MIXING-DEMIXING BEHAVIOR OF CALCIUM-ETHYLAMMONIUM MIXTURES IN OTAY MONTMORILLONITE

Evidence for demixing of exchange ions in smectites is generally based on or supplemented by X-ray powder diffraction measurements showing the occurrence of (1) a random interstratification over the whole (Mortland and Barake, 1964) or part of the surface composition range (McBride and Mortland, 1973, 1975; Barrer and Brummer, 1963), or (2) two distinct phases (segregation), each with its own characteristic spacing. The main variables involved in demixing are (1) the location and distribution of the exchange sites, (2) the structure and hydration properties of both exchangeable cations, and (3) the structure of the interlamellar (hydrated) exchangeable cation complex. Thus, in general, the very different interaction of the two cations with the silicate framework induces their demixing into interlayers rich in each cation.

On the other hand, such differences in interaction of the exchangeable cations with the negatively charged silicate surface may be considered responsible (at least in part) for the changes of their ion-exchange selectivity with composition (Barrer and Klinowski, 1979).

The purpose of the present study is to verify the possible relationship between the occurrence of demixing and the selectivity behavior of the cation pair calcium-ethylammonium. The choice of the cations is dictated by the ability to measure demixing in that a sufficient difference in spacing for both cationic forms must exist. A montmorillonite with high charge density (Otay) was used to allow comparison with literature data on lower charged bentonites.

EXPERIMENTAL

The <0.5-μm fraction of Na-montomorillonite (Otay, California, API No. 24) was thoroughly exchanged with Ca^{2+} and ethylammonium ($ETNH_3^+$). Salt-free homoionic suspensions (1% clay content) were obtained by dialysis, mixed in different proportions, and equilibrated by end-over-end shaking for 1 week. The samples were subsequently supercentrifuged and the supernatants discarded. Part of the homogenized centrifugate was transferred into small glass capillaries which were sealed immediately with a small torch and mounted in a Debye-Sherrer camera. The remaining part of the centrifugate was dried in air on glass plates, powdered in a mortar, and introduced into capillaries left open at one end. These samples were heated under vacuum at 60°C for 1 hr and then at 120°C overnight; they were then sealed and transferred to the Debye-Sherrer camera. $CuK\alpha$ radiation from a Siefert-Scintag X-ray diffraction apparatus was used for X-ray powder diffraction (XRD) examination.

A second series of XRD measurements was taken on samples prepared by overnight ion exchange of a 1% suspension of the Ca-exchanged smectite at 0.01 N $Ca(NO_3)_2$ with $ETNH_3^+$ solutions ranging in concentration from 5×10 to 2×10^{-2} M. The centrifugates were homogenized and examined by XRD in the wet and dry states as above. The amount of $ETNH_3^+$ adsorbed was measured in a duplicate experiment using ^{14}C-labelled $ETNH_3^+$.

RESULTS AND DISCUSSION

Figure 1 compares the d(001) spacings of the samples (wet and dry) obtained by direct ion exchange and by mixing salt-free suspensions. Below 60% $ETNH_3^+$ exchange (see Figure 1a), the 19.2-Å spacing corresponding to the pure Ca form was obtained, whereas above 60% $ETNH_3^+$ exchange, only the 13.2-Å spacing of the $ETNH_3^+$ form was observed. At 55 to 60% $ETNH_3^+$ loading a remarkably sharp transition zone was not-

ed, with reflections extending from 18.0 Å to about 13.0 Å (indicated by the vertical line in Figure 1a). These results indicate that homogeneous mixing occurred over almost the entire composition range, but with the special effect that each cation forced the other to adapt to its own characteristic state of swelling beyond exchange levels of 40% (Ca^{2+}) or 60% ($ETNH_3^+$).

In the samples obtained by one-week mixing of salt-free suspensions (see Figure 1c), both the Ca^{2+} and the $ETNH_3^+$ spacing were observed between 40 and 80% $ETNH_3^+$ content, indicating that demixing persists into crystallites which were already present in the original salt-free suspensions. Two conclusions may be drawn from these data:

(1) Both spacings may be detected together in the same pattern. In the direct ion-exchange experiment (Figure 1a) both spacings were *not* present together, thereby supporting the thesis of homogeneous mixing in the samples prepared by direct ion exchange.
(2) Preparations of clay mixtures from salt-free suspensions of the end members may lead to inhomogeneous cation distributions.

In contrast, drying the centrifugate from the ion-exchange experiment led to the typical pattern of an interstratified system (see Figure 1b), also found by Mortland and Barake (1964) for the Ca^{2+}-$ETNH_3^+$ system. This pattern is only possible if a reorganization occurred at lower water contents resulting in a demixing of Ca^{2+}- and $ETNH_3^+$-rich layers. Such a process upon drying was invoked by Vansant and Uytterhoeven (1972) to explain the apparent contradiction between random interstratification of Na^+- and alkylammonium-rich layers observed in dry systems (Barrer and Brummer, 1963) and the thermodynamic analysis of the Na-alkylammonium ion-exchange data which pointed towards homogeneous mixing.

Upon drying of the salt-free suspensions (see Figure 1d) only a 12–12.4-Å spacing was observed between 40 and 80% $ETNH_3^+$ content, whereas spacings corresponding to both Ca^{2+}- and $ETNH_3^+$-rich layers were observed in the suspension state, indicating a decided tendency to reorganize into regularly interstratified layers. According to the data in Figures 1a and 1b, the cation distribution in the dry interlayer may differ from that at the clay held in suspension and is therefore of doubtful relevance to the understanding of ion-exchange behavior.

The hydration properties of the interlayer changed drastically at about 55–60% $ETNH_3^+$ content. For $ETNH_3^+$ rich compositions the interaction of water with Ca^{2+} was decidedly different from that at the Ca-rich end, as was also shown by McBride and Mortland (1975) for Cu-tetramethylammonium and Cu-tetrapropylammonium mixtures. The sudden change in interlayer hydration at about 55–60% $ETNH_3^+$ exchange is however, *not* accompanied by a sudden change in selectivity, which is clearly shown by the rather smooth increase of the selectivity coefficient with the Ca-exchange level (Figure 2).

Interstratification in suspension covers $\sim$70 and 20% of the composition range for the Cu-tetramethyl ammonium and Cu-tetrapropylammonium systems, respectively, in Upton Wyoming montmorillonite (McBride and Mortland, 1975), but disappeared in our Ca^{2+}-$ETNH_3^+$ systems with Otay montmorillonite. Therefore, demixing is more likely to occur with increasing cation-selectivity difference and with increasing heterogeneity in charge distribution. Indeed, the Ca^{2+}-$ETNH_3^+$ selectivity is smaller than the Ca^{2+}-quaternary ammonium selectivity (Maes *et al.,* 1980), and Otay montmorillonite has a
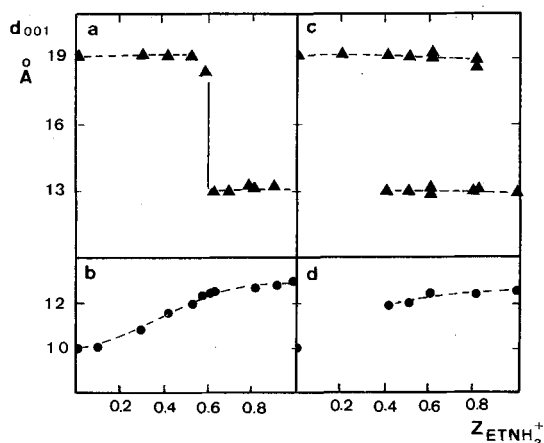
Figure 1. Variation of the d(001) spacings with the $ETNH_3^+$ fraction in wet (▲) and dry (●) mixtures of $Ca^{2+}ETNY_3^+$ Otay montmorillonites obtained from ion exchange (a and b) and by mixing the salt-free suspensions of the end members (c and d).

Figure 2. Natural logarithm of the $ETNH_3^+$-Ca^{2+} selectivity vs. the $ETNH_3^+$-occupancy in Otay montmorillonite. The Davies equation (Davies, 1962) was used to correct for solution-phase activity coefficients.

more homogeneous charge distribution than the lower charged montmorillonites (Maes *et al.*, 1979).

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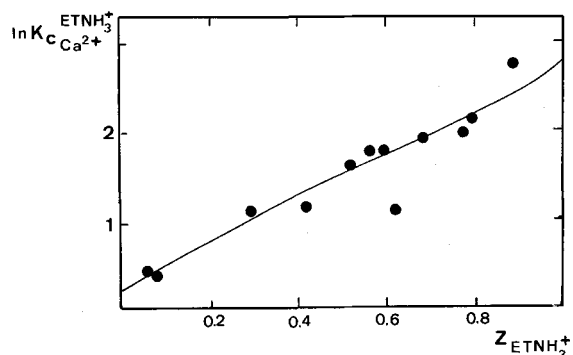
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