

HYSTERESIS IN THE BINARY EXCHANGE OF CATIONS ON 2:1 CLAY MINERALS: A CRITICAL REVIEW

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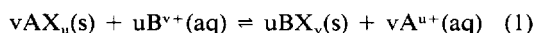
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Abstract—The binary exchange of cations on clays and soils is generally regarded as a thermodynamically reversible process. The literature on soil chemistry and geochemistry, however, abounds with reports on cation exchange reactions that appear to have only limited reversibility, i.e., that exhibit hysteresis. A satisfactory explanation of this phenomenon is still lacking, even though a number of mechanisms have been advocated, e.g., charge or site heterogeneity at the surface, differential hydration of cations, dehydration of the exchanger, crystalline swelling hysteresis, and inaccessibility of sites caused by domain or quasi-crystal formation. In the present article, the relevant literature is reviewed and analyzed critically. On the basis of available evidence, it is shown that exchangeable cations can be classified into three groups, defined in such a way that hysteresis has, in the literature, generally not been observed when exchange reactions involved cations belonging to the same group, but has often been found when the reactions involved cations from different groups. Furthermore, it is argued that none of the five mechanisms mentioned can, in and of itself, account fully for the observed exchange hysteresis. A conceptual model is proposed that combines elements of these five mechanisms and is able to describe, at least qualitatively, the effects of factors such as clay type, electrolyte concentration, and extent of dehydration.

Key Words—cation exchange, hysteresis, quasi-crystal, crystalline swelling, kinetics, smectites.

INTRODUCTION

Perhaps the most important chemical property of natural porous media is their ability to retain and exchange positively charged ions on colloidal surfaces. This property to a large extent conditions and controls the availability of macro- and micro-nutrients to plants, the mobility of positively charged chemical species such as K-fertilizers (Goulding, 1984) or heavy metals (McBride, 1989a), and generally affects the geochemical cycling of these cationic species. Concern about fertilizer efficiency, about the threat of soil salinization in many parts of the world, and about the fate of cationic contaminants in subsurface environments has motivated an important body of research on the exchange of cations in soils and, in particular, on the exchange of cations on the clay fraction of soils. A basic tenet of this research effort is the assumption that exchange reactions are thermodynamically reversible (Sposito, 1981; Bolt, 1982; Baveye and Charlet, 1987; McBride, 1989b; Tang and Sparks, 1993). For the generic reaction of exchange between the cations A^{u+} and B^{v+} on a soil, expressed as



where X^{-1} represents one equivalent of the soil's exchange complex, this assumption implies that exactly the same experimental exchange isotherm is obtained whether one starts with an exchanger fully saturated with A^{u+} (forward reaction) or with B^{v+} (backward reaction). Consequently, the practice of performing exchange experiments in only one direction, following

either the forward or the backward reaction, has become routinely adopted from the late 1970s onward.

Experimental data available in the literature (Fripiat *et al.*, 1965) suggest that some exchange reactions on clays and soils are indeed thermodynamically reversible (Figure 1a). However, there is also ample evidence that, under similar experimental conditions, a number of exchange reactions exhibit significant irreversibility, or "hysteresis." In these cases, the exchange isotherms corresponding to the forward and backward reactions do not coincide. As a result, the steady-state composition of the exchange complex of the soil or clay in contact with a given electrolyte solution depends on the past history of the system, as illustrated in Figure 1b.

Various molecular mechanisms have been suggested to account for this apparent irreversibility of many exchange reactions on clays and soils. These mechanisms involve such features as charge or site heterogeneity at the surface of the exchanger, differential hydration of the exchanging cations, dehydration of the soil or clay, crystalline swelling hysteresis, and inaccessibility of sites caused by domain or quasi-crystal formation. A satisfactory, complete explanation of the phenomenon of cation exchange hysteresis is still lacking, however.

In this context, the purpose of the present critical review is threefold. The first objective is to analyze in detail the experimental evidence available in the relevant literature on the hysteresis associated with the exchange of cations on soils and clays. The second

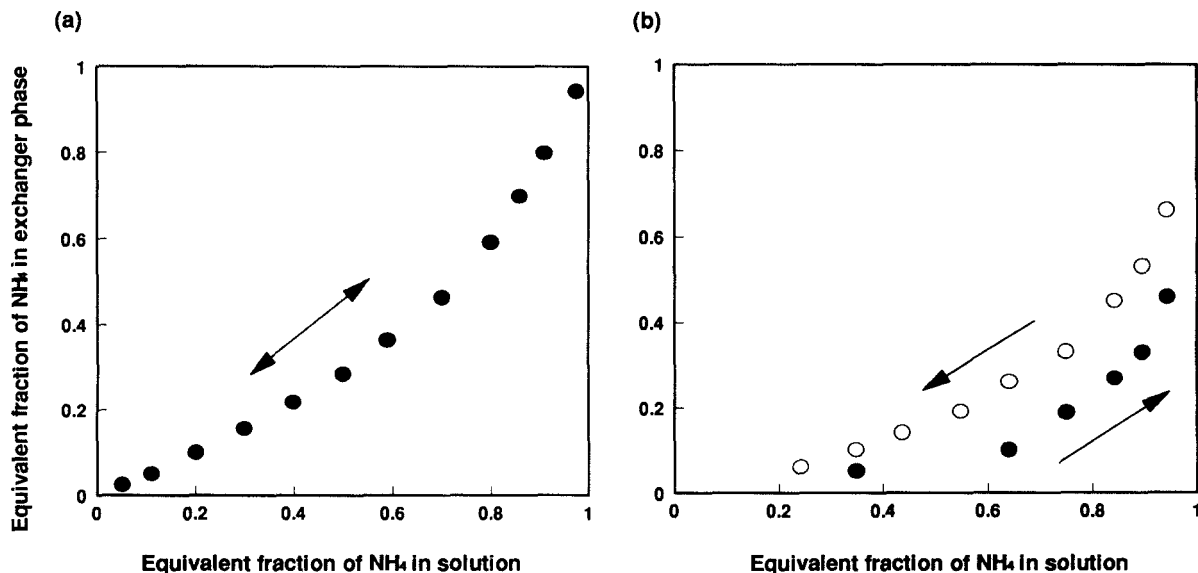


Figure 1. Isotherms corresponding to forward and backward exchange reactions on Camp Berteau montmorillonite (data from Fripiat *et al.*, 1965): a) non-hysteretic $\text{NH}_4\text{-Rb}$ exchange; b) hysteretic $\text{NH}_4\text{-Ba}$ exchange.

objective is to confront to this experimental evidence the various molecular mechanisms mentioned above and to analyze in detail their limitations. The final objective is to propose a conceptual model of the cation exchange hysteresis phenomenon in suspensions of 2:1 clay minerals. This model combines various elements of the above mechanisms and accounts, at least qualitatively, for the effects of factors such as clay type, electrolyte concentration, and extent of dehydration. Throughout the present article, attention is restricted to non-specific, binary cation exchange reactions. Although the apparent irreversibility associated with ternary exchange (Mukherjee, 1942; Morgun and Pachepskiy, 1987; Datta and Sastry, 1990) or specific adsorption reactions (Kiekens *et al.*, 1982; Comans *et al.*, 1991; Comans and Hockley, 1992) warrants further study, it is beyond the scope of this review.

EXPERIMENTAL EVIDENCE OF CATION EXCHANGE HYSTERESIS

As early as in 1921, Hisschemöller found marked hysteresis effects associated with the exchange reactions Na-NH_4 and Na-Ca on permutite, a synthetic aluminosilicate. Forward and backward exchange isotherms were observed to be clearly distinct, even though equilibration took place over periods of three days and, in some cases, even longer. Repeated transformations back and forth between the Na- and $\text{NH}_4\text{-}$ saturated forms of the exchanger made the hysteresis disappear. Storing the samples for half a year caused the isotherms to shift slightly, but hysteresis was still present.

The first reference to cation exchange hysteresis on clay minerals and colloidal fractions of soils was made

by Vanselow (1932), who studied a number of exchange reactions on bentonites, permutites, soil colloids, and zeolites. For each of these exchangers, Vanselow (1932) compared the selectivity coefficients associated with the forward and backward Na-K exchange reactions and found them to be significantly different. This difference was similar in all cases, suggesting that hysteresis affected the Na-K exchange to approximately the same extent on all materials tested. No hysteresis was found in the case of homovalent exchange reactions involving the pairs of divalent cations Ba-Ca and Ba-Cu . On the other hand, the heterovalent exchange between NH_4 and Ca was hysteretic on bentonite and on a soil colloid of unknown composition. To investigate this latter reaction further, Vanselow (1932), following Hisschemöller (1921), tried to eliminate hysteresis by carrying out, successively, five complete Ca-NH_4 transformations of a bentonite but this attempt was not successful. He also investigated the effect of temperature on the hysteresis associated with the Ca-NH_4 reaction; one experiment was carried out at room temperature for 5 hr, while another took place over 7 days at 75°C . The ratios of selectivity coefficients for the forward and backward reactions were not closer to unity in the second case. This led Vanselow (1932) to conclude that hysteresis was not only a matter of kinetics. According to him, the phenomenon of hysteresis could be related to changes in the crystal structure of the aluminosilicates.

In a paper covering various aspects of ion exchange on permutite, kaolinite, and montmorillonite, Wiegner (1935) referred to and analyzed several examples of ion exchange hysteresis described in the unpublished

work of Renold and Mitchell. Comparison of data for $\text{NH}_4\text{-Ca}$ exchanges on permutite, kaolinite, and bentonite showed that, in all cases, hysteresis decreased with the concentration of the electrolyte solution used and that it was most pronounced for permutite and least for bentonite. Wiegner explained these different levels of hysteresis in terms of "meta-structure," i.e., the presence of sites with different geometries, some of which bind ions more tightly than others (Marshall, 1964), depending on the order of entry. From this viewpoint, the meta-structure of permutite would be more highly developed than that of bentonite.

Giesecking and Jenny (1936) studied various exchange reactions in both forward and backward directions on colloidal Putnam clay (beidelite). The amount of electrolyte added in these experiments was expressed in terms of so-called symmetry concentrations, i.e., multiples of the milliequivalents of exchangeable ions in the system. A solution concentration of 1S, therefore, corresponded to a system with equal amounts of milliequivalents in solution and on the adsorption complex. The status of the exchanger was characterized by the percentage of adsorbed ions replaced. When the percentages found in the forward and backward reactions in 1S concentration did not add to 100%, Giesecking and Jenny (1936) concluded that the exchange reaction was hysteretic. The discrepancy was particularly noticeable in heterovalent exchange reactions. From the data reported by Giesecking and Jenny (1936), one may conclude that the K-Ca , $\text{NH}_4\text{-Ca}$, and Th-K exchange reactions exhibited hysteresis.

Schachtschabel (1940) studied several exchange reactions in both directions on kaolinite and montmorillonite. The experiments were carried out under constant total normality and with a fixed soil/solution ratio. Schachtschabel (1940) argued that, in the case of true equilibrium, the concentrations of any given ion should be the same for the reactions in both directions (starting with a 1S concentration). Large discrepancies, i.e., hysteresis effects, were found for $\text{NH}_4\text{-H}$, Ca-H , and Mg-H exchanges on montmorillonite. A small but measurable hysteresis was also associated with the $\text{NH}_4\text{-Ca}$ and $\text{NH}_4\text{-Mg}$ exchange reactions on the same clay. The Ca-Mg exchange, however, exhibited no hysteresis, an observation which Schachtschabel (1940) ascribed to the fact that the two ions have the same valence and similar hydration characteristics.

Mukherjee (1942) found that the Ba-K exchange on a colloidal Latekujan soil was hysteretic. The exchangers used in the experiments were labeled Ba-K -clay and K-Ba -clay, respectively. They resulted from the addition of BaCl_2 to a known amount of K -clay and, similarly, of KCl to the Ba -saturated form of the clay. Measurements of supernatant concentrations after 7 to 10 days revealed that the Ba:K ratio was unity both in the Ba-K -clay and in the K-Ba -clay, i.e., that the mixed clays had identical composition. To these mixed clay

samples, Mukherjee (1942) added a 1S concentration of BaCl_2 or KCl to study, respectively, the exchange of K by Ba or that of Ba by K . The experimental results indicated that KCl displaced a smaller amount of Ba from the K-Ba -clay than from the Ba-K -clay while BaCl_2 displaced a smaller amount of K from the Ba-K -clay than from the K-Ba -clay. Mukherjee (1942) concluded from these data that K and Ba in the two mixed Ba/K clays did not occupy identical exchange sites and that the cation that originally saturated the clay was most firmly bound and least replaceable. This latter conclusion corresponds with ideas expressed earlier by Wiegner (1935).

Kelley (1948) described a number of unpublished results of binary exchange experiments on Yolo soil. Hysteresis was found when the exchange reactions involved ions of different valence, such as with the pairs $\text{NH}_4\text{-Mg}$ and $\text{NH}_4\text{-Ca}$. On the other hand, the exchange between Ca and Mg did not exhibit any hysteresis, in agreement with Schachtschabel's (1940) findings.

The exchange data obtained by Mukherjee (1951), when analyzed using the procedure of Giesecking and Jenny (1936), suggest that the Na-K , Ca-NH_4 , and Ba-K exchange reactions on a number of kaolinitic and montmorillonitic soils are all hysteretic. On the other hand, these data also indicate that on these soils the Ca-Na exchange reaction is reversible.

Faucher and Thomas (1954) studied the K-Cs exchange on Chambers montmorillonite and did not find any hysteresis; the two exchange isotherms measured in batch for the forward and backward reactions coincided exactly. For purposes of discussion later in this paper, it is interesting to note that these authors dried their clay samples for 24 hr at 60°C before carrying out the actual exchange experiments.

Bose (1957) studied both forward and backward reactions of Na-K exchange on a clay membrane of montmorillonite (from Padegaon soil). The exchange was investigated by determining the activities of the cations on the basis of measured values of the electromotive force. Comparison of the two directions of the exchange reaction was expected to give the same activity of Na for a particular activity of K . As this was not found, Bose concluded that the exchange reaction exhibited hysteresis. Bose suggested that this was caused by K -fixation.

Tabikh *et al.* (1960) studied cation exchange hysteresis by comparing the Vanselow selectivity coefficients associated with the forward and backward reactions. These authors considered that when the product of the two selectivity coefficients was not equal to 1, the reactions were not completely reversible. Several systems were studied in which the clay was submitted to various drying treatments: 1) no drying, 2) dried on a steam bath at about 60°C , 3) dried to become a thick paste on a steam bath and further dried at room temperature,

4) dried by vacuum at 15°C, and 5) dried on a steam bath as in (2) and then ground to <0.1 mm. Four exchange reactions (Na–K, Na–Li, Ca–Mg, Rb–Mg) were investigated on three montmorillonitic clays (Colony, Belle Fourche, and Plymouth). In the cases where the clays were not dried (1), the reactions were completely reversible, whereas the corresponding dried systems showed marked hysteresis. In the latter cases, the dependence of the selectivity coefficients on the electrolyte concentration was, however, larger than in case (1), so that the product of the two selectivity coefficients was less accurate. The Na–K exchange reaction was also studied on a synthetic resin, where it was found reversible, even when the resin was dried prior to the exchange experiments. According to Tabikh *et al.* (1960), dehydration alters the exchange properties of montmorillonite, the extent of the process depending on the adsorbed cations involved and on the source of the clay. Collapse of interlayer spacings upon drying was suggested to be the cause of hysteresis. A sixth treatment involved resaturation with H and then with the original cation, after drying on a steam bath (treatment 2). These “recycled” samples did not exhibit any exchange hysteresis, indicating that the structural changes brought about by drying were reversible. Tabikh *et al.* (1960) let their K–Na exchange samples equilibrate for 48 hr, 9 days, or 15 days, and found no difference in the exchange constants of the reactions, concluding that failure to reach equilibrium was not the reason for the observed hysteresis.

Fripiat *et al.* (1965) studied the reversibility of a number of exchange reactions involving NH₄ and various alkaline and alkaline earth cations. Two exchangers, the Camp Berteau montmorillonite and the ion exchange resin Amberlite, were used. Both were stored in distilled water prior to the experiments. The cations that were exchanged against NH₄ were Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba. The exchange reactions were carried out in two directions at a total normality of 0.01 N. After equilibration by dialysis at 25°C for three or four days, the amounts of NH₄ in the equilibrium solution and in the exchange complex were evaluated. Exchange isotherms were then calculated, assuming that the CEC of the exchangers stayed constant throughout the experiments. Under these conditions, it was found that all exchange reactions on the resin were fully reversible, whereas, on the montmorillonite, the exchanges between NH₄ and, respectively, Li, Na, Mg, Ca, Sr, and Ba exhibited significant hysteresis. A more quantitative assessment of this phenomenon was obtained by determining the product of the forward and backward “equilibrium” constants. This product was exactly unity for the reversible exchange reactions and differed from 1.0 for those exhibiting hysteresis. The magnitude of the deviation from 1.0 was directly related to the area of the loop between the forward and backward exchange isotherms. On the basis of the val-

Table 1. Thermodynamic parameters relative to the exchange of NH₄⁺ with various cations on Camp Berteau montmorillonite.*

NH ₄ ⁺ exchange with:	$\bar{K}^*\bar{K}$	$\Delta Q_f - \Delta Q_b$ (J mol ⁻¹)
Li ⁺	0.570	1385
Na ⁺	0.730	787
K ⁺	1.000	0
Rb ⁺	1.000	0
Cs ⁺	1.020	0
Mg ²⁺	0.135	4937
Ca ²⁺	0.264	3305
Sr ²⁺	0.310	2908
Ba ²⁺	0.294	3017

* Data from Fripiat *et al.* (1965).

ues obtained for the thermodynamic equilibrium constants and for the free energies of the reactions in both directions, the heats of the forward and backward exchanges, ΔQ_f and ΔQ_b respectively (in J mol⁻¹), were computed. The magnitude of the difference $\Delta Q_f - \Delta Q_b$ was closely correlated with the observed hysteresis: Larger values of $\Delta Q_f - \Delta Q_b$ corresponded to a larger hysteresis loop between the forward and backward exchange isotherms and to a larger deviation from unity of the product of the equilibrium constants (Table 1). In the case of the reversible exchange reactions, the difference $\Delta Q_f - \Delta Q_b$ was equal to zero. Sample dehydration, advocated by Tabikh *et al.* (1960) to be the chief cause of cation exchange hysteresis, could not be responsible for the observations made by Fripiat *et al.* (1965) since these authors were careful never to let the clay dry during their experiments. Fripiat *et al.* (1965) suggested that hysteresis might be due to the difficulty that larger hydrated cations such as Li, Na, and the divalent cations may have in displacing the smaller hydrated NH₄-ions from the siloxane ditrigonal cavities.

Investigating systems at constant total normalities varying between 5 and 25 mmol_c l⁻¹ and using a dialysis technique, Van Bladel and Laudelout (1967) found hysteresis in the exchange reactions NH₄–Mg and NH₄–Ba on Camp Berteau montmorillonite. The extent of the hysteresis loop was least for the lowest total normality studied. The logarithms of the Gaines–Thomas selectivity coefficients for the forward and backward exchange reactions were found to vary linearly with the square root of twice the ionic strength. The slopes of these straight lines depended on the direction of the exchange. Extrapolation of these linear relations to vanishing ionic strength eliminated the irreversibility, which was therefore considered to be only apparent. Van Bladel and Laudelout (1967) suggested that cation exchange hysteresis is due to an imperfect dispersion of the clay suspensions used in the exchange experiments.

Deist and Talibudeen (1967) used the isotopes ^{42}K , ^{24}Na , ^{86}Rb , ^{45}Ca , and isotopic dilution techniques to study the K–Ca, K–Rb, and K–Na exchanges on different soils of unknown mineralogical composition. The CECs of these soils did not remain constant during the experiments, but instead varied with the composition of the exchange complex. Deist and Talibudeen (1967) attributed these changes in CEC to the collapse of interlayer spaces. In some soils, the exchange reaction K–Ca was found to be hysteretic.

Gilbert (1970) conducted a study to investigate the selectivity of Camp Berteau montmorillonite for Mg and Ca at different total normalities and temperatures. No significant difference was observed between the isotherms determined at the three concentration levels and two different temperatures applied. Comparison of the forward and backward isotherms did not reveal any hysteresis.

Gilbert and Van Bladel (1970) examined the influence of temperature and ionic strength on the selectivity of the Camp Berteau montmorillonite for Mn and NH_4 . Differences between the forward and backward exchange isotherms suggested that the NH_4 –Mn exchange exhibited hysteresis. Gilbert and Van Bladel (1970), like Van Bladel and Laudelout (1967) earlier, attributed the observed hysteresis to differences in the aggregation state of the clay.

Newman (1970) studied the sorption and desorption of K by mica in exchange with Na. The amount of K released or sorbed was calculated from the difference in solution concentration before and after equilibration. The experiment was done in boiling solutions (to speed up the process), and this introduced relatively large errors. Comparing different parts of the adsorption and desorption isotherms, Newman (1970) concluded that both an irreversible modification of the system and exchange hysteresis occurred. Newman (1970) linked the phenomenon of hysteresis to cation hydration and changes in the number of layers of interlayer water.

Maes and Cremers (1975) showed that the adsorption-desorption of Co and Zn on Na-saturated Camp Berteau montmorillonite was only partially reversible, depending on the pH and on the adsorbed amount of the divalent cation. The irreversibility at high divalent ion occupancy could be removed by lowering the pH. Under these conditions, however, the reaction was no longer stoichiometric; therefore, a specific adsorption process was probably involved.

Singhal *et al.* (1977) studied the effects of time, pH, ionic strength, and temperature on cation exchange reactions involving Ca and NH_4 on an Indian bentonite (Akli). Both forward and reverse directions of the exchange reaction reached equilibrium, or at least stable steady states, within 3 hr. Hysteresis was found in all experiments. The cation originally present on the exchanger was preferred during the exchange experiment,

provided the ionic strength was not adjusted to a constant level. In the case of constant ionic strength of the exchanging solutions, the exchanging cation was preferred above the one originally present. The main cause for this observed hysteresis was suggested to be the fixation of the cations in the micropores of the exchanger. Ni–Ca exchange on an illite (from Morris, Illinois) was found to be reversible by Singhal *et al.* (1978).

Using bentonite and resin membrane electrodes to measure electrolyte activities, Saha and Sastry (1984) studied the exchange of K and Na on a vermiculite, a bentonite, and a kaolinite. Upon addition of identical amounts of KCl or NaCl respectively to Na- and K-saturated clay samples, Saha and Sastry (1984) observed consistent differences between the activities of Na and K in solution in the exchange experiments involving the vermiculite and the bentonite. It is unclear to what extent the observed differences may have been due to changes in the cation exchange capacity of the clays during the exchange processes. Nevertheless, Saha and Sastry (1984) concluded that the K–Na exchange was hysteretic on vermiculite and bentonite, but not on kaolinite.

Gebhardt and Rosemann (1984) found hysteresis for the Cs–Ca exchange on marsh soils. The extent of the hysteresis depended on the type of soil. The Sr–Ca exchange did not exhibit hysteresis.

Laird (1987), studying the relationship between exchange selectivity and crystalline swelling, found a slight hysteresis in the Ba–Mg exchange on a synthetic fluorohectorite. Exchange isotherms were determined for the forward and backward exchange reactions by equilibration for 3 days with mixed BaCl_2 – MgCl_2 solutions of a total molarity of 0.1 M. The Ba- and Mg-clays were air dried and ground before usage. Laird (1987) suggested that the slight exchange hysteresis observed was related to hysteresis in crystalline swelling and changes in basal spacing of the clay.

The experimental evidence presented so far has involved the direct measurement of exchange isotherms or of thermodynamic quantities that can be readily deduced from exchange data. The article of Shainberg and Kaiserman (1971), on the other hand, presents evidence that is indirectly related to the phenomenon of cation exchange hysteresis. These authors measured the saturated hydraulic conductivity (HC_{sat}) of Wyoming bentonite membranes, variably saturated with Na and Ca, and observed that the HC_{sat} of the clay membranes depended on the experimental conditions used. The measured HC_{sat} values obtained by starting with the Ca-saturated clay and progressively increasing from 0 to 1 the equivalent fraction of sodium in the flowing solution were systematically higher than those for the reverse cases, obtained by starting with the Na-saturated clay. Shainberg and Kaiserman (1971) suggest that this may have been due to the cation exchange

reaction being hysteretic or, alternatively, to differences in the level of aggregation of the clay platelets, depending on the initial composition of the exchange complex (i.e., Na- or Ca-saturated).

To summarize the experimental evidence briefly reviewed above, it is convenient to arrange the various exchangeable cations in groups, an idea originally suggested by Fripiat *et al.* (1965) in connection with exchange reactions involving NH_4 . The groups in Table 2 are such that hysteresis, in the literature, has generally not been observed when exchange reactions involved cations belonging to the same group (e.g., K- NH_4 or Ca-Mg), but has often been found when the reactions involved cations from different groups (e.g., Na- NH_4 or Na-Ca). This classification in three groups and the various factors (e.g., clay type, electrolyte concentration, dehydration) that seem to affect the occurrence and extent of cation exchange hysteresis will be discussed further in subsequent sections of the present review.

HYSTERESIS AND KINETICS

Several authors (e.g., Kelley, 1948) have suggested that the hysteresis associated with the binary exchange of cations on clays and soils could be explained in terms of kinetics. This viewpoint is consistent with the principles of classical chemical thermodynamics (e.g., Denbigh, 1981), according to which any particular system in a given environment can only have one equilibrium state. Under conditions of constant temperature and pressure, this unique equilibrium state corresponds to the absolute minimum of the Gibbs free energy. From this conceptual standpoint, the history-dependent exchange compositions in Figure 1b are artifacts, resulting from a failure to reach equilibrium. If one waited long enough, the two curves forming the hysteresis loop in Figure 1b would theoretically collapse into a single exchange isotherm, indicative of a thermodynamically reversible reaction.

The available experimental evidence suggests that the time required for this collapse of the hysteresis loop to occur, i.e., the relaxation time of the exchanger-solution system, may be relatively long. Tabikh *et al.* (1960) varied between 48 hr and 15 days the total reaction time of a K-Na exchange on Wyoming bentonite and found no decrease in the apparent hysteresis over time. After storing permutite suspensions for half a year, Hisschemöller (1921) found that the isotherms had shifted slightly, but hysteresis had not disappeared. Vanselow (1932) carried out exchange experiments at 75°C, which should have increased the reaction rates appreciably, but found no evidence of reduced hysteresis. Newman (1970) found significant hysteresis in exchange experiments carried out with boiling electrolyte solutions.

These various results all suggest a very slow kinetics. They provide no information, however, on the relax-

Table 2. Classification of cations in three groups defined in such a way that hysteresis has been documented in the literature for binary reactions involving cations from different groups.

Group 1	Group 2	Group 3
Na ⁺	K ⁺	Ca ²⁺
Li ⁺	Rb ⁺	Ba ²⁺
	Cs ⁺	Sr ²⁺
	NH_4^+	Mg ²⁺
		Mn ²⁺
		Cu ²⁺
		Ni ²⁺

ation times of the exchanger-solution systems involved. These relaxation times may be of the order of months, years, or even longer. If the relaxation times are long, effectively infinite, compared with the time scale of observation of processes (e.g., electrolyte transport in soils) that one is interested in describing, it may be convenient, as suggested by Woods (1985), to view the stable, nonequilibrium (history-dependent) compositions of the exchangers as if they were true equilibrium states. This viewpoint has been traditionally adopted in soil physics to deal with the hysteresis characterizing the retention and transport of water in soils (e.g., Haines, 1930; Kool and Parker, 1987).

The above picture, in which a very slow kinetics is responsible for the hysteresis phenomenon, conflicts directly with what is known about the kinetics of cation exchange on clays and soils. The voluminous amount of research conducted in this area (e.g., Sparks, 1989; Tang and Sparks, 1993), has shown that cation exchange is slow on some minerals, like vermiculite and mica, but is very fast on kaolinite, illite, and the smectites, where it occurs within minutes or even seconds. Malcolm and Kennedy (1969), using a specific ion electrode technique, found that >70% of Ba-K exchange on kaolinite, illite, and montmorillonite occurred in less than 3 s. On kaolinite and illite, the exchange was "complete" after 30 seconds; while on the two montmorillonites used, it was so after only 3 min. More recently, Seyfried *et al.* (1989) reported that a Ca-Mg exchange on a sandy loam soil was too fast to be monitored using a stirred-flow chamber technique amenable, in principle, to study reactions with half-times as short as 18 s.

These observations can be reconciled with the slow reaction rate, argued above to be responsible for the hysteresis phenomenon, if one introduces the concept of a two-stage kinetics instead of the single-step kinetics that has been assumed for ion exchange in the past (e.g., Sparks, 1989). Immediately after being brought in contact with an electrolyte solution of a given composition, an exchanger undergoes a very fast reaction, characterized by a relaxation time τ_1 of the order of seconds or minutes (see schematic illustration in Figure

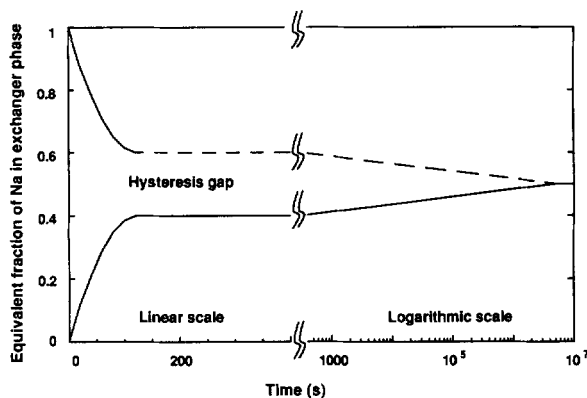


Figure 2. Schematic illustration of cation exchange as a two-stage kinetic process. The initial, fast step is associated with a relaxation time, τ_1 , of 2 minutes; the second step is much slower, characterized by a relaxation time, τ_2 , assumed here equal to 2 months.

2). The exchanger-solution system then enters into a second stage during which it slowly drifts toward thermodynamic equilibrium. The relaxation time, τ_2 , associated with this second stage may be of the order of months or years.

This concept of a two-stage kinetics, somewhat similar to that recently introduced by Comans *et al.* (1991) and Comans and Hockley (1992) to describe the sorption of Cs on illite, is consistent with all the experimental evidence briefly reviewed above. It is purely descriptive, however, and to be of practical value needs to be complemented by detailed information on the mechanism(s) responsible for the existence of two distinct rates of relaxation, and on the factors that affect τ_1 and, particularly, τ_2 .

PROPOSED MECHANISMS

Several mechanisms have been proposed in the relevant literature to account for the hysteresis associated with certain cation exchange reactions. In this section, five of these mechanisms are examined in detail within the kinetic framework outlined in the previous section.

Surface heterogeneity

As already mentioned earlier, Wiegner (1935) explained the hysteresis effects in terms of "meta-structure." He visualized the surfaces of clay platelets as highly irregular and presenting microscopic aberrations such as edges, ridges, summits, valleys, depressions, and channels. On the "elevated" areas, exchangeable cations would be bound less firmly than in the cavities. A clay saturated with a given cation X would have all of its "loose" and "firm" exchange sites occupied by X. Exchange with ion Y would result in a clay-XY characterized by a mixed adsorption complex, with X on the firm sites and Y on the loose sites.

Starting with a clay saturated with Y, one would obtain a clay-YX, with Y on the firm sites and X on the loose sites. At equal composition of the adsorption complex, i.e., identical equivalent fractions of adsorbed X and Y, the exchangers clay-XY and clay-YX would differ in the strength with which the ions are retained on the clay. Therefore, the relative replaceability of the ions X and Y on the clay would be different. The experimental observation by Mukherjee (1942) that desorption of two exchangeable cationic species in the presence of a third electrolyte depends on whether the clay is -XY or -YX lends credence to Wiegner's (1935) hypothesis.

Kelley (1948) has described Wiegner's (1935) conceptualization as a "purely mechanical interpretation." It also corresponds to a very static picture of the cation exchange process and indeed assumes implicitly that a given cation saturating an exchange site can remain "on" that site for an extended period of time. In reality, the available experimental evidence indicates that the residence times of cations in the vicinity of clay surfaces are short, even when the clay platelets are stacked in quasi-crystals (e.g., Borland and Reitemeier, 1950). Under these conditions, the adsorption strength of an exchange site is not able in and of itself to prevent the replacement of a saturating cation, e.g., X, by one of the other species, say Y. The same applies to the (possibly heterogeneous) selectivity of the exchange sites for cations X and Y. The tendency for the cation initially compensating the charge deficit of the clay at a given site to resist to the exchange must be due to some other mechanism, not necessarily related to either the adsorption strength or the exchange selectivity of the site.

Somewhat in the same spirit as Wiegner (1935), Fripiat *et al.* (1965) suggested that heterogeneity in the distribution of the surface charge sites may be responsible for the hysteresis observed in the exchange of cations on clays and soils. In the case of a heterogeneous distribution of surface charge sites, saturation of a clay with a divalent cation may create local defaults in the neutralization of the surface charge. It is then possible that cations that are not fully charge-compensated locally would exchange preferentially with a monovalent ion. On the other hand, monovalent ions that occupy sites that would be perfectly neutralized by one divalent ion, would exchange for this ion. Fripiat *et al.* (1965) correctly pointed out that this reasoning only applies to exchange reactions involving a monovalent and a divalent cation. It, therefore, lacks generality, since it cannot account for many of the cases of hysteresis described in the literature. In addition, like Wiegner's (1935) hypothesis, it fails to recognize the dynamic nature of the exchange of cations at the molecular level, and it does not account for the existence of the two very distinct relaxation times, τ_1 and τ_2 , described in the previous section.

Ditrigonal cavities and hydration of cations

According to Fripiat *et al.* (1965), the most likely explanation for the phenomenon of cation exchange hysteresis is the difficulty experienced by large hydrated cations to displace small cations like NH_4 , Cs, Rb, and K that fit snugly in the siloxane ditrigonal cavities on clay surfaces. This explanation is supported to some degree by Fripiat *et al.*'s (1965) data, which reveal a striking relationship between measured values of the difference ($\Delta Q_f - \Delta Q_b$) and the hydrated volume of the cations undergoing exchange with NH_4 (Figure 3).

The role of the siloxane ditrigonal cavities could be ascertained easily by comparing the cation exchange results obtained with clays having identical surface charge densities but different distributions of charge between tetrahedral- and octahedral layers. Nevertheless, as a general explanation of the phenomenon of cation exchange hysteresis, Fripiat *et al.*'s (1965) proposal suffers, like Wiegner's (1935), from the fact that it is based on a purely static view of exchangeable cations. If, e.g., NH_4 or Cs ions were not permanently and snugly installed in the siloxane ditrigonal cavities but were in fact, as is likely, continuously popping in and out of them at a very fast rate, nothing in the geometry of the cavities, in the absence of some other mechanism, could prevent clay-solution systems from decaying rapidly to equilibrium. Therefore, Fripiat *et al.*'s (1965) proposed mechanism could explain why the relaxation time, τ_1 , takes on a particular value for a given cation pair, but it cannot explain the existence of the second relaxation time, τ_2 . Furthermore, it does not account for the effects observed upon drying clays or upon changing the total normality or ionic strength of the electrolyte solutions. Finally, it can account for the hysteresis phenomenon only when it is associated with exchange reactions that involve cations from groups 1 and 2 (Table 2) or 2 and 3, but not 1 and 3.

Clay dehydration

Tabikh *et al.* (1960) suggested that the occurrence of cation exchange hysteresis can be explained by structural changes that take place during dehydration of the clay. In suspensions or in wet pastes, the clay platelets constitute a homogeneous adsorbent phase. The platelets themselves are wide apart, separated by large numbers of water layers. Upon drying, some or even all of these water layers disappear and the interplatelet spaces collapse. Upon rewetting, some of these collapsed platelets may not readily dissociate, leading to a dependence of the evolution of exchange reactions on the nature of the cation initially present on the exchange complex before the collapse occurred.

A test of this proposed mechanism is whether hysteresis is observed with exchangers that do not collapse upon dehydration. Synthetic resins do not change in terms of structure or aggregation status when they are

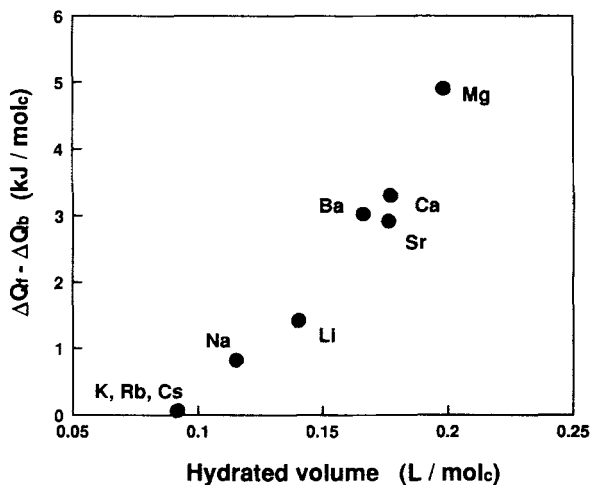


Figure 3. Difference in heat of exchange of various cations with NH_4^+ vs. the hydrated volume of the cations (after Fripiat *et al.*, 1965).

dried and, therefore, should not exhibit cation exchange hysteresis, according to Tabikh *et al.* (1960). Experimental data obtained by Tabikh *et al.* (1960) and Fripiat *et al.* (1965) indicate that this is indeed the case.

In spite of this partial confirmation, the mechanism proposed by Tabikh *et al.* (1960) is not compatible with a number of experimental results. Fripiat *et al.* (1965), for example, observed hysteresis in cation exchange experiments in which special precautions were taken never to let the clay dry. On the other hand, Faucher and Thomas (1954) did not find hysteresis during a Cs-K exchange on montmorillonite samples that had been dried. Therefore, clay hydration in itself does not constitute a complete explanation of the cation exchange hysteresis phenomenon.

Swelling hysteresis

If a dry Wyoming bentonite sample is brought into contact with a given electrolyte solution, it typically has a tendency to increase in volume, i.e., swell. Initially, this swelling occurs in discrete 2.5–3 Å steps, which correspond to the adsorption of successive water layers in the interplatelet spaces. If the smectite is saturated with K, NH_4 or Cs, this stepwise swelling, generally referred to as "crystalline" swelling, stops when the mean basal spacing has reached 14–15 Å (Table 3). On the other hand, under identical conditions, it stops at basal spacings around 19 Å when the smectite is saturated with divalent cations, and it is virtually limitless when the smectite is saturated with Na and Li, in which case the swelling is generally termed "osmotic." The basal spacings just mentioned are for Wyoming bentonite. Even though these basal spacings vary somewhat with the charge density of the clay (Quirk,

Table 3. Basal spacings of Wyoming bentonite in dilute solutions (<0.3 N).*

Ion	Basal spacing (Å)
Li ⁺	>20
Na ⁺	>20
K ⁺ , NH ₄ ⁺	15
Cs ⁺	13.8
Ca ²⁺ , Ba ²⁺	18.9
Mg ²⁺	19.2

* Data from Norrish (1954) and Norrish and Quirk (1954).

1968; Laird, 1987), the overall swelling pattern of Wyoming bentonite appears to be representative of those of smectites in general.

The fact that the above classification of swelling patterns in three distinct groups, depending on the nature of the saturating cation, follows very closely the grouping of Table 2 suggests that there may be a relation between interplatelet spacings and cation exchange hysteresis. Newman (1970) hypothesized that cation exchange hysteresis may be expected whenever there is a change in the number of water layers in the interplatelet spaces. However, in and of itself this change in the number of water layers is not sufficient to cause the observed cation exchange hysteresis. Indeed, if the addition or removal of a water layer in the interplatelet spaces occurs virtually instantaneously, it could affect to some extent the value of the relaxation time, τ_1 , but would have no bearing on the value of τ_2 .

Laird (1987), following Hurst and Jordine (1964) and Jordine *et al.* (1965), argued that both the addition and the removal of water layers in the interplatelet spaces are characterized by activation energy barriers. Overcoming these barriers may be a very slow process, with a long relaxation time. Therefore this hypothesis could in principle account for the hysteresis observed in the swelling of clays (e.g., Laffer *et al.*, 1966) and, consequently, for that observed in connection with cation exchange reactions, like the Ba–Mg exchange studied by Laird (1987).

This hypothesis accounts correctly for the relative extent of the hysteresis observed by Fripiat *et al.* (1965) for the exchanges between NH₄ and various divalent cations. Ba-saturated montmorillonite is less hydrated than the Mg-saturated form, and it exhibits a smaller hysteresis gap (Table 1). The relative extent of hysteresis associated with the exchanges NH₄–Li and NH₄–Na is also predicted correctly. However, on the basis of the number of water layers that have to be squeezed in or out of the interplatelet spaces, one might expect the exchange of NH₄ with Na or Li to be more hysteretic than that of NH₄ with any one of the divalent cations listed in Table 2. In fact, the reverse was observed experimentally by Fripiat *et al.* (1965).

The above hypothesis also leaves somewhat to be desired when one tries to invoke it to account for the

effect of the total normality, or the ionic strength, of the electrolyte solution on the exchange hysteresis. Various studies (e.g., Norrish and Quirk, 1954; Norrish, 1954; Posner and Quirk, 1964) have shown that decreasing the electrolyte concentration increases the extent of crystalline swelling. The range of concentrations used in these studies, from 0.1 to 4 mol, is however much higher than that commonly adopted in cation exchange experiments. Van Bladel and Laudelout (1967) observed the effect of electrolyte concentration on the hysteresis associated with the NH₄–Mg and NH₄–Ba exchange reactions. They did so in a range of total normalities in which, based on what is known about the swelling of the Camp Berceau montmorillonite, one would expect the basal spacings of the NH₄-, Mg-, and Ba-saturated clay to have remained consistently at their maximum value. Therefore, clay swelling hysteresis cannot account for at least some of the observations on cation exchange hysteresis that have been reported in the literature. This is hardly surprising in view of the fact that, in clay suspensions, basal spacings are only one of a number of parameters necessary to characterize the geometrical and dynamical interactions of clay platelets.

Domain or quasi-crystal formation

Van Bladel and Laudelout (1967) argued that “much of the apparent irreversibility of ion exchange reactions is simply a consequence of the imperfection of the dispersion of heavily flocculated clay suspensions.” They further considered that this imperfect dispersion may have led to the relative inaccessibility of a portion of the exchange sites on the clay platelets during their experiments.

Neither Van Bladel nor Laudelout, in any of their writings (e.g., Gilbert and Van Bladel, 1970; Laudelout, 1987) went beyond this somewhat sketchy description of the mechanism they proposed for the phenomenon of cation exchange hysteresis. Nevertheless, experimental evidence obtained independently by other authors lends credence to Van Bladel and Laudelout’s (1967) viewpoint.

It is indeed well established in colloidal chemistry that, under certain conditions, clay platelets in suspension form so-called domains or quasi-crystals (Aylmore and Quirk, 1959; Blackmore and Miller, 1961; Quirk and Aylmore, 1971). These are packets of clay platelets in more or less parallel alignment. The extent of the packets, or the number of single platelets per packet, depends on various factors, including the nature of the ion adsorbed, the electrolyte concentration, the clay type, and the clay concentration. As mentioned earlier, these are precisely the factors that appear to influence the hysteresis associated with cation exchange reactions.

The number of platelets per quasi-crystal of montmorillonite has been determined using methods like

light scattering (e.g., Banin and Lahav, 1968; Dufey and Banin, 1979; Schramm and Kwak, 1982), viscosimetry (e.g., Shainberg and Otoh, 1968; Schramm and Kwak, 1982), high resolution transmission electron microscopy (e.g., Shomer and Mingelgrin, 1978), and small-angle neutron or X-ray scattering (e.g., Cebula *et al.*, 1979). A summary of the results obtained with these various techniques is given in Table 4. The approximate upper bound for the number of clay platelets per quasi-crystal of Ca-montmorillonite was obtained by Greene *et al.* (1973) on the basis of electron micrographs.

Again it is easy to recognize in Table 4 the same three groups already identified in the previous section (Table 2), suggesting that there is a close relationship between cation exchange hysteresis and the number of platelets per quasi-crystal of (homogeneously saturated) montmorillonite. The existence of such a relationship would account for the effect of the total normality of the solution on the hysteresis associated with cation exchange reactions, observed for example by Van Bladel and Laudelout (1967). Indeed, the experimental results obtained by Fitzsimmons *et al.* (1970) and Greene *et al.* (1978) via optical density measurements and by Novich and Ring (1984) using photon correlation spectroscopy indicate that the average number of clay platelets per quasi-crystal increases significantly with the total electrolyte content of the solution in which the clay is suspended. The fact that air drying of smectite suspensions causes an increase in the average size of quasi-crystals (Shainberg and Otoh, 1968; Blackmore and Miller, 1961), in conjunction with the observations of hysteresis made by Tabikh *et al.* (1960), lends credence to Van Bladel and Laudelout's (1967) hypothesis.

The effect of the composition of the exchange complex on the formation or breakdown of montmorillonite quasi-crystals has been investigated by a number of authors (Banin and Lahav, 1968; Shainberg and Kaiserman, 1969; Schramm and Kwak, 1982). In these studies, montmorillonite suspensions with equivalent fractions of adsorbed sodium, E_{Na} , ranging from 0 to 1 were obtained by mixing appropriate amounts of Na- and Ca-saturated montmorillonite suspensions and by letting the mixtures reach an apparent equilibrium. The experimental results suggest that up to an E_{Na} of about 0.5 the clay platelets form quasi-crystals; whereas for values of E_{Na} above 0.5, the clay platelets are largely dissociated.

The formation and breakdown of the quasi-crystals in suspension appears to also affect significantly the behavior of exchangeable cations. Low angle X-ray diffraction studies of mixed Na-Ca-montmorillonite suspensions show that up to a threshold E_{Na} of about 0.5, the Ca ions saturate the exchange sites in the interplatelet spaces inside the quasi-crystals, whereas the Na ions are located on the outer surfaces of the quasi-

Table 4. Ranges reported in the literature for the number of platelets per quasicrystal of montmorillonite, assuming full dispersion in the Li-saturated case.

Ion	Platelets/quasicrystal
Li ⁺	1.0
Na ⁺	1.0-1.7
Rb ⁺ , K ⁺ , Cs ⁺ , NH ₄ ⁺	1.4-3.0
Mg ²⁺ , Ba ²⁺	2.7-7.0
Ca ²⁺	2.7->20

crystals (Glaeser and Mering, 1954; Fink *et al.*, 1971; Levy and Francis, 1975). At E_{Na} values above 0.5, this "demixing" phenomenon gives way to a more homogeneous distribution of the cations on the exchange sites. Therefore, the inaccessibility of exchange sites referred to by Van Bladel and Laudelout (1967) is borne out by experimental evidence for E_{Na} values in the range 0 to 0.5.

Van Bladel and Laudelout's (1967) proposed mechanism nevertheless falls short of explaining completely the phenomenon of cation exchange hysteresis. Indeed, it does not account for the fact that exchange reactions involving cations from group 3 in Table 2 are not hysteretic, even though smectites saturated with these cations are all "incompletely dispersed." Furthermore, a complete model of the cation exchange hysteresis phenomenon should explain in detail how the imperfect dispersion of the clay platelets causes hysteresis, and account for the role that cation demixing plays in this process.

CONCEPTUAL MODEL OF CATION EXCHANGE HYSTERESIS

The similarity between the groupings in Tables 2-4 suggests that swelling hysteresis and the formation of quasi-crystals are both simultaneously involved in causing the cation exchange hysteresis phenomenon.

To describe a possible scenario for this combined action, it is convenient to use the schematic illustration of Figure 4, the lower portion of which, from a to d, was first introduced by Ball (1981). The first monovalent cations added to a suspension of a smectite saturated with a divalent cation tend to adsorb reversibly and rapidly on the outer surface of the quasi-crystals (point b). Because of their lower charge, their entrance into the interplatelet regions would be accompanied by the addition of several water layers and would result in the propping open of the interplatelet regions. This, effectively, would lead to the breakdown of the quasi-crystals into smaller quasi-crystals, with increased axial ratios. Because of the large activation energy barrier associated with this process, its kinetics is extremely slow as long as the equivalent fraction of the monovalent cation in solution remains low. At higher concentrations of the monovalent cation in solution (point c), the probability of some of the monovalent cations

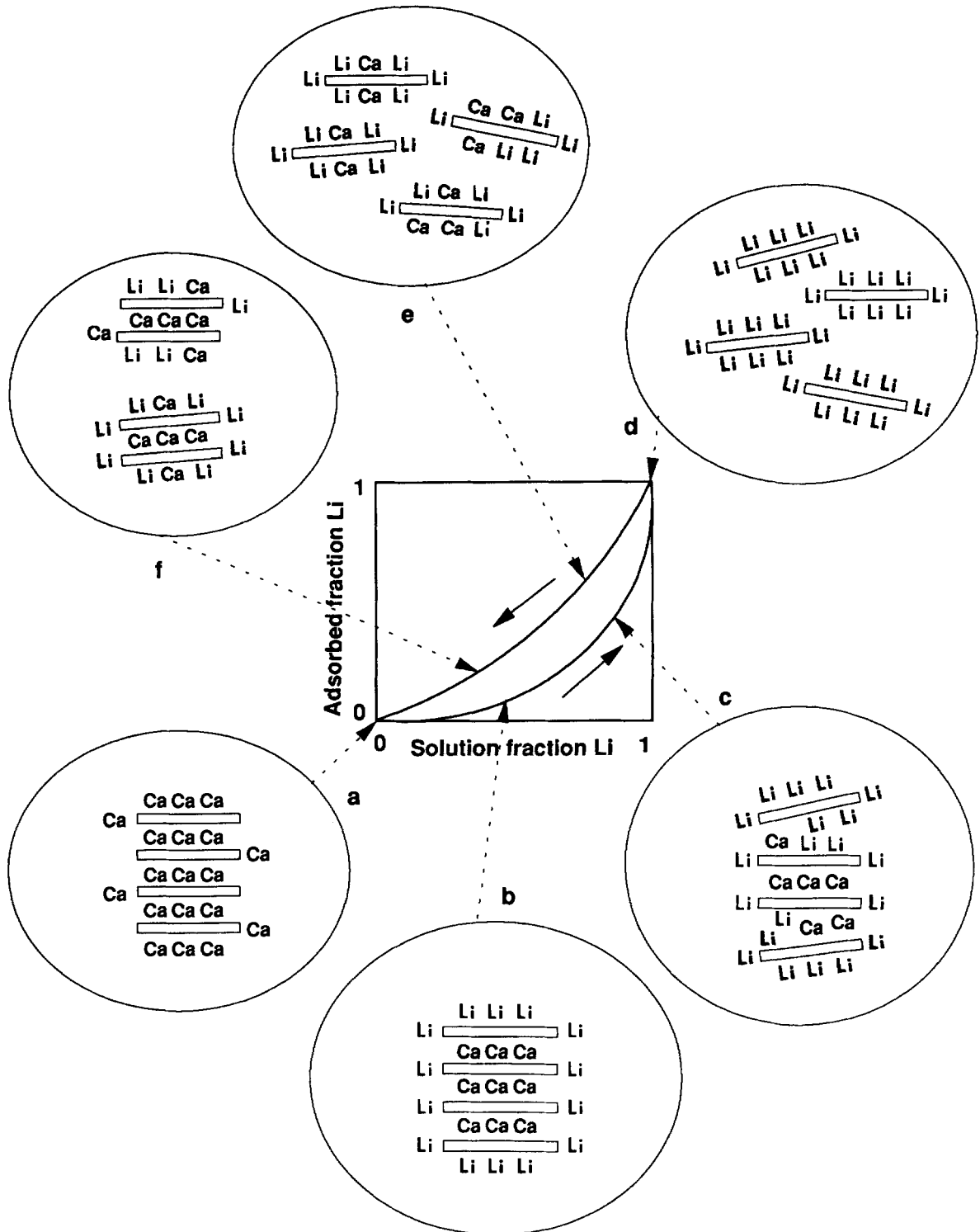


Figure 4. Hypothesized distribution of cations and changes in aggregation status during a Li-Ca exchange cycle in a smectite suspension.

being able to overcome this activation energy barrier is increased and the clay platelets become more and more dissociated. When the majority of the quasi-crystals have been dispersed, little further change in either surface properties or platelet dimensions occurs and the exchange reaction proceeds with a very fast kinetic until the exchanger is fully saturated with the monovalent cation (point d). The backward reaction starts with the exchanger saturated with the monovalent cation and fully dispersed. Under these conditions, the totality of the exchanger surface is therefore accessible to the divalent cations (point e). The exchange is virtually instantaneous. Brownian motion makes the clay platelets constantly bump into each other. As a result of these encounters, doublets of platelets may form (point f). An activation energy barrier hampers this process as long as the concentration of the divalent cation in solution remains low. As this concentration is increased, the probability of formation of doublets, triplets, etc., becomes more and more significant, i.e., its kinetics becomes faster. Eventually, when the electrolyte solution no longer contains any monovalent cation, the suspension reverts to its initial state (point a), with all the exchange sites saturated by divalent cations.

This scenario applies to binary exchange reactions involving Li. When, instead, Na is involved in the exchange reaction, the picture has to be modified somewhat because Na-saturated smectites have a tendency to form quasicrystals (Table 4). Therefore, in this case, point d should correspond to a partially aggregated suspension instead of a fully dispersed one for Li-saturated clays. In the case of Rb-, Cs-, K-, and NH₄-saturated smectites, this aggregation tendency is even stronger (Table 4) and results in quasi-crystals with interplatelet spacings that are smaller than in the Ca-, Ba-, or Mg-saturated clays (Table 3). The concept of energy barrier introduced earlier should still apply to this situation. The only difference with the Li-saturated case is that the energy barrier to be overcome in the replacement of divalent cations by monovalent cations now is associated with the removal of a water layer from the interplatelet space rather than with the addition of one or more water layers, as in Figure 4.

This scenario makes clear the key role played by the activation energy barriers associated with the process of interplatelet swelling. It also clarifies, in this context, the influence of the quasi-crystals on the extent of the hysteresis loop. Indeed, the bigger the quasi-crystals are at a point a (Figure 4), the smaller is the exchanger surface accessible initially to the monovalent cation, and the bigger one expects the difference will be between the geometric configurations of the clay suspensions at the points b and f, corresponding to the same solution composition.

An implicit premise of the above scenario is that the process of formation or breakdown of quasicrystals upon decrease or increase, respectively, of the mono-

valent cation concentration in solution are very slow, occurring over times commensurate with the relaxation time, τ_2 , introduced in the previous section. Experimental evidence obtained by Shainberg and Kaiserman (1969) seems to strongly contradict the validity of this assumption. These authors followed the kinetics of formation and breakdown of Ca-saturated quasi-crystals of Wyoming bentonite. They did so by recording the changes in light transmission as a function of time when Ca-bentonite suspensions of 0.05% (w/v) concentrations were added in various proportions to Na-bentonite suspensions of the same concentration in the titrating vessel placed in the light path of a spectrophotometer. Quasi-crystal formation was found to be virtually instantaneous whereas the breakdown of Ca-saturated quasi-crystals took approximately 10 min. Similar results were obtained by Frenkel and Shainberg (1981) using a stopped flow spectrophotometer and mixtures of Na-saturated and, respectively, Ca-, Mg-, Al-, Fe-, and Al-saturated Wyoming bentonite. These results are however sharply contradicted by the observations made by Greene *et al.* (1973) and, more recently, by Novich and Ring (1984).

Greene *et al.* (1973) used light scattering techniques and monitored the development of flow birefringence to follow the rearrangement of elementary platelets of Ca-saturated Wyoming bentonite into quasi-crystals. They found that the speed of shaking and the volume of suspension per flask significantly affected the thickness and lateral extent of the quasi-crystals. At the highest shaking rate, the optical density of the clay suspensions, directly related to the size of the quasi-crystals, was still steadily increasing four weeks after the beginning of the experiments. Novich and Ring (1984), on the other hand, used photon correlation spectroscopy to monitor the coagulation of suspensions of a number of clay minerals. They present data for illite indicating that the rate of quasi-crystal or domain formation remained constant over a 20 min period after the beginning of the experiment. Both Green *et al.*'s (1973) and Novich and Ring's (1984) data refer to the formation of quasi-crystals, while Shainberg and Kaiserman's (1969) evidence relates to both formation and breakdown processes. Undoubtedly, further research is needed in this area. Nevertheless, the observations by Greene *et al.* (1973) that high-energy ultrasonic radiation was unable to completely disperse Ca-bentonite platelets associated in quasi-crystals suggests that the latter are extremely stable and gives some credence to the assumption made above.

CONCLUSIONS AND PERSPECTIVES

Because the arguments put forth earlier in favor of the mechanism involving crystalline swelling and quasicrystal formation also apply to the conceptual model outlined in the previous section, this model appears to account at least qualitatively for most of the experimental evidence on cation exchange hysteresis avail-

able in the literature. In particular, it explains the effect of the total normality of the electrolyte solution, the effect of dehydration, and the influence of the nature of the cations involved in the exchange reaction. In this last respect, it is consistent with the grouping of cations in Table 2. Interestingly, however, it also raises a number of critical questions concerning the way the behavior of clay suspensions has been studied in the past. In experiments dealing with the formation and breakdown of quasi-crystals in mixed Na–Ca systems (Banin and Lahav, 1968; Schramm and Kwak, 1982), for example, researchers have routinely adopted the procedure of mixing together homoionic Na- and Ca clays in various proportions to obtain targeted exchanger phase compositions. Within the framework of the conceptual model presented in the present paper, one would expect the results obtained using this procedure to differ significantly from those obtained with clay suspensions that have undergone a forward or backward exchange reaction prior to light scattering or viscosity measurement.

The conceptual model introduced in the present paper also causes to some extent the traditional distinction between cation exchange and cation "fixation" (e.g., of K on vermiculite) to become somewhat blurred. What has been referred to as fixation in the past could indeed very well correspond to a case where the relaxation time τ_1 (Figure 3) is negligibly small (or the extent of the reaction characterized by this relaxation time is insignificant) and where τ_2 is extremely long. Within the context of the model of the previous section, this case would reside at one extreme of a continuum whose other limit would correspond to exchange reactions with a finite τ_1 and a vanishing τ_2 . Between those two poles, one would find exchange reactions varying widely in terms of both τ_1 and τ_2 . The experimental determination of the values of these relaxation times and of the parameters that affect them awaits further research.

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