

THE EFFECT OF HYDROXY-ALUMINUM PRECIPITATION ON THE EXCHANGE PROPERTIES OF MONTMORILLONITE¹

Key Words—Cation Exchange, Hydroxy-aluminum Precipitate, Interlayer Precipitate, Montmorillonite, Selectivity Coefficient, Tactoid.

The exchange isotherms of Na-Ca on montmorillonite were determined by Banin (1968). It was found that the selectivity coefficient was not constant but changed with the relative fraction of the adsorbed ions. Banin associated this variation with the structural properties of the mineral, namely, tactoid formation in the calcium state, and the presence of different exchange sites affecting the energy of exchange. Shainberg and Kemper (1966) calculated that the affinity of the internal surface of calcium is 2–4 times greater than that of the external surface. As long as the platelets were completely separated, the two ions were randomly distributed in the exchange complex. When tactoids formed, demixing took place, and the sodium ions concentrated on the external surfaces of the packets (Mering and Glaeser, 1953; Shainberg and Otoh, 1968).

When suspensions of montmorillonite were titrated with Al-salt and base, Al precipitated as hydroxy-aluminum complexes (Weismiller *et al.*, 1967). Results of X-ray powder diffraction showed that at least some of these precipitates occurred as interlayers between the clay platelets (Rich, 1960; Barnhisel and Rich, 1963; Keren *et al.*, 1977). A number of workers have reported a reduction in cation-exchange capacity (CEC) of clays following the formation of Al-interlayers (Rich, 1960; Shen and Rich, 1962; Frink, 1965; Carstea, 1968; Keren *et al.*, 1977).

In addition to altering the exchange capacity of the clay, such interlayers may affect the *selectivity* properties of the clay surface. The present investigation was undertaken to determine the effect of hydroxy-Al interlayers on the selectivity coefficient at Na-Ca exchange of the clay mineral montmorillonite.

EXPERIMENTAL

Hydroxy-Al interlayer preparation

A sample of Wyoming montmorillonite (API reference clay mineral No. 25), obtained from Ward's National Science Establishment, was used. The <2- μ m particles in the calcium form were prepared by the method described by Keren *et al.* (1977). Aluminum chloride was added to the suspensions at the rate of 16 meq/g of clay. The 16-meq/g rate provides sufficient precipitate to cover the clay surface (Keren *et al.*, 1977). Hydroxy-Al precipitates were formed by adding 0.5 N NaOH solution at the rate of 0.2 ml/min with a syringe pump (Sage Instruments, Model 355) to a continuously stirred suspension containing 1 g clay. The hydroxy-Al precipitates were prepared at OH/Al mole ratios near 2.80 and pH 7.5 (Keren *et al.*, 1977). After the addition of NaOH, the volume was adjusted to 100 ml and the mixture was shaken continuously for an additional 6 hr. The clay-hydroxy-Al complexes were not allowed to dry.

CEC determination

The CEC of the clay was determined by Na²² analysis using a Packard Instrument Co. 5000 series Auto-Gamma spectrometer system. The CEC of the clay and of the hydroxy-Al-clay complexes was determined by washing with Na²²-labeled 0.1 N NaCl having a known c/min of Na²² per meq Na, washing

out the excess NaCl with ethanol, and counting the Na²² remaining on the clay. The CEC was based on the dry weight of the clay at 110°C, not including the weight of the hydroxy-Al precipitate. The CEC of the pure clay and of the clay-hydroxy-Al complex was 0.90 and 0.31 meq/g, respectively.

Ion-exchange isotherms

Samples of montmorillonite and montmorillonite-hydroxy-Al complexes were equilibrated with Na²²-labeled NaCl and CaCl₂ at various ratios at a total concentration of 0.1 N. The isotherms were studied at 25 \pm 1°C. The amount of Na that adsorbed on the clay at equilibrium was determined by counting the Na²² remaining on the clay, knowing the c/min of Na²² per meq Na, the volume and concentration of the solution that remained on the clay after centrifugation, and the amount of clay in the sample.

Since the pH of the equilibrium solution was 7.5, the net charge of the hydroxy-Al precipitate was apparently minimal; thus, the CEC of the hydroxy-Al precipitate was negligible, compared with the CEC of the clay.

RESULTS AND DISCUSSION

The Na-Ca exchange isotherms and the selectivity coefficient for the pure clay and for the clay-hydroxy-Al complexes are given in Figures 1 and 2, respectively. The selectivity coefficient, K_{Ca}^{Na} , is defined as

$$K_{Ca}^{Na} = \frac{\bar{X}_{Na}^2 \cdot X_{Ca}}{\bar{X}_{Ca} \cdot \bar{X}_{Na}^2} \quad (1)$$

where X and \bar{X} are the equivalent fractions of the cations in the solution and in the clay, respectively.

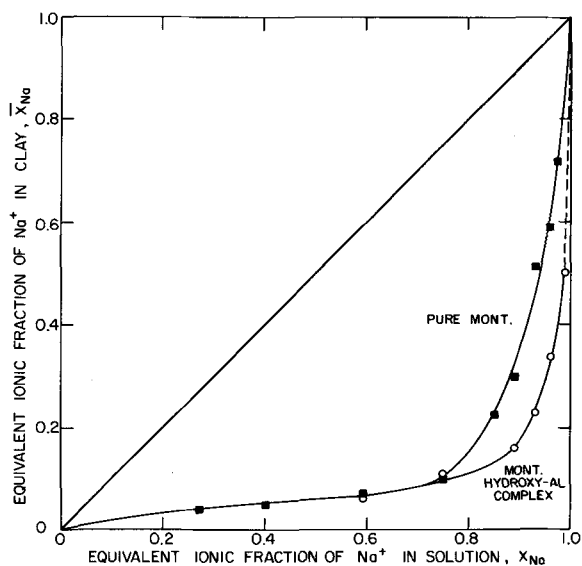


Figure 1. Na-Ca exchange isotherms of a montmorillonite and montmorillonite-hydroxy-Al complex at a total salt concentration of 0.1 N.

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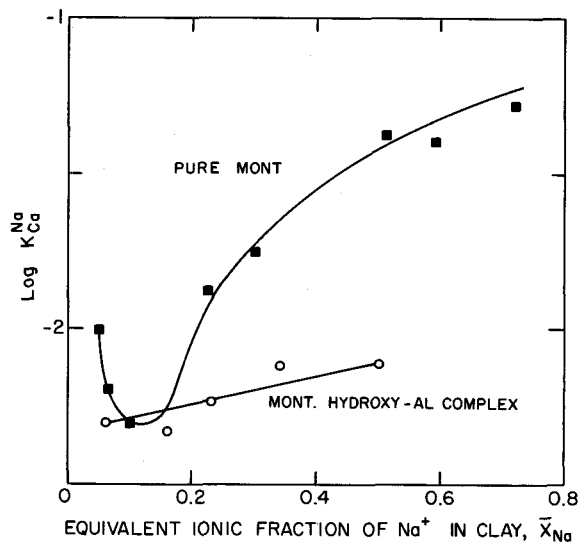


Figure 2. Selectivity coefficient, K_{Ca}^{Na} , as a function of the equivalent ionic fraction of sodium in a montmorillonite and montmorillonite-hydroxy-Al complex.

The results indicate that the calcium was strongly preferred by the clays. This was as predicted from Donnan's equilibrium considerations for a di-monovalent ion exchange (Helfrich, 1962). The preference of the montmorillonite-hydroxy-Al complex for calcium was greater than that of pure montmorillonite in the range $X_{Na} > 0.2$. The selectivity coefficient for the pure clay was not constant; it changed with the sodium ion fraction in the clay and had a minimum in the range $0.1 < X_{Na} < 0.2$. This variation can be attributed to the structural properties of the mineral, namely, tactoid formation in the Ca state and the presence of different exchange sites affecting the energy of exchange (Banin, 1968). The minimum in the selectivity coefficient occurred when the monovalent ion content was equal to the exchange capacity of the outer surface of the tactoid. It was found that the breakdown of the tactoids started at this point (Shainberg and Otoh, 1969; Bar On *et al.*, 1970). Introducing more sodium ions into the exchange complex increased the space between the platelets, and finally they separated from each other. Since the affinity of the internal surfaces for calcium was 2–4 times greater than that of the external surfaces (Shainberg and Kemper, 1966), the preference for monovalent ions increased as more and more plates were separated. Whereas the selectivity coefficient for the pure clay was not constant, the change for the clay-hydroxy-Al complex was very small. Since the selectivity coefficient of the clay-hydroxy-Al complex was similar to the selectivity coefficient of the pure clay in the minimum point, this may indicate that tactoids are formed in montmorillonite when a hydroxy-Al interlayer is present and when those tactoids are stable along the isotherm. The gradual increase in the selectivity coefficient with the equivalent ionic fraction of ex-

changeable sodium was probably due to the increase in the space between the platelets of a small portion of the tactoids where the interaction between the interlayer precipitate and the clay surface was weak. It is also possible that a small portion of the tactoids was essentially without an interlayer, and thus the introduction of sodium into the exchange complex may have broken the packets down, increasing the selectivity coefficient.

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