INTERPRETATION OF THE VARIABILITY OF SELECTIVITY COEFFICIENTS FOR EXCHANGE BETWEEN IONS OF UNEQUAL CHARGE ON SMECTITES[1]

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Abstract—Ion-exchange experiments in expanding clay minerals conducted over a wide range of surface ionic compositions and ionic strength produce variable mass-action selectivity coefficients. When the exchanging ions are of unequal charge, tactoid structure appears to influence selectivity, although configurational entropy of adsorbed ions may also generate variable selectivity. The degree of deviation from ideal mass-action exchange is related to the dissimilarity of the ions undergoing exchange. Data involving trivalent ion adsorption on smectites suggest that mass-action is a poor approximation when the adsorbing and desorbing ions have different hydration energies and charge. No form of exchange equation is successful in describing ion exchange for a wide range of experimental conditions, although the fluctuation of the selectivity coefficient follows consistent trends with changing experimental conditions. The strong adsorption of high-charge ions on clays is not exothermic, but must be driven by the increasing disorder of ions and/or water.

Key Words—Cation exchange, Cation selectivity, Entropy, Mass action, Selectivity coefficient, Smectite.

INTRODUCTION

The equations for exchange on surfaces between ions of unequal charge have received considerable attention, at least partly as a result of the non-constant nature of the mass-action ion selectivity coefficient. Although modifications have been made to the mass-action equation in order to maintain a constant coefficient (Krishnamoorthy and Overstreet, 1949; Eriksson, 1952), no exchange model has been developed that predicts the changing selectivities that are especially evident at low ionic strength (Marshall, 1964). The mass-action coefficient is generally found to be dependent upon the ionic composition of the exchanger (Maes *et al.*, 1976; Barrer and Falconer, 1956) and the total ionic strength of the solution at equilibrium (Laudelout *et al.*, 1968). The functional dependence on surface composition and ionic strength is generally more pronounced for trivalent metal ion adsorption (Frysinger and Thomas, 1960; McBride and Bloom, 1977) than for divalent ion adsorption (Gaines and Thomas, 1955). Heterogeneity of surface exchange sites might account for composition-dependent selectivities, as has been suggested for Co^{2+}-Na^+ and Cu^{2+}-Na^+ exchange on montmorillonite (Peigneur *et al.*, 1975; McBride, 1976). However, exchange studies of numerous types of surfaces have shown similar systematic variations of selectivity with surface composition, suggesting that exchange between ions of unequal charge is not accurately described by mass-action concepts. Rather than assume a systematic variation of the heat of reaction (ΔH) with surface composition (resulting from site heterogeneity

or ion-ion interaction), one can interpret large changes of selectivity in terms of entropy changes accompanying exchange reactions in clay systems. Marshall (1964) stated that entropy changes in the exchange of ions of different charge is an important factor and noted that exchange systems deviate greatly from the simple Gaines and Thomas (1953) thermodynamic model which allows calculation of *averaged* ΔS and ΔH values of exchange from the temperature-dependence of the mass-action "equilibrium coefficient." Because this coefficient is given by a form of the exchange equation based upon mass-action concepts and is assumed to be the "equilibrium constant," the calculated free energy of reaction (ΔG) at a given surface composition is arbitrary and model-dependent. Using this approach, relatively large values of ΔS for exchange between monovalent and divalent ions on exchangers have been recorded (Coleman, 1952; Gaines and Thomas, 1955). While hydration structure of ions probably plays an important role in determining the value of ΔS for an ion-exchange reaction, the extent to which adsorbed divalent or trivalent ions are restricted by electrostatic attraction to individual surface sites may greatly influence ΔS. For example, exchange of Cs^+ by Sr^{2+} on montmorillonite was accompanied by a calculated increase in entropy (Gaines and Thomas, 1955), which may be partially a result of the displacement of highly localized, weakly hydrated Cs^+ ions on the surface by more strongly hydrated, more mobile Sr^{2+}. The reaction of Na^+-montmorillonite with a number of divalent heavy metals also produced increases in entropy and was endothermic (Maes *et al.*, 1976). Similarly, replacement of K^+ by Ca^{2+} on a strong-acid exchange resin produced a large increase in entropy (Coleman,

1952), possibly due in part to a large reduction in translational freedom of K^+ upon adsorption when compared to the more mobile behavior of adsorbed Ca^{2+}. The trend is the same for Ca^{2+}, Sr^{2+}, and Ba^{2+} adsorption on Na^+-zeolites, where ΔS values are positive, but much larger for the strongly hydrated Ca^{2+} when compared to Sr^{2+} and Ba^{2+} (Sherry, 1969).

The present study investigates several clay-exchange systems involving ions of unequal charge and attempts to explain observed deviations of data from mass-action behavior. The extent to which systematic variations in the equilibrium coefficient can be explained by changes in entropy and energy at the exchanger surface is also evaluated.

MATERIALS AND METHODS

A Na^+-saturated montmorillonite ($<2 \mu m$) from Upton, Wyoming, was prepared by standard methods of dialysis and freeze-dried. Weighed quantities (0.100 g) of the freeze-dried Na^+-montmorillonite were equilibrated for one day at $20 \pm 1°C$ with 50 ml of $CdNO_3$ solution. The ionic strength and Na^+ concentration were controlled at three levels by the presence of 0.01, 0.05, and 0.10 M $NaNO_3$. Equilibrium activities of Cd^{2+} were determined using an Orion Cd specific ion electrode. The use of NO_3^- salts prevented the possibility of Cd-anion complex formation in solution. The electrode was accurate enough to allow calculation of exchange coefficients at low Cd^{2+} adsorption levels but not at high levels where initial and equilibrium Cd^{2+} concentrations were not greatly different.

As an example of exchange between a divalent and trivalent ion, Ca^{2+}-saturated Upton montmorillonite was prepared by standard dialysis procedure (CEC = 94 meq/100 g) and equilibrated with several concentrations of $LaCl_3$ solution. The exchanges were conducted for one day at room temperature using 0.100 g of Ca^{2+}-montmorillonite in 100 ml volumes of solution. Supernatants were separated by centrifugation and analyzed for La^{3+} by flame photometry. Two exchange isotherms were obtained, with the concentration of excess $CaCl_2$ in solution adjusted to 0.001 M and 0.01 M. X-ray powder diffraction analysis of the Ca^{2+}- and La^{3+}-saturated clay films indicated similar d-spacings for the wet and dry states—19 Å and 14 Å, respectively.

RESULTS AND DISCUSSION

The usual theoretical approach used in exchange between ions of different charge can be demonstrated for displacement of a monovalent cation, M^+, by a divalent ion, M^{2+}:

$$2\overline{M^+} + M^{2+} \rightleftharpoons \overline{M^{2+}} + 2M^+$$
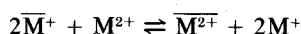
where the bar represents the adsorbed state of the ion. The mass-action equilibrium "constant" (or coefficient) is then defined as:

$$K_{MA} = \frac{[\overline{M^{2+}}]}{[\overline{M^+}]^2} \cdot \frac{(M^+)^2}{(M^{2+})} \tag{1}$$

where the square brackets represent equivalent fractions of adsorbed ions and round brackets indicate solution activities. The value of K_{MA}, however, is composition-dependent, and "surface activity" coefficients are generally introduced into the expression so that an equilibrium constant, K, can be defined:

$$K = \frac{f_{2+}}{f_+^2} \cdot \frac{[\overline{M^{2+}}]}{[\overline{M^+}]^2} \cdot \frac{(M^+)^2}{(M^{2+})} = \frac{f_{2+}}{f_+^2} \cdot K_{MA} \tag{2}$$

The assignment of variations in the selectivity coefficient to composition-dependent activity coefficients of the adsorbed ions (f_{2+}, f_+) is arbitrary and produces no further understanding of the exchange process, nor does it allow prediction of the functional relationship between K_{MA} and surface ion composition. Since the "activities" of adsorbed ions as defined in Eq. (2) are not analogous to those of ions in solution (Thomas, 1965) and cannot be assumed to be simply related to surface concentrations of ions, an approach to exchange using a model that avoids surface activity concepts would be preferred. Statistical thermodynamic models of exchange (Harvey *et al.*, 1966; Barrer and Falconer, 1956; Davis, 1950) can be used in principle to determine the chemical potential of adsorbed ions without making the approximation of solution-like behavior. Compared with solution ions, adsorbed ions are restricted in translational and rotational motion, with the result that their entropies as well as energies are changed.

The entropy change during the exchange reaction, ΔS^0_{ex}, is the resultant of several entropy contributions. For A^{2+}-B^+ exchange, ΔS^0_{ex} is given by (Hutcheon, 1966):

$$\Delta S^0_{ex} = S^0_{A(ads)} + 2S^0_{B(sol)} - S^0_{A(sol)} - 2S^0_{B(ads)}$$

where $S^0_{A(ads)}$ and $S^0_{B(ads)}$ are the standard entropies of the adsorbed metal ions A^{2+} and B^+ and their associated water molecules, and $S^0_{A(sol)}$ and $S^0_{B(sol)}$ are the standard entropies of the metals and their hydration water in solution. Rearranging the above equation:

$$(S^0_{A(ads)} - 2S^0_{B(ads)}) - (S^0_{A(sol)} - 2S^0_{B(sol)}) = \Delta S^0_{ex} \tag{3}$$

one can observe that a positive entropy of exchange may arise from a value of $(S^0_{A(ads)} - 2S^0_{B(ads)})$ which is less negative than $(S^0_{A(sol)} - 2S^0_{B(sol)})$. The latter term is expected to be large and negative because of the much greater order of hydration water about divalent ions. Thus, considering Cd^{2+}-Na^+ exchange, $(S^0_{Cd(sol)} - 2S^0_{Na(sol)}) = -14.6 - 2(14.4) = -43.4$ e.u. Since M^{2+}-M^+ exchange on clays has ΔS^0_{ex} values on the order of 6 e.u. (Gilbert and van Bladel, 1970), then:
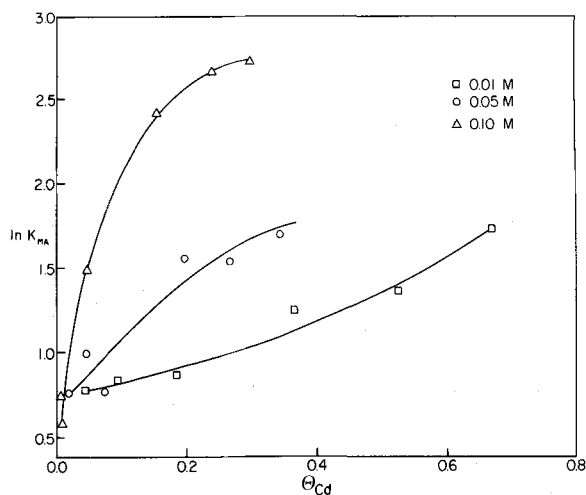
Figure 1. The relationship between fraction of exchange sites occupied by Cd^{2+}, θ_{Cd}, ionic strength and mass-action selectivity coefficient, K_{MA}, in the Cd^{2+}-Na^+-montmorillonite system at room temperature.

$$(S^0_{Cd(ads)} - 2S^0_{Na(ads)}) - (-43.4) \cong +6 \text{ e.u.}$$

Clearly, $(S^0_{Cd(ads)} - 2S^0_{Na(ads)})$ must be negative, but smaller in magnitude than the standard state entropy difference of the same ions in solution. Such a result could be explained by a disordering of water molecules as Cd^{2+} moves to exchange sites and Na^+ is displaced to solution. Since M^{2+}-smectites have limited interlamellar dimensions ($\sim$10 Å), it is likely that a partial loss of outer-sphere hydration water is necessary for Cd^{2+} to be adsorbed, while the desorption of Na^+ does *not* involve a compensating gain in outer-sphere hydration structure because of its weak energy of hydration. This entropy of hydration, ΔS_{hyd}, for the exchange reaction should remain essentially constant per mole of ions exchanged *unless* the interlamellar dimensions of the clay are a function of surface ion composition.

A second entropy contribution arises from the ordering of adsorbed ions on surfaces, called configurational entropy, ΔS_{conf}. This term must be introduced because the process of adsorption confers a degree of ordering on the cations which they did not possess in solution. Derivation of the configurational entropy for M^{2+}-M^+ exchange is difficult, since divalent ions balance two charge sites, and site geometry can only be guessed. However, attempts to obtain theoretical expressions of configurational entropies for exchange between ions of unequal charge have been made (Harvey *et al.,* 1966; Barrer and Falconer, 1956; Davis, 1950); however, for expanding clays such entropy models are probably too simple (*vide infra*). Regardless of the exact model, surface-localized ions possess configurational entropy, ΔS_{conf}, that is a function of ad-
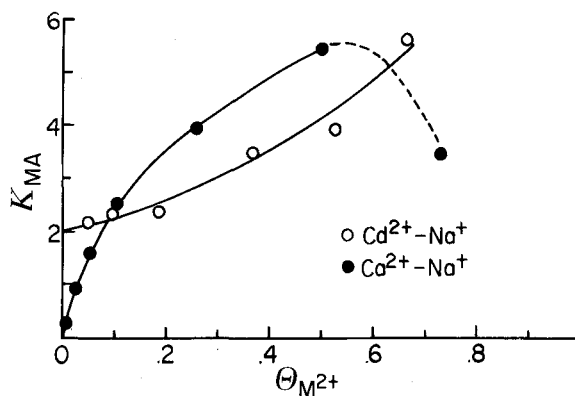

Figure 2. Effect of divalent ion adsorption level on K_{MA} for the cases of Cd^{2+} and Ca^{2+} exchange on Na^+-montmorillonite at room temperature and an ionic strength of 0.01 M.

sorption level. As a result, the mass-action exchange coefficient does not remain constant at different levels of exchange. For M^{2+}-M^+ exchange, the more localized nature of the monovalent ion on surfaces compared with the divalent ion would be expected to produce a positive ΔS_{ex} as the displacement of ordered M^+ ions by less ordered M^{2+} increased the entropy of the clay phase. In addition, the positive entropy, ΔS_{conf}, is not likely to be constant as a function of surface ionic composition. These predictions are consistent with observed results; i.e., free energies of M^{2+}-M^+ ion exchange change with adsorption level, and entropies for M^{2+} adsorption on M^+-clays are invariably positive.

The mass-action exchange coefficient, K_{MA}, for Cd^{2+}-Na^+ exchange varies as a function of the fraction of surface sites occupied by Cd^{2+}, θ (Figure 1). The increase in K_{MA} with increasing θ suggests that preference for Cd^{2+} over Na^+ is higher when greater amounts of Cd^{2+} are adsorbed. A similar result has been obtained for other M^{2+}-Na^+ exchange systems (Maes *et al.,* 1976). The relationship between K_{MA} and θ follows the same trend at higher ionic strength, but becomes much more pronounced (Figure 1). Since the mass-action equation is based on the assumption of solution-like behavior of adsorbed ions, this variation of K_{MA} suggests that adsorbed Na^+ may be somewhat more restricted in mobility at higher values of θ, resulting in an apparent increase in preference for Cd^{2+}. Alternatively, it is possible that the *energy* of Cd^{2+} adsorption increases at higher ionic strength and higher θ or that Cd^{2+} is forced to lose more outer-sphere hydration water upon adsorption at higher θ. It is interesting that K_{MA} is essentially constant for different ionic strengths at very low θ, but indicates a much higher preference for Cd^{2+} at higher ionic strengths when θ is increased. This relationship indicates that at higher Cd^{2+} adsorption levels, an increase in Na^+ activity in solution (i.e.,

higher ionic strength) causes a desorption of Cd^{2+} which is much less than that predicted by the classical mass-action equation.

The non-constant nature of K_{MA} at a given ionic strength with changing surface composition appears to be typical for M^{2+}-M^+ exchange on smectites as shown by data for Ca^{2+}-Na^+ exchange (Figure 2). The data cannot be fit to any single exchange equation over a range of ionic strengths *and* surface ion compositions. Despite the observation that initial adsorption of M^{2+} ions on M^+-smectites at low ionic strengths strongly favors M^{2+} relative to M^+ ions as shown by adsorption isotherms (McBride, 1976; Garcia-Miragaya and Page, 1977), Figures 1 and 2 show that K_{MA} is actually smallest at low M^{2+}-adsorption levels. A reasonable explanation of these results can be given when it is realized that greater quantities of adsorbed M^{2+} increase tactoid formation from dispersed clay platelets, an explanation that has been developed previously (Banin, 1968). The data suggest, then, that the interlayer regions of tactoids prefer divalent to monovalent ions more than external surfaces, in agreement with other results and theoretical calculations (Keren, 1979; Shainberg and Kemper, 1966).

The results are also consistent with demixing models which are based on the premise that tactoid formation causes M^{2+} ions to concentrate in interlamellar regions while M^+ ions occupy external sites (Shainberg and Otoh, 1968; Fink *et al.,* 1971). One effect of higher ionic strength may be to induce tactoid formation at lower values of θ, thereby increasing the clay's preference for M^{2+} ions. In any event, changing platelet structure during exchange probably influences the relative ion preference enough to produce the observed complex relationships between K_{MA} and surface ion composition for M^{2+}-M^+ exchange (Gaines and Thomas, 1955; Hutcheon, 1966; Maes *et al.,* 1976). K_{MA} tends to reach a maximum and then decrease at θ values above 0.5–0.6 (Figure 2), suggesting that since tactoid formation is well established when more than half of the exchange sites are occupied by M^{2+} ions (McBride, 1976; Fink *et al.,* 1971), entropy considerations may dominate at high θ. When most exchange sites become occupied by a given ion, the relative preference for that ion must decrease as shown by arguments based on configurational entropy (McBride, 1979).

Trivalent ions are preferred to M^+ and M^{2+} ions on clays (Frysinger and Thomas, 1960; McBride and Bloom, 1977). Although exchange equations have been developed to describe adsorption of M^{3+} ions (Krishnamoorthy and Overstreet, 1949), the data suggest that the complementary cation competes only to a limited degree with the M^{3+} ion. As a result, the mass-action equation (and related equations) greatly overestimate the ability of the low-charge ion to desorb M^{3+} when exchange data at different ionic strengths are com-
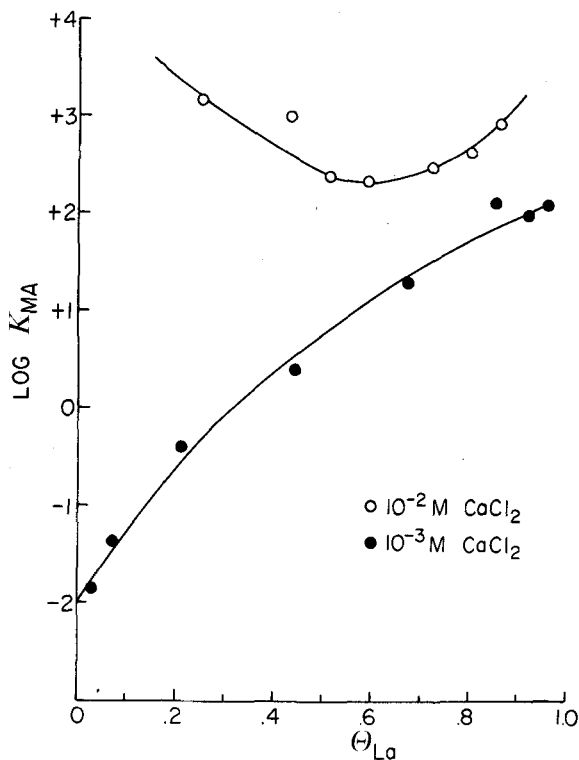

Figure 3.   The relationship between the mass-action selectivity coefficient, K_{MA}, and fraction of exchange sites occupied by La^{3+} for La^{3+}-Ca^{2+} exchange on montmorillonite in the presence of 10^{-2} M and 10^{-3} M $CaCl_2$.

pared, and the data are often better fitted to an equation which ignores the concentration of the complementary ion in solution (McBride and Bloom, 1977). For example, the value of K_{MA} for La^{3+} adsorption on Ca^{2+}-montmorillonite is not only much less composition-dependent, but also greater in magnitude at higher equilibrium concentrations of Ca^{2+} (Figure 3). Very similar results have been obtained for Al^{3+}-Ca^{2+} exchange (McBride and Bloom, 1977), indicating that the mass-action equation is more satisfactory in these systems at high than at low ionic strength. The constancy of selectivity coefficients in previous studies has generally been obtained at relatively high ionic strength, and exchange equations have generally not been tested at lower ionic strength where variability of the exchange "constant" might be expected (Marshall, 1964). The M^{3+}-M^{2+} exchange systems, like the M^{2+}-M^+ systems, show an increase in K_{MA} when the concentration of the low charge ion is increased in solution. Results from Al^{3+}-K^+ exchange suggest that M^{3+}-M^+ systems behave similarly, with the mass-action selectivity coefficient for the M^{3+} ion increasing with increasing ionic strength (Nye *et al.,* 1961).

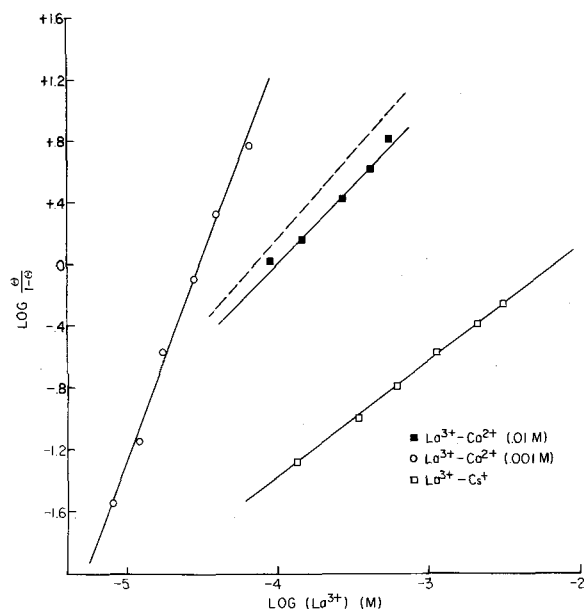It has been generally assumed that selectivity of clays

Figure 4. Relationship between the La^{3+} adsorption function, $\theta/1 - \theta$, and the solution activity of La^{3+} for La^{3+}-Ca^{2+} exchange in 10^{-2} M and 10^{-3} M $CaCl_2$, and La^{3+}-Cs^+ exchange. Data for Al^{3+}-Ca^{2+} exchange in 10^{-2} M $CaCl_2$ are represented by the broken line.

for M^{3+} ions is a result of strong electrostatic forces. However, a trivalent ion must balance three charge sites while maintaining a large hydration sphere, producing a situation that may not be energetically favorable compared to the adsorption of weakly hydrated M^+ ions. To counter this effect, displacement of low-charge ions on clays by M^{3+} produces a net decrease in the ordering of water molecules in solution, while the accompanying *increase* in ordering of surface water is limited by the interlamellar volume. For Ca^{2+}-La^{3+} or Ca^{2+}-Al^{3+} exchange, no apparent change in interlamellar spacing occurs in suspension. As a result, the ΔS^0_{ex} for M^{3+} adsorption may have a large positive value, overcoming the possibly endothermic nature of the adsorption process and producing a strong preference for the high-charge ion. Exchange data on the Ca^{2+}-La^{3+} montmorillonite system at several temperatures indicate increasing preference for La^{3+} at higher temperatures. Using the thermodynamic relationship:

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

it is easily shown that the spontaneous adsorption of La^{3+} on Ca^{2+}-clay has a positive ΔS^0_{ex}. Therefore, entropy rather than electrostatic energy, drives the strong adsorption of La^{3+} (and Al^{3+}) on clays. Tactoid formation should be a less important factor in M^{3+}-M^{2+} exchange than M^{2+}-M^+ exchange, but this does not prevent K_{MA} from varying widely for different La^{3+} adsorption levels or ionic strengths. The mass-action model is apparently least successful in predicting ex-

change equilibrium between ions with very different charge and hydration properties.

If adsorption of M^{3+} ions is considered to be a chemisorption process, where the concentration of the complementary ion is considered to have a relatively small effect upon the adsorption, then the activity of M^{3+} in solution is determined by the extent of surface coverage, θ (McBride and Bloom, 1977):

$$(M^{3+}) = K\left(\frac{\theta}{1 - \theta}\right)^n \qquad (5)$$

where K is a constant and n = 1. This function describes La^{3+} adsorption on Ca^{2+}-montmorillonite in 0.01 M $CaCl_2$ (Figure 4). Al^{3+} adsorption data on Ca^{2+}-montmorillonite at the same ionic strength are found to be comparable (broken line, Figure 4), indicating that Al^{3+} is adsorbed with about the same affinity as La^{3+}. At lower ionic strength (0.001 M $CaCl_2$), the La^{3+} adsorption function has a much higher slope (Figure 4), although the data can be fit to Eq. (5) with n $\cong$ 0.38.

Data for La^{3+}-Cs^+ exchange on montmorillonite (from Krishnamoorthy and Overstreet, 1950), when corrected for the activity coefficient of La^{3+} in solution, also fit Eq. (5) with n $\cong$ 1.3 (Figure 4). For a given quantity of adsorbed La^{3+}, a much higher concentration of La^{3+} is maintained in solution for the La^{3+}-Cs^+ than the La^{3+}-Ca^{2+} clay system as a result of the stronger energy of bonding of Cs^+ by the clay relative to Ca^{2+}. The value of n in Eq. (5) seems to depend upon the complementary ion as well as the ionic strength.

The problem with exchange experiments performed at constant (i.e., relatively high) ionic strength is that the solution concentration of the less strongly adsorbed ion is generally not varied greatly. Considering M^{2+}-M^+ exchange (Eq. (1)), a nearly constant $(M^+)^2$ term and the necessary relationship that $\overline{M^{2+}} = 1 - \overline{M^+}$ if adsorbed metals are measured as equivalent fractions, then:

$$(M^{2+}) = K'\frac{\theta}{(1 - \theta)^2}$$

where $\theta = \overline{M^{2+}}$. This expression has almost the same form as the Langmuir adsorption equation even though exchange data can fit this equation and still produce a constant K_{MA}. Equations of this form (e.g., Eq. (5)) often fit exchange data rather well under certain conditions.

CONCLUSIONS

Analysis of ion-exchange data from this study and previous investigations shows that any single form of exchange equation is unlikely to describe quantitatively exchange reactions on expanding clays over a wide range of experimental conditions. This result derives in part from the non-rigid nature of the clays, with the cation composition of the surfaces affecting ion selec-

tivity by changing exchange-site geometry. The mass-action equation produces selectivity coefficients that vary considerably for M^{2+}-M^+ exchange, and extremely for M^{3+}-M^{2+} exchange as the ionic strength and surface ionic composition are varied. The failure of the mass-action selectivity coefficient as an approximate "exchange reaction constant" has previously been observed; however, this study indicates that the deviations from "mass-action" behavior are consistent with arguments involving reaction entropy, and that the deviations show the following consistent relationships:

(1) An increase in solution concentration of the low-charge (weakly adsorbed) ion causes the selectivity coefficient, K_{MA}, to indicate a greater preference for the high-charge ion.

(2) An increase in surface concentration of the high-charge ion generally increases the selectivity coefficient for that ion up to a maximum ($\theta > 0.5$), beyond which preference for the high-charge ion may decrease.

(3) Deviation from mass-action exchange behavior is greatest for M^{3+}-M^{2+} and M^{3+}-M^+ systems, less for M^{2+}-M^+ systems, and least for M^{2+}-M^{2+} or M^+-M^+ systems.

(4) Strong adsorption of high charge ions on clays is a result of an entropy gain associated with the disordering of water or an increase in ion disorder at exchange sites.

The mass-action equation can be expected to produce a reasonably constant selectivity coefficient in cases where all of the adsorbed ions are "solution-like" in terms of their surface disorder (i.e., high rotational and translational mobility). Otherwise, the ordering of ions by localization at sites produces an entropy of exchange whose magnitude is dependent upon the level of adsorption of a given ion and the degree to which the adsorbed and desorbed ions are "solution-like." It is expected that the development of ion-exchange models may be assisted by the qualitative concepts developed in this study.

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Резюме—Показано, что ионно-обменные эксперименты, проведенные на расширяющихся глинистых минералах в пределах поверхностных ионных составов и ионных сил дают переменные коэффициенты масс-действенной селективности. Когда обменные ионы имеют неравный заряд, тактоидная структура, по видимому, влияет на селективность, хотя конфигурационная энтропия адсорбированных ионов тоже может вызывать переменную селективность. Степень отклонения от идеального масс-действенного обмена связана с различием ионов, вовлеченных в обмен. Данные, включающие трехвалентную адсорбцию ионов смектитами, указывают на то, что масс-действие является плохим приближением, когда адсорбирующие и десорбирующие ионы имеют разные энергии гидратации и заряд. Ни одна форма уравнения обмена не является подходящей для описания ионного обмена для широкого диапазона экспериментальных условий, хотя колебание коэффициента селективности следует последовательным тенденциям с изменением экспериментальных условий. Сильная адсорбция глинами ионов с высокими зарядами не является экзотермической, а должна поддерживаться увеличивающимся разупорядочиванием ионов и/или воды. [N.R.]

Resümee—Experimente zum Ionenaustausch in quellfähigen Tonmineralen, wobei deren Oberflächen eine unterschiedliche Ionenzusammensetzung und Ionenstärke aufwiesen, führen zu unterschiedlichen Selektivitätskoeffizienten. Wenn die austauschenden Ionen von ungleicher Ladung sind, scheint eine taktoide Struktur die Selektivität zu beeinflussen, obwohl auch die Konfigurationsentropie des adsorbierten Ions eine unterschiedliche Selektivität hervorrufen kann. Der abweichungsgrad vom idealen Austausch nach dem Massenwirkungsgesetz steht in Zusammenhang mit der Unterschiedlichkeit der Ionen, die am Austausch teilnehmen. Ergebnisse bei der Adsorption dreiwertiger Ionen an Smektit deuten darauf hin, daß das Massenwirkungsgesetz eine ungenaue Annäherung ist, wenn das zu adsorbierende und das zu desorbierende Ion unterschiedliche Hydratationsenergien und Ladungen haben. Keine Art von Austauschgleichung kann den Ionenaustausch für einen großen Bereich von experimentellen Bedingungen genau beschreiben, obwohl die Änderung des Selektivitätskoeffizienten bei sich ändernden experimentellen Bedingungen bestimmten Trends folgt. Die starke Adsorption von hochwertigen Ionen an Tonen ist nicht exotherm, sondern muß durch die zunehmende Unordnung der Ionen und/oder des Wassers bewirkt werden. [U.W.]

Résumé—Des expériences d'échange d'ions dans des minéraux argileux en expansion faits sur une large gamme de compositions ioniques et de force ionique de surface produisent des coéficients de sélectivité d'action en masse variables. Lorsque les ions échangeants sont de charge inégale, une structure tactoide semble influencer la sélectivité, quoique l'entropie de configuration des ions adsorbés peut aussi générer une sélectivité variable. Le degré de déviation de l'échange d'action en masse idéal est apparenté à la dissimilar ité des ions subissants l'échange. Des donneés impliquant l'adsorption d'ions trivalents sur des smectites suggère que l'action en masse est une pauvre approximation lorsque les ions adsorbants et désorbants ont des énergies d'hydration et une charge différentes. Aucune forme d'équation d'échange ne réeussit à décrire l'échange d'ions pour une large gamme de conditions expérimentales, quoique la fluctuation du coéficient de sélectivité suit des directions régulières suivant des changements de conditions expérimentales. L'adsorption forte d'ions à haute charge sur les argiles n'est pas exothermique mais doit être poussée par le désordre croissant d'ions et/ou d'eau. [D.J.]