Calcium-Magnesium Exchange in Montmorillonite and Vermiculite*

Rachel Levy and I. Shainberg

Division of Soil Physical Chemistry and Head, Division of Soil Physical Chemistry, Volcani Institute of Agricultural Research, Bet Dagan, Israel

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Abstract: An experimentally determined Ca-Mg exchange isotherm of montmorillonite is reported. The selectivity coefficient of this exchange over a wide range of Mg saturation was calculated and found constant.

Standard free energies of exchange, thermodynamic equilibrium constants and activity coefficients of the exchangeable Ca and Mg ions in vermiculite and montmorillonite, were predicted from knowledge of the microstructure of these two clays, assuming that coulombic forces are the main ones playing a role in the interaction between the counterions and the charged clay surface. The standard free energies of exchange ($\Delta G^{\circ}{}_{Ca}^{Mg}$ = 238 cal/mole) predicted a preference for Ca in montmorillonite and a preference for Mg in vermiculite ($\Delta G^{\circ}{}_{Ca}^{Mg}$ = −1665 cal/mole). The predicted thermodynamic equilibrium constants were compatible with the experimentally determined selectivity coefficients $K_{Ca}^{Mg} = 0 \cdot 67$ as compared with $K_{sCa}^{Mg} = 0 \cdot 68$ in montmorillonite, which remains constant over all the range of Mg saturation, and $K_{Ca}^{Mg} = 16 \cdot 7$ as compared with $K_{sCa}^{Mg} = 13 \cdot 9$ in vermiculite at 95% Mg saturation. The activity coefficients of Ca and Mg counterions in montmorillonite were found to be fCa = $2 \cdot 0 \times 10^{-3}$ and fMg = $2 \cdot 2 \times 10^{-3}$, respectively, and to remain constant. The activity coefficients of exchangeable Ca and Mg in vermiculite were found to be fCa = $7 \cdot 1 \times 10^{-5}$ and fMg = $3 \cdot 5 \times 10^{-5}$, respectively, at an equivalent fraction of unity. The activity coefficient of exchangeable Mg increased as the saturation with Mg decreased, and was found to be $1 \cdot 7 \times 10^{-3}$ in the range of the low Mg saturation.

The microstructure, the isomorphic substitution and the surface charge density provided an understanding of the changes taking place in the activity coefficients of the counterions.

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