Thermodynamic Study of Na-K-Ca Exchange Reactions in Vermiculite

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Abstract: The exchange of Na, K, and Ca ions in vermiculite has been studied between 50 and 150 ° C at a total normality of 0.1. The free energy changes were negative in the Na → K, Ca → K, and Na → Ca exchange reactions, and the cation preference in the vermiculite was Na < Ca < K in the temperature range examined. The enthalpy changes, calculated by application of the van't Hoff equation to the relation between equilibrium constant and temperature, were positive. The cation preference in the vermiculite seems to have been largely controlled by the increase in entropy which was due to the positive values of the entropy change term in the solid for the Na-K and Ca-K exchanges and the positive values of the entropy change in the solution for the Na-Ca exchange. From a thermodynamic analysis of the cation-mixing properties in vermiculite, the observed free energy change in the Na-K exchange was determined solely by the differences of the intrinsic electrostatic binding energy of the cations on the clay surface. That in the Na-Ca exchange was interpreted by taking into account an extra interaction energy of Ca-Ca pairs in addition to the intrinsic energy change. Furthermore, an additional interaction energy between K ions and the clay surface appears to have been added to the free energy change in the Ca-K exchange. In the Na → K and Ca → K exchange reactions a structural modification occurred in the K-equivalent fraction ($X\text{-}\square_K$) range 0.05 − 0.6, and a regularly interstratified phase of 15-Å and 10-Å members was formed at $0.05 < X\text{-}\square_K < 0.4$.

Key Words: Cation exchange • Entropy • Free energy • Interstratification • Thermodynamics • Vermiculite

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