Probing the double-layer structure at the rutile-water interface with x-ray standing waves

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Introduction

Although the ion distribution near solid-liquid interfaces [known as the electrical double layer (EDL)] has been studied for nearly 150 years, progress in understanding its structure has been limited by the lack of techniques that can probe extended structures at the liquid-solid interface [1]. In this study, we demonstrate the use of the x-ray standing wave (XSW) technique to reveal important aspects of the EDL structure (shown schematically in Fig. 1), including the locations of ions in the condensed layer and the partitioning of ions between the condensed and diffuse components of the EDL [2].
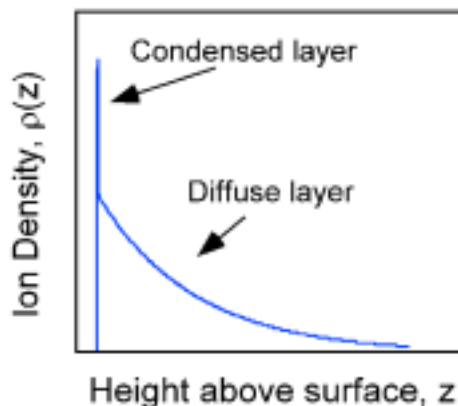

Figure 1: Important aspects of the EDL structure (shown schematically) including the locations of ions in the condensed layer and the partitioning of ions between the condensed and diffuse components of the EDL.

Methods and Materials

The TiO$_2$ polymorph rutile has been studied extensively and is known to be chemically stable over a broad range of pH values. Experimental solutions were prepared by dissolving reagent-grade RbCl, RbOH, and Sr(NO$_3$)$_2$ in nanopure deionized water. Solution pH values, adjusted by using HNO$_3$ and NaOH, ranged from 2.98 to 10.92. Solution ionic strengths ranged from 590 to 4240 mM. Rb was exclusively present as Rb$^+$ in all solutions, and $\geq$ 98.5% of Sr was present as Sr^{2+}.

The Bragg diffraction XSW technique has been described previously [3, 4]. An XSW field is generated by a coherent superposition of the incident and reflected x-ray beams during Bragg diffraction. The XSW period is equal to the d-spacing of the diffraction planes, and the position of the XSW antinodes shifts inward by d/2 relative to the diffraction planes as the incident angle, θ, is scanned through the Bragg reflection. The atomic distribution (characterized by the coherent position and coherent fraction, respectively) is determined by monitoring the modulation of the fluorescence yield of a specific atomic species near the Bragg condition.

Results and Discussion

In situ XSW measurements for Sr^{2+} and Rb$^+$ ions at the rutile (110)-aqueous interface are summarized in Fig. 2 for a range of Sr and Rb concentrations at alkaline pH where the rutile (110) surface is negatively charged. The data clearly show a well-defined coherent fraction for both Sr^{2+} and Rb$^+$ ions, albeit at very different solution concentrations. The significant value of the measured coherent fraction directly implies that both of these ions are specifically adsorbed to the rutile (110) surface.
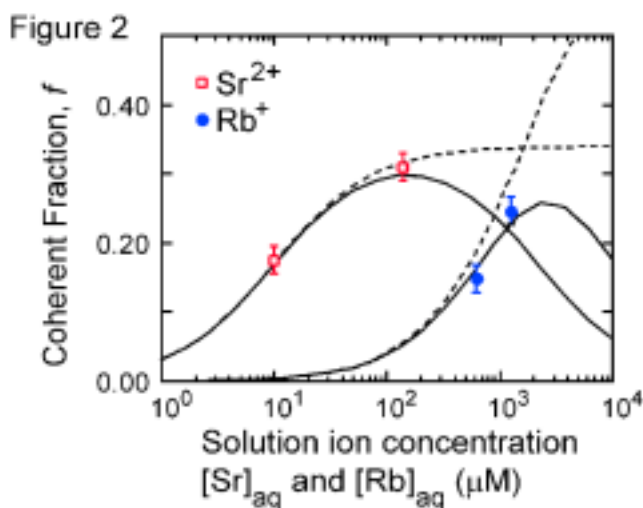

Figure 2: *In situ* XSW measurements for Sr^{2+} and Rb$^+$ ions at the rutile (110)-aqueous interface summarized for a range of Sr and Rb concentrations at alkaline pH.

An interesting feature of the data in Fig. 2 is that the small but significant measured coherent fraction increases with the cation solution concentration. To understand this result, we note that the experimental coherent fraction, F_{exp}, of the EDL is the weighted average of the geometrical factor, a_H, of

the ions in the condensed, diffuse, and bulk layers. If we assume a diffuse ion distribution based on the Gouy-Chapman model, the measured coherent fraction for the EDL can be written as equation 1:

$$F_{exp} = \Theta_c \, a_H/(\Theta_c + \Theta_d + \Theta_{bulk}) \approx \Theta_c/(\Theta_c + \Theta_d), \quad (1)$$

where Θ_i are the projected coverages of the condensed (c), diffuse (d), and bulk solution layers. Consequently, the variation of the measured coherent fraction reflects the changes in the EDL partitioning between the condensed and diffuse layers.

Additional measurements of the condensed layer structure are derived from the coherent position (which is sensitive to the condensed layer structure of the EDL), measured both *in situ* and *ex situ*. These results show that the mono- and divalent ions of Sr and Rb are located at different heights above the rutile surface. By coupling these measurements to *ex situ* surface extended x-ray absorption fine structure (SEXAFS) measurements, we have also derived a detailed description of the Sr adsorption structure that suggests a tetradentate adsorption geometry.

Acknowledgments

References

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