A comparative thermochemical study of ion exchange at metal oxides-solution interfaces using flow microcalorimetry

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Surface charge development at interfaces between metal oxides and aqueous solutions play a fundamental role in environmental, geological, and technological settings. Our ability to harness metal oxides potential in technological applications and safeguard the future of our environmental resources under realistic conditions hinges on our ability to adequately model the entire suite of interfacial chemical reactions (ion exchange, protonation, adsorption, etc.) that contribute to, and is influenced by, the development of surface charge. A host of theoretical principles, experimental techniques and computational methods have been utilized to study the complex spectrum of interfacial reactions. Yet conspicuously missing are thermodynamic data, specifically those coming from direct calorimetric measurements. The literature on energetics and enthalpies (ΔHs) of surface reactions remains scarce despite the usefulness of thermodynamic data in linking molecular-level structure with the macroscopic properties of charge development. By using flow microcalorimetry to measure the enthalpies of ion exchange (ΔH_{exch}) as a direct probe of surface charge across various surfaces and using different 1:1 electrolytes, this study aims to investigate the role of i) surface bulk dielectric constants (ε_s), ii) electrolytes distance parameters (radii), and iii) surface functional groups acid dissociation constants (pKas). The two general groups of surfaces chosen for this study are metal oxides and phyllosilicate minerals. The ΔH_{exch} will be obtained using 50 mM solutions of the electrolytes held at constant pHs, chosen to cover a range of surface charging behaviors. Some initial data shows a close similarity in the ΔH_{exch} measured using Cl and NO_3 on Al- and Fe-oxides, surfaces with intermediate ε. On Si-oxides, preliminary data seems to indicate that ΔH_{exch} will vary with the chemical properties of the cations used. Further trends in measured ΔH_{exch} will be noted and interpreted in light of the above mentioned factors. This thermochemical data set will be a great complement to theoretical and modeling studies of surface charge development on metal oxides.