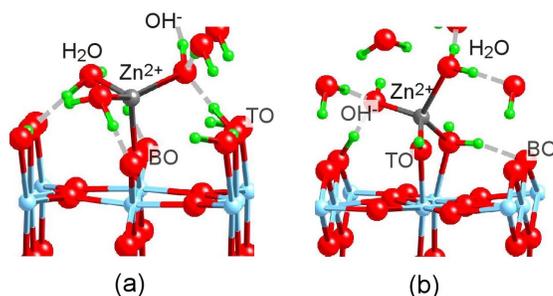


Figure 2. Adsorption geometry of adsorbed Zn^{2+} cations at the TiO_2 rutile (110)-aqueous interface. Two distinct adsorption geometries are observed: (a) monodentate above the bridging oxygen and (b) bidentate between terminal oxygens. Hydrogen bonds are represented with dashed lines.