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FORMATION OF HIGHLY SELECTIVE CESIUM-EXCHANGE SITES IN MONTMORILLONITES

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Abstract—Ion-exchange sites with very high selectivity for Cs ($\Delta G^{Cs^+}_{Ca^{2+}}$ = 40 kJ/eq) similar to illite were generated in a controlled way in montmorillonites by (1) repeated wetting-drying cycles and by (2) charge reduction using the Hofmann-Klemen effect. An almost continuous range of sites with selectivities varying from $\ln K^{Cs^+}_{Ca^{2+}} = 33$ to 5 was observed.

Key Words—Cation exchange, Cation selectivity, Cesium, Hofmann-Klemen effect, Montmorillonite, Wetting-drying.

INTRODUCTION

A small fraction of the cation-exchange capacity of illites and micas is known to be selective for cations of low hydration energy such as Cs, Rb, and K. Very high affinities for Cs in clay minerals have been assigned to the presence of collapsed (10-Å) layers, either naturally present (illite) (Sawhney, 1972 and references therein) or induced, e.g., by heating montmorillonite to 600°–700°C (Tamura, 1964). The crystallographic nature of the different sites is uncertain. At least three types of sites, interlayer-edge, interlayer, and outer basal-surface sites, of decreasing selectivity have been proposed to explain the Cs (Brouwer *et al.,* 1983; Sawhney, 1972) and K (Sawhney, 1972; Bolt *et al.,* 1963) selectivity of illite.

Brouwer *et al.* (1983) demonstrated that the observed high selectivity of illite corresponds to thermodynamically reversible ion-exchange reactions rather than to a sometimes-mentioned irreversible fixation. The exchange of Cs^+, Rb^+, K^+ vs. Ca^{2+}, Sr^{2+}, Ba^{2+}, or Na^+ was described in terms of three sites each showing a characteristic exchange selectivity for the different exchanging pairs. A very small number of sites (0.1 meq/100 g) showed an exceedingly high selectivity for Cs^+ with respect to Ca^{2+} (40 kJ/eq) and rather strong selectivity differences between Cs^+ and Rb^+ (6 kJ/eq). The second site (0.6 meq/100 g) exhibited an intermediate selectivity for Cs^+ (17 kJ/eq) and did not discriminate between Cs^+ and Rb^+. The remainder of the cation-exchange capacity was assigned to the sites on the basal surfaces of the clay; they showed the usual Cs^+-Ca^{2+} selectivity (5.7 kJ/eq).

In an attempt to unravel the nature of the high-energy sites, we report here the progressive creation of high selectivity sites in montmorillonite by various wetting-drying and charge-reduction pretreatments.

EXPERIMENTAL

Two series of montmorillonites with increasing amounts of high-energy sites were prepared as follows:

(1) By prolonged alternate wetting and drying (W-D cycle) of K^+-montmorillonite, the turbostratic structure of montmorillonite disappears and a three-dimensional mica-like mineral is created (Gaultier and Mamy, 1978; Plançon *et al.,* 1979). The degree of reorganization of swelling montmorillonite into a collapsed, more ordered mica-like structure depends on the number of W-D cycles and also on the layer charge of the smectite (D. D. Eberl, U.S. Geological Survey, Denver, Colorado, personal communication, 1985). A series of montmorillonites was prepared in this manner in which an increasing amount of high-energy sites formed because of the development of an increasing number of collapsed layers (structurally comparable to illite) are formed.

(2) A second series of montmorillonites was prepared in which the charge was reduced by Li^+ incorporation after 24 hr heating at 240°C, a process which is known as the Hofmann-Klemen effect (Hofmann and Klemen, 1950).

The <0.5-μm fraction of Camp Berteau (C.B.) montmorillonite was separated and stored as a 2% suspension in 1 M $NaNO_3$.

(1) The Na-saturated montmorillonite was exchanged for K^+, dialyzed to 10^{-2} N KNO_3, and subjected to alternate wetting and drying cycles (W-D cycles). Clay suspensions (2%) were dried in air at 80°C in a furnace and ground in a mortar. Subsequently, the clays were redispersed to the original clay content (2%) by 24-hr stirring. Samples were with-

Table 1. ln K_c values and site-group capacities (meq/100 g) for simulating the Cs^+-Ca^{2+} equilibria at 25°C of potassium-exchanged Camp Berteau montmorillonite subjected to alternate wetting-drying cycles.

	ln $K_{c\,Ca^{2+}}^{Cs^+}$			
Wetting-drying cycles	Type I site 33.8	Type II site 25	Type III site 13.8	Type IV site 5
	Site-group capacity			
0	0.0002	0.005	0.1	110
2	0.007	0.012	0.4	104
5	0.015	0.012	0.4	98
10	0.02	0.02	0.8	74

drawn as suspensions after 0, 2, 5, and 10 W-D cycles, exchanged for Ca^{2+} using 0.05 M $Ca(NO_3)_2$ solutions, and dialyzed to 0.005 M $Ca(NO_3)_2$. Cs^+-Ca^{2+} and Rb^+-Ca^{2+} ion equilibria were measured at very low $Cs^+(Rb^+)$ occupancy (<1%) by mixing known volumes of the clay suspension with mixed solutions of Cs^+-Ca^{2+} or Rb^+-Ca^{2+} at 0.01 total normality. ^{137}Cs and ^{86}Rb were used for equilibrium distribution monitoring. Equilibrium was obtained by overnight end-over-end shaking at 25°C. The systems were centrifuged in a temperature-controlled centrifuge and the supernatant assayed radiometrically for either ^{137}Cs or ^{86}Rb.

(2) The K^+-montmorillonite was also dried (24 hr) at 500°C, subsequently exchanged for Ca^{2+} (0.05 M $Ca(NO_3)_2$), and dialyzed to 0.005 M $Ca(NO_3)_2$. The Cs^+-Ca^{2+} ion equilibrium was measured under conditions similar to those used for the W-D samples.

(3) Reduced-charge montmorillonites (RCM) were obtained by well-known methods (Maes and Cremers, 1977) which essentially consisted of exchanging a Na-saturated material with different levels of Li^+, freeze drying it, and heating it to 240°C for 24 hr. Portions of the samples were subsequently expanded in ethylene glycol and ethanol. They were then re-exchanged with Na^+ (in $NaNO_3$), washed salt free, and stored as freeze-dried powders. Samples were either used as such or were stored for 48 hr over NH_3 vapor before use. The latter procedure was reported to expand all collapsed layers (Farmer and Russell, 1967). Samples were then exchanged with Ca^{2+} using 0.05 M $Ca(NO_3)_2$, and dialyzed to 0.005 M $Ca(NO_3)_2$. The Cs^+-Ca^{2+} ion equilibrium was measured under conditions described above.

The Ca cation-exchange capacity (Ca-CEC) of the different clay samples was measured using isotopic dilution methods (^{45}Ca) (Peigneur *et al.*, 1975).

RESULTS AND DISCUSSION

K-montmorillonite subjected to various wetting-drying cycles

Submitting the K-exchanged montmorillonite to an increasing number of W-D cycles resulted in a decrease in its Ca-CEC from 1.1 (no W-D treatment) to 1.04 (2 W-D cycles), 0.99 (5 W-D cycles), and 0.74 (10 W-D cycles) meq/g (Table 1). These results are comparable to observations made on Wyoming bentonite by Gaultier and Mamy (1978) and Plançon *et al.* (1979) and can be explained by interlamellar K-fixation in collapsed (10-Å) clay layers. Because these clay layers failed to swell in water and consequently did not exchange for Ca, the Ca-CEC decrease can be used as a measure of clay layer collapse.

The Cs^+-Ca^{2+} and Rb^+-Ca^{2+} selectivity data are shown in Figures 1a and 1b, respectively, as a function of the log of the amount of $Cs^+(Rb^+)$ adsorbed in meq/100 g. Corrections for solution phase-activity coefficients using the Debye Huckel equating treatment are included and amount to about -0.16 in ln K_c terms (Cs^+ and Rb^+).

The general pattern of the selectivity curves is comparable to those found for the same equilibria in illite clay (Brouwer *et al.*, 1983) and indicate that different sites with widely different selectivities for Cs(Rb) were present. Increasing selectivities were observed with increasing number of W-D cycles in both the Cs^+-Ca^{2+} and the Rb^+-Ca^{2+} experiments. These phenomena were probably caused by the creation of increasing numbers of high selectivity sites which resulted from the reorganization of swelling montmorillonite into collapsed mica-like structures. The solid lines in Figures 1a and 1b correspond to a simulation of the selectivity profile using four different groups of sites, each group being characterized by its ln K_c value and its cation-exchange capacity. The data are summarized in Tables 1 and 2.

The model used to describe the selectivity profiles is the multi-site ion-exchange model of Barrer and Klinowski (1972). Using the equivalent fraction scale for the adsorbent, the M^+-M^{2+} selectivity in any site group i is defined as

$$_{M^{2+}}^{M^+}K_c{}^{i} = \frac{\overline{(M_i{}^+)^2}}{\overline{M_i{}^{2+}}} \cdot \frac{a_{M^{2+}}}{a_{M^+}{}^2},$$

in which bars indicate surface phases. The overall M^+-M^{2+} selectivity is:

$$_{M^{2+}}^{M^+}K_c{}^{overall} = \frac{(\Sigma X_i\overline{M_i{}^+})^2}{\Sigma X_i\overline{M_i{}^{2+}}} \cdot \frac{a_{M^{2+}}}{a_{M^+}{}^2},$$

in which X_i = equivalent fraction of the ith site group with respect to the total CEC, and $\overline{M^+}$, $\overline{M^{2+}}$ are the equivalent fractions of $M_i{}^+$ and $M_i{}^{2+}$ in the ith site group.

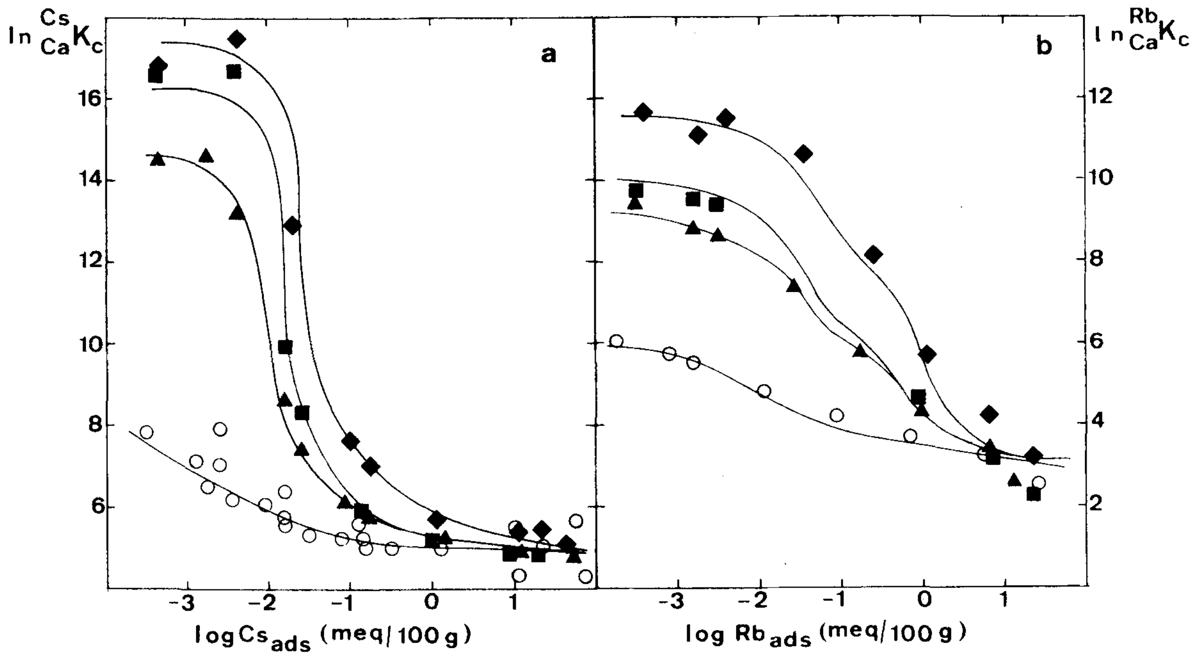

Figure 1. Plot of ln K_c vs. Cs- (a) and Rb-exchange (b) levels (meq/100 g) in original Camp Berteau montmorillonite (○) and Camp Berteau montmorillonite subjected to 2 (▲), 5 (■), and 10 (◆) wetting-drying cycles. Curves are simulated using data shown in Table 1 (Cs^+-Ca^{2+} equilibria) and Table 2 (Rb^+-Ca^{2+} equilibria).

Cs^+-Ca^{2+} selectivity

At least four types of sites were necessary to simulate the experimental data. For Cs^+-Ca^{2+}, type I and II sites had a very high selectivity for Cs with ln K_c = 33.8 and 25, respectively. Type III sites had an intermediate selectivity (ln K_c = 13.8), and type IV sites had a low selectivity corresponding to the interlayer or basal surface sites in montmorillonite. The selectivity of all site types was assumed constant throughout the W-D series.

With increasing W-D cycles increasing amounts of type I, II, and III sites were created (see Table 1). The number of type-IV sites, which are assumed to be the expanded interlayer, decreased as the total CEC decreased. After 10 W-D cycles, 0.02 meq/100 g of type I and II sites were found with a selectivity comparable to the high-energy sites in illite (ln K ~ 30). The total amount of type I and II sites (0.04 meq/100 g) reached about half the amount found in illite (0.1 meq/100 g). Additional W-D cycles would probably have increased the total number of high-energy sites further. A few high-energy sites were observed in the original Camp Berteau montmorillonite which were probably due to mica impurities, as observed by Talibudeen and Goulding (1983).

All Cs^+-Ca^{2+} selectivity profiles (Figure 1a) leveled off at a ln K_c value of about 5, independent of the number of W-D cycles, and were probably due to planar site selectivity. This value is identical to the one calculated from ln $K_{\mathrm{Na}^+}^{\mathrm{Cs}^+}$ (Maes and Cremers, 1978) and ln $K_{\mathrm{Na}^+}^{\mathrm{Ca}^{2+}}$ (Maes and Cremers, 1977) for Camp Berteau montmorillonite. Alternate W-D cycles thus did not influence the planar site selectivity. The Cs^+-Na^+ selectivity decreases as mean interlayer charge density decreases (Maes and Cremers, 1978). The CEC decrease in the present studies resulted from layer col-

Table 2. Site-group capacities (meq/100 g) and ln K_c values (in parentheses) used for simulating the Rb^+-Ca^{2+} equilibria at 25°C for K-exchanged Camp Berteau montmorillonite subjected to alternate wetting-drying cycles.

Wetting-drying cycles	Type I site	Type II site	Type III site	Type IV site
0	0.0002 (28)	0.005 (24.5)	0.2 (13.8)	110 (3.2)
2	0.007 (27.5)	0.012 (23)	0.4 (16.5)	104 (3.2)
5	0.015 (27.5)	0.012 (23)	0.4 (16.5)	98 (3.2)
10	0.02 (27.5)	0.2 (23)	0.8 (16.5)	74 (3.2)

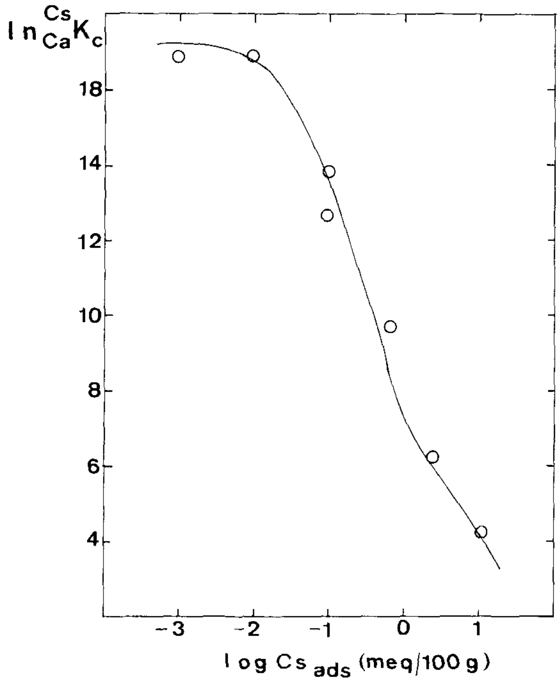

Figure 2. Plot of ln K_c vs. Cs-exchange level (meq/100 g) in K^+-exchanged Camp Berteau montmorillonite heated to 500°C. Curve is simulated using data shown in Table 3.

lapse, leaving the mean interlayer charge density unaltered and consequently also the selectivity. The fact that interlayer charge is heterogeneously distributed among the interlayers but also within each interlayer is in line with this reasoning (Lagaly, 1981).

Rb^+-Ca^{2+} selectivity

The procedure used to simulate the Rb^+-Ca^{2+} selectivity was the same as the Cs^+-Ca^{2+} selectivity simulation. Table 2 summarizes the variables used. A good simulation of the experimental data was obtained (see Figure 1b), keeping in mind that variations of a few units in ln K in the "trace" region were expected (Brouwer *et al.*, 1983).

Throughout the series of W-D samples the Rb^+-Ca^{2+} selectivity on site I was much smaller than the Cs^+-Ca^{2+} selectivity. ln $K_{Rb^+}^{Cs^+}$ was equal to 3.15 ($\Delta G = -7.7$ kJ/eq) which is identical to the Cs^+-Rb^+ equilibrium on the high affinity site in illite and which Brouwer *et al.* (1983) assigned to the exchange of dehydrated Cs^+ and Rb^+ ions at the interlayer-edge positions (Brouwer *et al.*, 1983). Site II showed only a small preference for Cs^+ with respect to Rb^+ (ranging from −0.6 to −1.6 kJ/eq), whereas site III appeared to show a slight preference for Rb^+ (ranging from 0 to −3.3 kJ/eq). The selectivity at high loading (site IV) was compatible with commonly found values on montmorillonite (Bruggenwert and Kamphorst, 1979).

Table 3. Site-group capacities (meq/100 g) and ln K_c values (in parentheses) used for simulating the Cs^+-Ca^{2+} equilibria at 25°C in K-montmorillonite heated to 500°C.

	Type I site	Type II site	Type III site	Type IV site
ln $K_{c\,Ca^{2+}}^{Cs^+}$	33.8	25	13.8	5.5
Capacity	0.03	0.3	2.5	47.2

K-montmorillonite heated to 500°C

Figure 2 shows the variation of ln $K_{c\,Ca^{2+}}^{Cs^+}$ as a function of the Cs^+-exchange level in a K-montmorillonite heated to 500°C for 24 hr. The residual Ca-CEC was 0.5 meq/g. The selectivity behavior was simulated (see Table 3) using the same ln K_c values as for the alternate W-D cycle treatment indicating that comparable type of sites were created. The total number of high affinity sites (2.83 meq/100 g) exceeded the number in illite (0.7 meq/100 g) by a factor of 4.

Reduced-charge montmorillonites

Figure 3a shows the variation of ln $K_{c\,Ca^{2+}}^{Cs^+}$ as a function of the Cs-exchange level for all RCM samples. The notation refers to the fractional capacity, expressed with respect to the Ca-CEC of 1.1 meq/g of the original (unheated) montmorillonite. All RCM samples were expanded with ethylene glycol and ethanol. Those samples that received an additional NH_3 treatment are indicated in Table 4 by NH_3 in brackets. X-ray powder diffraction patterns were not taken.

A general increase in selectivity was observed with increasing charge reduction or decreasing Ca-CEC of the RCMs. The experimental data were simulated by using 4 types of sites, the ion-exchange capacities, and selectivity coefficients of which are summarized in Table 4. With decreasing layer charge on montmorillonite, the total amount of sites I, II, and III increased, keeping the selectivity coefficient constant throughout the series of samples. The capacity of type IV sites ("planar" surfaces) as expected decreased with charge reduction. The natural log of the selectivity coefficient of type-IV sites, however, decreased form 5.15 in the original montmorillonite to 2.5 in 0.13 Ca-RCM, a phenomenon which can be described by charge-density effects and calculated by combining the charge-density influence on the Na^+-Cs^+ and Na^+-Ca^{2+} equilibria in these RCMs (Maes and Cremers, 1977, 1978).

Cs^{2+}-Ca^{2+}selectivity

Storage of RCM samples over NH_3 vapor for 48 hr (Farmer and Russell, 1967) opened up more clay layers than the ethylene-glycol and alcohol treatments and resulted in higher Ca-CECs (see Table 5). NH_3 treatment had no effect on the Ca-CEC of the 0.96 Ca-RCM and the 0.84 Ca-RCM, and the resulting Cs^+-Ca^{2+} behaviors were identical (Figures 3a and 3b). With NH_3

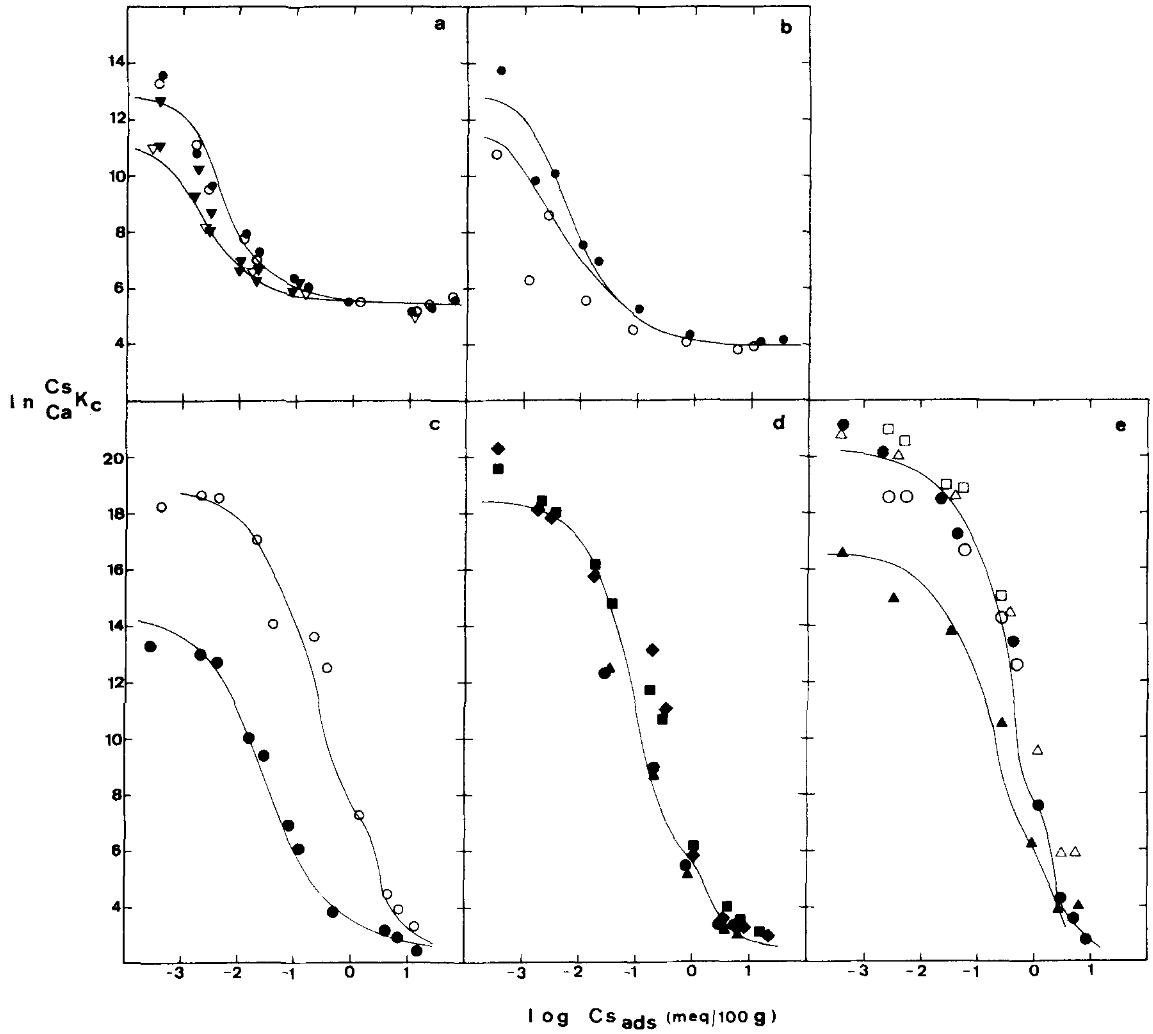

Figure 3. Plot of ln K_c vs. Cs-exchange level (meq/100 g) in different reduced-charge montmorillonites (RCM): (a) 0.96 Ca-RCM (○); 0.95 Ca-RCM (△); 0.96 Ca-RCM-(NH_3) (●); 0.95 Ca-RCM-(NH_3) (▲); (b) 0.84 Ca-RCM (○); 0.84 Ca-RCM-(NH_3) (●); (c) 0.42 Ca-RCM (○); 0.64 Ca-RCM-(NH_3) (●); (d) 0.54 Ca-RCM-(NH_3) (●); 0.50 Ca-RCM-(NH_3) (▲); 0.46 Ca-RCM-(NH_3) (■); 0.43 Ca-RCM-(NH_3) (◆); (e) 0.13 Ca-RCM (○); 0.16 Ca-RCM (△); 0.25 Ca-RCM (□); 0.29 Ca-RCM-(NH_3) (●); 0.33 Ca-RCM-(NH_3) (▲). Curves are simulations using data shown in Table 4.

treatment the Ca-CEC of the 0.42, 0.16, and 0.13 Ca-RCMs increased to 70.4 (0.64 Ca-RCM-NH_3), 31.4 and 36.8 meq/100 g (0.33 Ca-RCM-NH_3) because of the additional swelling of collapsed clay layers. The overall Cs^+-Ca^{2+} selectivities (Figures 3c and 3e) and the high-energy site capacity correspondingly decreased (Table 4), in agreement with the decrease of high affinity sites. It is unclear why NH_3 treatment of the 0.16 Ca-RCM produced a higher Ca-CEC (0.29 Ca-RCM-NH_3) but showed a lower selectivity profile.

The number of high-affinity sites generated in the RCM samples was a function of the residual Ca-CEC irrespective of the swelling treatment (NH_3 or not) of the sample. This relationship provided evidence for the association of high-energy sites with collapsed layers. The creation of high-energy sites was, however, not solely a function of CEC because the NH_3-treated samples (Ca-RCM-NH_3) were not completely consistent with the untreated samples (Ca-RCM).

DISCUSSION

The agreement between the Cs^+-Ca^{2+} and Rb^+-Ca^{2+} selectivity behavior in illite and in modified montmorillonite suggests the involvement of similar sites. The agreement, however, does not mean that identical sites were involved in both systems. Indeed, the simulation analysis merely shows that at least three or four, and possibly more sites must be postulated and that

Table 4. ln K_c values and site-group capacities (meq/100 g) used for simulating the Cs^+-Ca^{2+} equilibria at 25°C of different reduced-charge montmorillonites exposed or not to NH_3 vapor.

ln $K_c{}^{Cs^+}_{Ca^{2+}}$	Type I site 33.8	Type II site 25.0	Type III site 13.8	Type IV site (given in parentheses)
0.96 Ca-RCM 0.95 Ca-RCM 0.96 Ca-RCM-(NH_3) 0.95 Ca-RCM-(NH_3)	0.0025–0.001	0.012–0.008	0.02–0.1	105 (5.15)
0.84 Ca-RCM 0.84 Ca-RCM-(NH_3)	0.002–0.001	0.012	0.2	93 (3.85)
0.64 Ca-RCM-(NH_3)	0.003	0.04	0.4	70 (2.55)
0.54 Ca-RCM-(NH_3) 0.50 Ca-RCM-(NH_3) 0.46 Ca-RCM-(NH_3) 0.43 Ca-RCM-(NH_3)	0.018	0.1	1.0	53.8 (2.35)
0.42 Ca-RCM	0.018	0.2	2.0	44 (2.50)
0.33 Ca-RCM-(NH_3)	0.005	0.13	1.3	34 (2.35)
0.29 Ca-RCM-(NH_3) 0.25 Ca-RCM 0.16 Ca-RCM 0.13 Ca-RCM	0.02	0.3	1.5	18 (2.35)

the characteristic free energy values for the Cs^+-Ca^{2+} exchange ranged from about 40 to about 6 kJ/eq. It is evident that slight shifts in site density and characteristic K_c values can produce equally good fits and, by increasing the number of site groups, better descriptions of the data can be obtained. The essential feature is that heat treatments of montmorillonite generate a range of sites with different selectivity, rather than a limited number of sites, as proposed for illite (Brouwer *et al.*, 1983).

It is further evident, from the contents of Tables 1–4, that the smaller the site-group capacities the higher was the selectivity. This relationship corresponds to islands of high-selectivity sites of type I surrounded by regions of sites of types II, III, and IV of increasing capacity. The highest selectivity corresponded to a collapsed center (10-Å) in agreement with the representation of exchange of dehydrated cations (Brouwer *et al.*, 1983). In sites of type IV, full swelling occurred corresponding to selectivities on the planar sites. In the intermediate region a whole range of sites with different "equivalent anionic radius" may be viewed as corresponding to a range of selectivities in line with current views that selectivity differences mainly originate from the opposing effects of cation hydration and coulombic interaction with the framework charge (Eisenmann, 1962).

The present model also explains that for structural reasons the dependence of high and intermediate selectivity sites on CEC differed in the two series of samples studied here. The reduction of CEC was indeed due to two different mechanisms:

(1) Collapse of K^+-interlayers in the W-D samples and the 500°C heat treatment led to unexchangeable interlayers or interlayer regions mostly occupied by K^+.

(2) *In situ* charge neutralization in the RCM samples led to charge-density-dependent differences in swelling and the collapse of very low charged interlayers or interlayer regions. This difference is illustrated by the fact that the selectivity of sites of type IV decreased with charge density in the RCM samples, in contrast to the W-D samples.

The greater variability in sites in the montmorillonite samples contrasted with illite where three sites were sufficient to describe the data. The likely explanation is that in illite the high-energy sites were located at edges of the crystallites, whereas in

Table 5. Calcium cation-exchange capacities (meq/g) of reduced-charge montmorillonites (RCM) before and after expsure to NH_3.

Before NH_3-treatment	After NH_3-treatment
1.053 (0.96 Ca-RCM)	1.054 (0.96 Ca-RCM-NH_3)
0.936 (0.85 Ca-RCM)	0.924 (0.84 Ca-RCM-NH_3)
0.458 (0.42 Ca-RCM)	0.704 (0.64 Ca-RCM-NH_3)
0.179 (0.16 Ca-RCM)	0.314 (0.29 Ca-RCM-NH_3)
0.139 (0.13 Ca-RCM)	0.368 (0.33 Ca-RCM-NH_3)

the montmorillonite samples more sites of intermediate selectivity were probably present in the interlayers.

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