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AN INTERPRETATION OF CATION SELECTIVITY VARIATIONS IN M^+–M^+ EXCHANGE ON CLAYS[1]

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Abstract—The decreasing preference of montmorillonite for K^+ relative to Na^+ as the clay adsorbs increasing amounts of K^+ is shown to be the general rule for the exchange of strongly hydrating ions by weakly hydrating ions. Variability in the mass-action selectivity coefficient is interpreted in terms of a composition-dependent surface entropy, which is a function of the chemical properties of the exchanging ion as well as the nature of the adsorption sites. The generally used mass-action form of exchange equation may only be applicable to exchange systems in which both ions have solution-like mobility at the exchanger surface. It is suggested that experimental variables such as ionic strength can greatly influence the degree of fit of data to a given ion-exchange equation.

Key Words—Adsorption, Cation exchange, Montmorillonite, Selectivity, Statistical mechanics.

INTRODUCTION

The development of ion-exchange equations has a long history, and several reviews discussed the numerous models that have been used (Walton, 1949; Marshall, 1964; Reichenberg, 1966). Despite the various approaches to exchange, selectivity coefficients (i.e., K_c values) for ions on colloids are known to vary with the ionic composition of the exchanger (Marshall, 1964) as well as with the ionic strength of the solution (Laudelout *et al.*, 1968). As a result, the exchange equations have only qualitative predictive value, although they are used to calculate a selectivity coefficient for each different ionic composition of the exchanger. The relation between "activities" of adsorbed ions and the fraction of surface exchange sites occupied by the ions is described by the functional dependence of K_c on the ionic composition of the surface. In general, mass-action forms of exchange equations are used to calculate K values, but other equations have been found to produce more constant selectivity coefficients for divalent–monovalent ion exchange (Eriksson, 1952; Krishnamoorthy and Overstreet, 1949). It is suggested in the present study that modifications to the mass-action equation result from the fact that adsorbed ions are not solution-like in all respects, and that their "activities" are not simple functions of mole or equivalent fractions of these ions in the exchanger. In addition, many of the proposed exchange models have been based on data from systems that maintained relatively high ionic strengths as well as a narrow range of exchanger composition, so that constancy of the exchange equations has not been rigorously tested (Marshall, 1964). The purpose of this paper is to investigate the variability of the selectivity of montmorillonite for K^+ relative to Na^+ as a function of surface composition and ionic strength, and to present an interpretation of selectivity variations based upon statistical mechanical considerations of ions adsorbed on sites with different degrees of mobility.

MATERIALS AND METHODS

Exchange experiments involving Na^+ and K^+ were conducted with 0.100 g samples of K^+-saturated or Na^+-saturated Upton, Wyoming, montmorillonite (prepared by standard methods of dialysis) in 100-ml volumes of solution. After 24 hr of shaking, the suspensions were centrifuged and the supernatants analyzed for Na^+ and/or K^+ using flame photometry. The following three experiments were carried out: (a) adsorption of K^+ on Na^+-montmorillonite in the absence of excess NaCl, with measurement of the equilibrium concentration of K^+, (b) adsorption of K^+ on Na^+-montmorillonite with excess NaCl (0.01 M) present, with measurement of the equilibrium concentration of K^+, (c) adsorption of Na^+ on K^+-montmorillonite in the absence of excess salt with measurement of equilibrium concentrations of Na^+ and K^+. Experiment (c) was conducted twice to verify reproducibility. The surface coverage terms, $[\overline{K^+}]$, representing the fraction of exchange sites occupied by K^+, were calculated from the equilibrium K^+ concentration using a cation-exchange capacity (CEC) of 96.5 meq/100 g for the K^+-montmorillonite. This CEC value was determined for duplicate samples by exchanging K^+ from the clay with 3 washes of 0.1 M $CaCl_2$ and measuring the displaced K^+ by flame photometry. The CEC of the Na^+-montmorillonite, as determined by a similar method, was 77 meq/100 g, indicating that the dialysis procedure used in preparation of the clay had produced excessive surface hydrolysis.

RESULTS AND DISCUSSION

The selectivity coefficient, K_c, for the adsorption of K^+ on Na^+-montmorillonite can be defined as:

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$$K_c = \frac{[\overline{K^+}]}{[\overline{Na^+}]} \cdot \frac{(Na^+)}{(K^+)} \quad (1)$$

where $[\overline{K^+}]$ and $[\overline{Na^+}]$ are equivalent fractions of the clay exchange sites occupied by K^+ and Na^+, and (K^+) and (Na^+) are the solution activities at equilibrium. A plot of K_c as a function of $[\overline{K^+}]$ demonstrates the non-constant nature of the selectivity (Figure 1). The adsorption of K^+ on Na^+-montmorillonite with excess NaCl (0.01 N) present produced K_c values in the range of 1–2.5, with the preference for K^+ decreasing as greater quantities of K^+ were adsorbed. These results are comparable to those of Gast (1972), which indicated a K_c of 3–4 with a lower ionic strength (0.001 N). In the absence of excess salt, with the adsorption of Na^+ on K^+-montmorillonite, the value of K_c was larger and indicated a much more pronounced decrease in selectivity for K^+ at greater levels of adsorbed K^+ (Figure 1). A leveling off of K_c at $\overline{K^+}$ values above 0.8 was caused by proton competition with Na^+ for exchange sites when low concentrations of Na^+ were present (i.e., $\leq 10^{-5}$M). With low Na^+ concentrations, H^+ concentrations resulting from dissolved CO_2 became significant, displacing as much as 7% of the K^+ ions from the K^+-montmorillonite before any Na^+ had been added to the system. Subsequent additions of Na^+ to solution displaced H^+ from exchange sites in preference to K^+, and no significant quantities of H^+ were on exchange sites at $[\overline{K^+}]$ values below 0.8. This is a reasonable result based upon preliminary experiments which gave K_c values for Na^+–H^+ exchange in the range of 2 to 5 in favor of Na^+.

In an experiment involving the exchange of Na^+-montmorillonite by K^+ in the absence of excess salt, the competitive effect of H^+ was even more pronounced until levels of K^+ in solution became high enough to exclude protons from the surface. The result was a much greater quantity of Na^+ released than K^+ adsorbed on clays with a high Na^+ content. Because the Na^+-montmorillonite in the absence of added salt was more susceptible to the hydrolysis reaction, the data were not analyzed for variation in K_c as a function of surface composition. An ion exchange equation including H^+, Na^+, and K^+ would have been necessary to adequately describe this system.

A number of other exchange studies have indicated composition-dependent selectivity variations. A decrease in preference of Na^+-montmorillonite for Cs^+ at high levels of adsorbed Cs^+ (Lewis and Thomas, 1963; Gast, 1972) has been observed, with similar but less pronounced decreases of K_c for Cs^+ on K^+-montmorillonite (Faucher and Thomas, 1954). Exchange between Na^+ and Rb^+ on montmorillonite (Gast, 1972) and between Na^+ and K^+ on erionite (Sherry, 1979) has also shown the effect. Data on cation exchange in crosslinked (i.e., rigid) resins have suggested that the

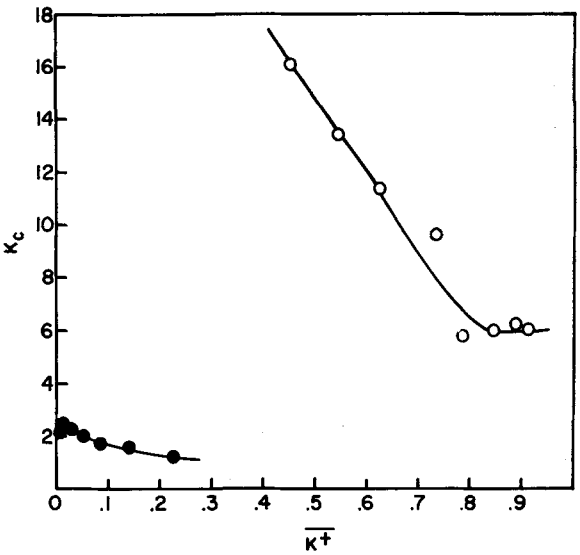


Figure 1. Relationship of the selectivity coefficient, K_c, to equivalent fraction of adsorbed K^+ for adsorption of K^+ on Na^+-montmorillonite in 0.01 N NaCl (●), and adsorption of Na^+ on K^+-montmorillonite with no excess salt (○).

phenomenon of selectivity variation as a function of surface composition is the rule rather than the exception (Reichenberg, 1966). In all types of exchangers, the preference for the larger (i.e., less strongly hydrated) cation decreased as the exchange sites were more completely occupied by that cation. This general relationship is shown in Figure 2, with $\Delta \log K_c$ (the difference in the value of $\log K_c$ at 0.2 and 0.8 equivalent fractions of exchange sites occupied by the larger cation) related to Δr, the difference in ionic radii of the ions. In general, then, exchange of an ion of small radius by one of large radius is characterized by preference for the larger ion which becomes less pronounced (or may even reverse) as the exchange proceeds. For example, the value of K_c reduced by more than one order of magnitude for K^+–H^+ and Cs^+–Li^+ exchange on strong acid resins when the preferred ion was increased from 20 to 80% coverage of the exchange sites. Similarly, experiments conducted on montmorillonite and synthetic laponite using weakly hydrating organic cations such as $(CH_3CH_2)_3NH^+$ to displace metallic M^+ ions showed dramatic decreases in preference for the organic cations at high adsorption levels (Theng, 1974; Vansant and Peeters, 1978). Conversely, numerous experiments have shown relatively constant values of K_c as a function of exchanger composition when the cations are of similar hydration energy, such as Li^+ and Na^+ (Gast, 1972; Sherry, 1979).

The form of the ion-exchange equation used to obtain K_c is based upon the hypothesis that "activities" of surface-adsorbed ions are proportional to the fraction of sites occupied (Kerr, 1928; Vanselow, 1932). This

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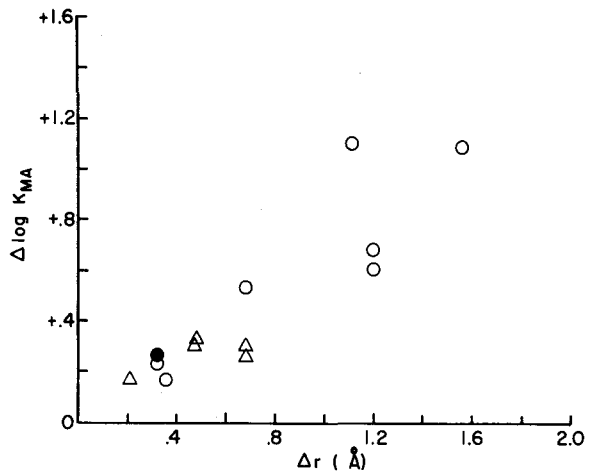


Figure 2. Relationship between Δ log K_c (difference between K_c at $[\overline{M^+}] = 0.2$ and $[\overline{M^+}] = 0.8$) and Δr (difference in radii of the two ions undergoing exchange). Estimates of Δ log K_c are obtained from the studies of Gast (1972) (△), Faucher and Thomas (1954) (●) on montmorillonite, and the studies of resins by Reichenberg (1966) (○).

requires the assumption that surface-adsorbed ions form an ideal binary "solution" (Garrels and Christ, 1965), with any departure from ideal behavior observed as small variations in K_c with changing surface-ion composition. The non-ideality can then be expressed in terms of "activity coefficients" of adsorbed ions, f_+, which deviate from unity for non-ideal mixtures of surface-adsorbed ions. However, systematic variation of the "activity coefficient" of an ion as a function of the equivalent fraction of that ion on the exchanger (Walton, 1949), suggests that a better ion-exchange equation could be developed. It has long been known that ion "activities" on surfaces appear to have a nonlinear relationship to surface composition, so that mole or equivalent fractions of an ion on surface sites cannot generally be taken as a measure of that ion's "activity" or chemical potential. The empirical Kielland equation for the activity coefficient of an adsorbed ion, A^+:

$$\log f_{A^+} = C \cdot [\overline{A^+}]^2$$

where C is constant, is evidence for nonlinear relationship between surface "concentration" and surface activity (Kielland, 1935).

Reasons for "non-ideal" behavior (i.e., composition-dependent K_c) can be suggested. Heterogeneity of adsorption sites is possible, although the fact that K_c variation is more dependent upon the properties of the ions in M^+–M^+ exchange than the type of exchanger seems to rule out this effect. Large variations in K_c occur for strong-acid resins where site heterogeneity would seem unlikely. A second explanation might involve interaction energies which depend upon the ionic composition of the surface. Thus, the assumption can be made that, for A^+–B^+ exchange, B^+ ions on neighboring sites have a greater interaction energy than A^+ ions on neighboring sites (Barrer and Klinowski, 1977). This phenomenon seems unlikely for exchange between ions of the same charge, although it may be significant when the adsorbed ions are of unequal charge.

The hypothesis proposed in this study is that an exchanger surface occupied by two ions with much different hydration energies cannot be considered an ideal binary "solution." Since the mass-action Eq. (1) is based upon a solution-phase analogy (see, for example, Sposito and Mattigod, 1979), with both ions assigned the same degree of mobility in the adsorbed state, systematic variations of K_c will occur with changing composition as a result of the different quantities of configurational entropy attributable to ions localized on exchange sites compared to more mobile ions. Considering the extreme examples of localized (loc) and mobile (mob) ions on a surface, the chemical potential of the ions, μ^s, can be derived by statistical mechanics for each case (Adamson, 1976) if one assumes that equations for the potentials of individual adsorbed ions can be developed in much the same way as for adsorbed molecules:

$$(\mu^s)_{loc} = kT \ln \left(\frac{\theta}{1-\theta}\right) - kT \ln Q^s \qquad (2)$$

$$(\mu^s)_{mob} = kT \ln \theta - kT \ln Q^s \qquad (3)$$

where θ is the fraction of exchange sites occupied by the ions, and Q^s is the partition function of the adsorbed ions. The first term in Eq. (2) and (3) represents the partial molar configurational entropy of the adsorbed ions. Thus, if an exchanger approached complete saturation with localized ions ($\theta \rightarrow 1$), the chemical potential of the ions attributable to surface entropy would increase rapidly as $\ln[\theta/(1-\theta)]$ became a large number. However, if the sites approached complete saturation by mobile ions, the surface entropy term would approach zero. This nonsymmetrical behavior would greatly reduce the preference for a localized ion relative to a mobile ion at high adsorption levels, since there are fewer and fewer ways of placing localized ions on sites as most of the sites become occupied by localized ions.

If it is assumed that the free energy of a mixed-ion surface can be expressed as the sum of the contribution of ions A^+ and B^+ to the free energy, and if both ions are assumed mobile on the surface, Eq. (3) can be used to express the chemical potential of the ions:

$$\mu_A{}^s = kT \ln[\overline{A^+}] - kT \ln Q_A{}^s$$

$$\mu_B{}^s = kT \ln[\overline{B^+}] - kT \ln Q_B{}^s.$$

Since the chemical potentials of A^+ and B^+ in solution are given by:

$$\mu_A = \mu_A{}^0 + RT \ln(A^+)$$

$$\mu_B = \mu_B{}^0 + RT \ln(B^+)$$

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then, in an exchange system (with a fixed exchanger content) these expressions for the surface and solution chemical potentials can be related at equilibrium (Krishnamoorthy and Overstreet, 1949):

$$\mu_A{}^s - \mu_B{}^s = \mu_A - \mu_B \tag{4}$$

producing the generally accepted mass-action form of M^+–M^+ exchange equation:

$$K = \frac{[\overline{A^+}]}{[\overline{B^+}]} \cdot \frac{(B^+)}{(A^+)} \tag{5}$$

where K is a constant determined by the value of $\mu_A{}^0$, $\mu_B{}^0$, $Q_A{}^s$ and $Q_B{}^s$. Exchange between ions with similarly mobile behavior should produce a constant selectivity coefficient, K_c. Thus, for Na^+–Li^+ exchange on montmorillonite, K_c, does not vary widely (Gast, 1972). In addition, ion exchange on nonrigid resins (not crosslinked) also tends to produce a constant K_c value (Reichenberg, 1966). However, for the nonsymmetrical case of exchange with one ion showing localized behavior, Eq. (2) may be a better expression of the chemical potential of the localized ion. The exchange constant then becomes:

$$K' = \frac{[\overline{A^+}]}{[\overline{B^+}]^2} \cdot \frac{(B^+)}{(A^+)} \tag{6}$$

where ion A^+ is the least mobile ion. Since K′ is related to K_c by the following expression:

$$K' = \frac{K_c}{\left(1 - [\overline{A^+}]\right)}$$

K_c would be expected to have a large value at low levels of adsorbed A^+, and a lower value at high levels of adsorbed A^+. Thus, the selectivity variations observed in clay and resin exchange described earlier are explained at least qualitatively by a different degree of surface localization for the two ions involved in the exchange.

When both exchange ions have localized behavior, the proposed model predicts an exchange constant given by:

$$K'' = \frac{[\overline{A^+}]^2}{[\overline{B^+}]^2} \cdot \frac{(B^+)}{(A^+)} \tag{7}$$

This form is suggestive of the empirical Rothmund-Kornfeld exchange equation, written for M^+–M^+ exchange as:

$$\left(\frac{[\overline{A^+}]}{[\overline{B^+}]}\right)^x = \frac{k(A^+)}{(B^+)}$$

where x has a value near unity for smectites, but a value near 2 for exchange between large, weakly hydrating ions on synthetic aluminosilicates (Walton, 1949). Thus, Ag^+–K^+ and Ag^+–Tl^+ exchange produced x values of 2.17 and 2.00, respectively (Walton, 1949). Since K^+–$NH_4{}^+$ and Rb^+–Cs^+ exchange on montmorillonite (Walton, 1949; Gast, 1972) had $x \sim 1$, the site geometry of the exchanger may have an influence on the degree to which adsorbed ions can be considered mobile.

Previous derivation of the mass-action Eq. (5) assuming that both adsorbed cations, A^+ and B^+, are localized (Davis, 1950) can be shown to be thermodynamically incorrect. This derivation allows an infinitesimal increase in the number of exchange sites occupied by A^+, $\partial N_{\bar{A}}$, to occur while no change in the number of sites occupied by B^+, $N_{\bar{B}}$, occurs. This, of course, is not possible in a two-ion system with a fixed quantity of exchange sites. Thus, chemical potential of surface-adsorbed A^+ *cannot* be defined as:

$$\mu_A{}^s = (\partial G/\partial N_{\bar{A}})_{N_{\bar{B}}}$$

Barrer and Klinowski (1977) recognized this problem, and redefined the chemical potentials in terms of the ions associated with their sites. Thus, the chemical potential of A^+ with its site L_A, is given by:

$$\mu_{AL_A} = (\partial G/\partial N_{AL_A})_{BL_B} = (\partial G/\partial N_{\bar{A}})_{BL_B}$$

It is conceptually possible to vary the quantity of AL_A while holding BL_B constant by adding pure A^+-exchanger to the system. However, the total number of exchange sites in the system must then be changed. The requirement of a system with variable exchange site content introduces new problems to the derivation of an exchange equation. From classical thermodynamics, the total change in free energy of an exchange system:

$$\overline{A^+} + B^+ \rightleftharpoons A^+ + \overline{B^+}$$

can be written as:

$$dG = \mu_A{}^s\, dN_{\bar{A}} + \mu_B{}^s\, dN_{\bar{B}} + \mu_A\, dN_A + \mu_B\, dN_B \tag{8}$$

where $\mu_A{}^s$, $\mu_B{}^s$ are the chemical potentials of adsorbed A^+ and B^+ and μ_A, μ_B are the chemical potentials of solution-phase A^+ and B^+. In a given A^+–B^+ exchange system, the total quantity of exchanger is not varied. As a result the following relationships hold:

$$dN_{\bar{A}} = -dN_{\bar{B}}$$
$$dN_B = -dN_{\bar{B}}$$
$$dN_A = -dN_{\bar{A}}$$

When these equations are substituted into Eq. (8), all compositional changes on the exchanger and in solution can be expressed in terms of $N_{\bar{A}}$:

$$dG = (\mu_A{}^s - \mu_B{}^s - \mu_A + \mu_B)\, dN_{\bar{A}} \tag{9}$$

At exchange equilibrium, the free energy must be a minimum with respect to variations in number of moles of A, B, $\bar{A}$, and $\bar{B}$; therefore, the coefficient

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of $dN_{\bar{A}}$ in Eq. (9) must be zero. As a result, the chemical potentials of adsorbed and solution ions are related:

$$\mu_A{}^s - \mu_B{}^s = \mu_A - \mu_B \qquad (10)$$

This relationship has been used in derivations of the mass-action form of ion-exchange equation (Krishnamoorthy and Overstreet, 1949; Davis, 1950; Gaines and Thomas, 1953; Barrer and Klinowski, 1977). Since Eq. (10) *requires* conservation of mass, one cannot avoid the problem of definition of chemical potential by allowing the quantities of adsorbed A^+ to vary by the creation of exchange sites. This would invalidate the expression $dN_{\bar{A}} = -dN_{\bar{B}}$, and Eq. (10) could not then be considered valid. An increase in adsorbed A^+ *must* be accompanied by a decrease in adsorbed B^+ if Eq. (10) is to be used.

Spontaneous M^+–M^+ ion exchange generally produces an *average* negative change in entropy (Sherry, 1969; Gast and Klobe, 1971), much of which is probably due to a change in order of water in the exchanger and solution phase. While this change in ordering of water may determine to a large extent the *magnitude* and *average* ΔS of exchange, variations of ΔS as a function of surface-ion composition must be attributed to configurational entropy, since the entropy change of water per mole of ions exchanged should remain about the same at all surface compositions. Variations in K_c are then caused by changing surface order of ions. However, large changes in the value of K_c can also be produced by different experimental conditions, such as ionic strength (Figure 1). For M^+–M^+ exchange, many experiments in the literature have controlled ionic strength with relatively high concentrations of salt in solution. The result is that one variable in the exchange equation is essentially fixed. For Na^+–K^+ exchange at high NaCl concentrations, the value of (Na^+) in Eq. (1) is constant, and the equation can be rewritten:

$$(K^+) = c\,\frac{[\overline{K^+}]}{1 - [\overline{K^+}]}$$

where $c = (Na^+)/K_c$ and $[\overline{K^+}] = 1 - [\overline{Na^+}]$. This equation is of Langmuir form, indicating that ion-exchange experiments which set one of the two ions in solution constant or nearly constant may not be testing the constancy of the mass-action coefficient, K_c, but rather the validity of a Langmuir equation for the adsorption of a single ion. When the activities of both exchange ions in solution are allowed to vary over a wide range, K_c also varies widely (see, for example, McBride and Bloom, 1977).

CONCLUSIONS

The mass-action form of ion-exchange equation is based upon assumptions that are not valid for all exchange reactions. Thus, composition-dependent selectivity variations can be explained in terms of the site-localized nature of weakly hydrated ions. It is suggested that knowledge of the chemical nature of exchange sites and adsorbed cations can produce exchange equations that more accurately describe the equilibrium between exchangers and ions. What has been interpreted as non-ideal behavior of mixed-ion exchangers can then be understood in terms of different degrees of cation mobility on exchange sites. In principle, complete knowledge of the cation-site interaction would eliminate the necessity for surface "activity coefficients" of ions on homogeneous exchangers.

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Резюме—Показано, что уменьшающееся предпочтение монтмориллонита к K^+ относительно Na^+ в процессе адсорбции глиной увеличивающихся количеств K^+ является общим правилом обмена сильно гидратирующих ионов на слабо гидрирующие ионы. Изменчивость коэффициента селективности действующих масс объясняется зависимой от состава поверхностной энтропией, которая является функцией химических свойств обменного иона, а также природы мест адсорбции. Обычно используемая форма уравнения обмена действующих масс может бытьприменена только к обменным системам, в которых оба иона имеют растворо-подобную подвижность на поверхности обменника. Предполагается, что экспериментальные переменные такие как ионная сила могут сильно повлиять на степень соответствия полученных величин данному уравнению обмена ионов.

Resümee—Es wird gezeigt, daß die abnehmende Bevorzugung des Montmorillonites für K^+ im Vergleich zu Na^+, obwohl der Ton zunehmende Mengen an K^+ adsorbiert, die allgemeine Regel für den Austausch stark hydratisierender Ionen gegen schwach hydratisierende Ionen ist. Die Schwankung des Massenwirkungs Selektivitätskoeffizienten wird als eine von der Zusammensetzung abhängende Oberflächenentropie interpretiert, die eine Funktion der chemischen Eigenschaften des austauschenden Ions ist und von der Art der Adsorptionsstelle abhängt. Die im allgemeinen verwendete Austauschgleichung auf Basis des Massenwirkungsgesetzes kann nur bei Austauschsystemen angewendet werden, in denen beide Ionenarten eine lösungsähnliche Beweglichkeit auf der Austauscheroberfläche haben. Es ist anzunehmen, daß experimentelle Variable, wie z.B. die Ionenstärke, den Grad des Zutreffens von Daten auf eine gegebene Ionenaustauschgleichung stark beeinflussen können.

Résumé—On a montré que la préférénce décroissante de la montmorillonite pour K^+ par rapport à Na^+ à fur et à mesure que l'argile adsorbe des quantités croissantes de K^+ est la règle générale pour l'échange des ions fortement hydratants par les ions faiblement hydratants. La variété du coefficient de sélectivité d'action massive est interprétée en termes d'une entropie de surface dépendante de la composition, qui est une fonction des propriétés chimiques de l'ion en échange aussi bien que de la nature des sites d'adsorption. L'équation d'échange sous forme d'action massive généralement utilisée peut seulement être appliquée à des systèmes d'échange dans pesquels les deux ions ont une mobilité de solution à la surface d'échange. On suggère que les variables telles la force ionique peut fortement influencer le degré d'ajustement de données à une équation d'échange d'ions donnée.

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