

Adsorption of oxalate on rutile to 150°C: Experimental and surface complexation modeling studies

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Chemical interactions occurring at the interface of mineral surfaces and aqueous solutions impact a broad range of geochemical and environmental process, materials and chemical sciences, and technological processes. Consequently, solid-solution interfaces have been studied broadly, with the majority of studies conducted at room temperature. However, numerous mineral–aqueous solution interactions of interest in the geosciences and for technological applications take place at elevated temperatures. For rutile (α -TiO₂) extensive experimental studies have examined the surface protonation and cation adsorption into the hydrothermal regime (10–250°C). Additionally, the CD-MUSIC model has been used as a framework to integrate molecular-scale information to rationalize cation adsorption to 250°C. In contrast, limited data are available for the adsorption of anions, specifically organic anions, as a function of temperature.

This contribution will build on the hydrothermal cation adsorption data by presenting macroscopic pH titration data examining the adsorption of oxalate on rutile from 10 to 150°C, in NaCl media. Comparable to cation adsorption on rutile, oxalate increases the development of proton charge curves; moreover, oxalate adsorption is enhanced at elevated temperature. At all temperatures, adsorption of oxalate commences at pH above the p*H*_{znp}c value. All experimental results were rationalized using a CD-MUSIC model combination. Application of the CD-MUSIC model considered available data providing coordination geometries for oxalate/bioxalate–rutile interactions derived from theoretical and spectroscopic studies. Additionally, changes in oxalate/bioxalate surface speciation as a function of pH were evaluated. The present study successfully extends the application of the CD-MUSIC model to elevated temperatures for rationalizing organic anion adsorption behavior.