A comparative study of the energetics of alkali and alkali metal cation exchange reaction on rutile, quartz and Mxene surfaces using immersion and flow calorimetry

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In this study, the heats of exchange (Q_{exch})associated with Li^+, Na^+, and K^+, as well as with Mg^{2+}, Ca^{2+} and Ba^{2+} on Rutile (α-TiO_2), Quartz (α-SiO_2), and MXene ($Ti_3C_2T_x$) have been measured using two calorimetric techniques: flow adsorption microcalorimetry and immersion calorimetry under the same experimental condition (i.e. pH, ionic strength and pCO_2). The goal of this work was to compare data set obtained from different calorimetric techniques and different solids to investigate potential similarity that may prove useful for further studies. Results showed that on all three surfaces Q_{exch} are strongly correlated to the differences in the bulk solvation enthalpies (ΔH_{solv}) between the incoming exchanging cation and that of the desorbing cation from the surface. These strong correlations highlight the role of hydration properties in cation exchange reactions on all three solids and point to a potentially unifying trend for these reactions. When normalized to the mole of metal in the structure (Ti for Rutile and Mxene, and Si for quartz) , Q_{exch} for both quartz and rutile surfaces were of the same magnitude while those for MXene were significantly larger (by ~ 44X) than those on rutile. This difference seems to be related to the intercalation of cations between the MXene layers and will be further investigated The lack of differences between rutile and quartz, solids with markedly different charge properties, highlights the strong control the aqueous phase exerts on interfacial reactions

Comparing results from the two calorimetric techniques (flow and immersion) showed that Q_{exch} were similar in magnitude albeit there were some differences in the signs of the calorimetric heats that will be further explored.