Interpretation of the Variability of Selectivity Coefficients for Exchange Between Ions of Unequal Charge on Smectites[1]

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Abstract: Ion-exchange experiments in expanding clay minerals conducted over a wide range of surface ionic compositions and ionic strength produce variable mass-action selectivity coefficients. When the exchanging ions are of unequal charge, tactoid structure appears to influence selectivity, although configurational entropy of adsorbed ions may also generate variable selectivity. The degree of deviation from ideal mass-action exchange is related to the dissimilarity of the ions undergoing exchange. Data involving trivalent ion adsorption on smectites suggest that mass-action is a poor approximation when the adsorbing and desorbing ions have different hydration energies and charge. No form of exchange equation is successful in describing ion exchange for a wide range of experimental conditions, although the fluctuation of the selectivity coefficient follows consistent trends with changing experimental conditions. The strong adsorption of high-charge ions on clays is not exothermic, but must be driven by the increasing disorder of ions and/or water.

Key Words: Cation exchange • Cation selectivity • Entropy • Mass action • Selectivity coefficient • Smectite

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