

Relationship between ionic strength and the proton interaction of clay minerals

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The fine-grain size and large surface area of clay minerals makes them an important solid phase in catalyzing organic and inorganic reactions in aqueous environments. Specifically, it is their surface reactivity and adsorption capacity for both metal cations and anions over a wide range of environmental pH conditions that makes them critical to consider in environmental remediation. The aqueous environment, ionic strength will also influence the adsorption behavior of metals and organics. In this study, we investigate variations in the point of zero proton net charge (PZNPC) and acidity constants (K values) of three clays (kaolinite, illite and montmorillonite) at seven ionic strengths (ranging from 0.001M to 0.1M) in order to characterize the relationship between the PZNPC, the K values, site concentrations and ionic strengths for the three clays. Two methods for calculating PZNPC were used to assess how changes in ionic strength impact the PZNPC. Nonelectrostatic surface complexation models were employed to calculate the site concentrations and acidity constants for each clay. The results show that the PZNPC of clay minerals changes linearly with the logarithm of ionic strength, with the PZNPC of kaolinite, illite and montmorillonite ranging from 6.67 to 5.67, 9.23 to 8.84, and 9.76 to 9.60, respectively. The second method generally agrees with the range of PZNPC of the first method, with values of 6.65 to 5.53, 9.79 to 9.20, and 10.14 to 9.99 for kaolinite, illite and montmorillonite, respectively. We define the K values of the permanently charged site and amphoteric site as K_a (permanently charged site), K_{a+} (protonation of amphoteric site), and K_{a-} (deprotonation of amphoteric site). We further demonstrate that there is a linear relationship between the acidity constants and logarithm of ionic strength. The $\log K_a$ values ranges from -10.1 to -9.6, -6.3 to -5.5, and -6.0 to -5.5 for kaolinite, illite and montmorillonite, respectively. For the amphoteric site, the K_{a-} values range from -7.7 to -6.5, -11.4 to -10.4, and -11.1 to -10.6 and the K_{a+} values range from 4.7 to 5.6, 9.5

to 9.8, and, 9.8 to 10.1 for the above clays respectively. Collectively, our data suggest that knowing the ionic strength of an environment and its corresponding effect on the surface reactivity of clay minerals is critical to realizing their full range of potential during environmental remediation work.