

KINETICS AND MECHANISMS OF ION EXCHANGE ON SOIL CONSTITUENTS (POTASSIUM, THERMODYNAMICS, INTRAPARTICLE DIFFUSION)

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Abstract

A study was conducted to evaluate kinetics methodologies and the feasibility of using kinetics to determine thermodynamic parameters for K-Ca exchange on soils and clay minerals. Additionally, the elucidation of rate-limiting steps for ion exchange was performed using different kinetics techniques. Thermodynamic parameters using the Argersinger (mole fraction) and Gaines and Thomas (equivalent fraction) conventions were compared, in magnitude and trend. Selectivity coefficients and surface phase activity coefficients using the two conventions did not compare in magnitude, however, they showed similar trends when these coefficients were reduced to common thermodynamic parameters, such as the equilibrium constant K_c and the standard free energy ΔG° of exchange, the two conventions not only resulted in similar inferences on ion behavior but also in the same magnitude of values at a given temperature. To evaluate the use of kinetics to determine thermodynamic parameters, the Argersinger convention was employed for the equilibrium approach while a kinetics approach was studied using miscible displacement, batch and vortex mixed batch techniques. Except for the vigorously mixed vortex method, the thermodynamic parameters for the two approaches did not compare. However, when diffusion was greatly reduced as the rate-limiting step, as with the vigorously mixed vortex method, the data indicated that a kinetic approach can be successfully used to gather thermodynamic information about ion exchange processes. The order of reduction of the influence of diffusion on K-Ca exchange by the kinetic methods evaluated was: vortex > batch = stirred > miscible displacement > static. Using an additive resistance relations model, rate-determining steps under static conditions were elucidated. Both film and intraparticle diffusion were found to be rate-determining on vermiculite. In kaolinite and the Chester soil, film diffusion was the rate-limiting step.