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Cation-exchange equations used in soil science — A review

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Summary

In soil science literature a number of equations have been used to describe the cation-exchange equilibrium in soils and clays. The models of the exchange process underlying these equations are examined in detail. The assumptions inherent to these models and the ensuing limitations of the resulting equations are discussed. Some suggestions are given on the direction of future developments in this field.

Introduction

Since the development of synthetic ion-exchange resins numerous publications have appeared in chemistry periodicals covering the exchange behavior of these and related materials, culminating in rather complete works on the phenomenon of ion exchange in general, as e.g. Helfferich's *Ion exchange* (1962).

Prior to this period the interest in ion-exchange was largely confined to soil chemists, who have been professionally involved in ion-exchange ever since J. T. Way around 1850 indicated that soils may adsorb substantial amounts of cations in an exchangeable form. As a result the present day soil scientist is confronted with, on one hand, an inheritance stemming from the work of his predecessors in soil chemistry, on the other hand a description and formulation of the ion-exchange phenomena in physicochemical literature. The practical soil chemist, looking for equations of satisfactory predictive value, thus sometimes finds himself in a situation of 'embarras du choix' which formulation should be preferred for his particular purpose. The situation is then aggravated by the fact that most workers on the subject have used their own preferred nomenclature and choice of symbols, and too often assumptions inherent in a particular approach have either become lost in subsequent usage or were never stipulated clearly.

It is for this reason that it will be attempted to present a review of 'cation-exchange equations' as they are being used in soil science, pointing out the particular assumptions involved, elaborating on the existing relationships between them, and indicating practical applicability, if possible. In doing so, one often finds that the interpretation of a particular type of approach, in the light of present day knowledge, differs from the standpoint of the original investigator. In this comparative discussion of the different formulations of cation-exchange in soils no weight was given to chronological order.

Definition of quantities and symbols

Although in several instances the exchange reaction between cations and soil constituents may be partly irreversible, and although often the 'cation-exchange capacity' of a soil depends, among others, on the pH value of the system, this is of no concern for the comparison of the approaches to be made. Thus it will suffice to consider, at least for the time being, systems containing an amount of exchanger with a constant capacity to adsorb reversibly certain cations and unable to adsorb anions (although these may be repelled due to the presence of an electrostatic field). Furthermore the discussion will be limited to cation pairs, with an accent on the more interesting heterovalent case, i.e. mono-di-valent exchange. Also, the anions being of minor concern, these will be treated as if one species is present only.

Treating a system containing an amount of exchange material suspended in an aqueous solution, one recognizes the following *experimentally accessible* quantities, once exchange equilibrium has been established between, say, mono- and divalent cations:

a) liquid content of the system, V, in ml per gram exchanger;

b) equilibrium concentrations (if necessary obtained from an equilibrium dialyzate), c_0^{+}, c_0^{++}, c_0^{-}, in meq. per ml equilibrium solution;

c) total amounts present in the system of the different ions (obtained by a stripping procedure or from the determination of the isotopically exchangeable pool of ions), $\Sigma(+)$, $\Sigma(++)$, $\Sigma(-)$, in meq. per gram exchanger.

With the help of these experimental quantities one may define unambiguously the 'surface excess' of the different ions with respect to the solvent, as:

$$\begin{aligned} \gamma^{+}(+) &= \Sigma(+) - Vc_0^{+} && \text{meq./g} \\ \gamma^{+}(++) &= \Sigma(++) - Vc_0^{++} && \text{meq./g} \\ -\gamma^{+}(-) &= Vc_0^{-} - \Sigma(-) \quad \{= \gamma^{-}(-)\} && \text{meq./g} \end{aligned} \tag{1}$$

in which $\gamma^{+}(i)$ indicates the *excess* of ion i, which for anions, in the absence of chemical adsorption of the latter, tends to be a negative number due to anion repulsion. For this reason one often uses the surface deficit, $\gamma^{-}(\text{an}) = -\gamma^{+}(\text{an})$, which is then positive.

Summation of the above quantities gives the definition of the cation-exchange capacity in meq. per gram of exchanger, γ, as:

$$\gamma = \gamma^{+}(+) + \gamma^{+}(++) + \gamma^{-}(-) = \Sigma(+) + \Sigma(++) - \Sigma(-) \tag{2}$$

or in general:

$$\gamma = \text{Sum}\left\{\gamma^{+}(\text{cat}) + \gamma^{-}(\text{an})\right\} = \text{Sum}\left\{\Sigma(\text{cat}) - \Sigma(\text{an})\right\}$$

Obviously, when $\gamma^{-}(\text{an}) > 0$, the excesses of the cations present do not sum up to the cation-exchange capacity, thus:

$$\text{Sum}\left\{\frac{\gamma^{+}(\text{cat})}{\gamma}\right\} < 1$$

Inasfar as in soil science it appears convenient to define the amounts adsorbed of different cations present in such a manner that the sum total of these does yield the cation-exchange capacity, one must introduce a convention for the partition of the anion deficit over the different cations present. Such a convention always contains a somewhat arbitrary element, since the system as a whole contains at least two species of cations and two species of anionic charges (the exchanger charge and that of the anions present) which are not coupled in any particular manner. Nevertheless it appears convenient to apportion the total amount of anions present over the cations present, proportionally to the equilibrium concentrations of the latter. Then one defines the amounts of cations, present as salts, as the proportional parts of the total amount of anions in the system. This also implies that now the anion deficit (in its totality, if more than one species of anion is present) is divided over the cations concerned, again proportionally to the equilibrium concentrations. Accordingly the 'amount adsorbed', $(\mathrm{cat})_{\mathrm{ads}}$, constitutes the excess of that cation with respect to the amount of its salt present in the system. Introducing finally the fractional amount adsorbed (or the equivalent fraction adsorbed), $N(\mathrm{cat}) = (\mathrm{cat})_{\mathrm{ads}}/\gamma$, one finds for the present system:

$$N^{+} = \left\{\gamma^{+}(+) + \frac{c_{o}^{+}}{(c_{o}^{+} + c_{o}^{++})}\gamma^{-}(-)\right\}/\gamma = \left\{\Sigma(+) - \frac{c_{o}^{+}}{(c_{o}^{+} + c_{o}^{++})}\Sigma(-)\right\}/\gamma$$

$$N^{++} = \left\{\gamma^{+}(++) + \frac{c_{o}^{++}}{(c_{o}^{+} + c_{o}^{++})}\gamma^{-}(-)\right\}/\gamma = \left\{\Sigma(++) - \frac{c_{o}^{++}}{(c_{o}^{+} + c_{o}^{++})}\Sigma(-)\right\}/\gamma \quad (3)$$

$$1 = N^{+} + N^{++} = \left\{\gamma^{+}(+) + \gamma^{+}(++) + \gamma^{-}(-)\right\}/\gamma = \left\{\Sigma(+) + \Sigma(++) - \Sigma(-)\right\}/\gamma$$

The exchange equation is then a functional relationship between N^{+}, N^{++}, c_{o}^{+} and c_{o}^{++} (at equilibrium).

Thermodynamic considerations

Prior to a consideration of the existing exchange equations, which all involve the introduction of certain assumptions based on the model used for describing the exchange phenomenon, it appears interesting to follow the outcome of the application of purely formal thermodynamic reasoning to the exchange reaction involved. If this reaction is written, for the present case, as:

$$\mathrm{exch}(++) + 2\ \mathrm{salt}(+) \rightleftarrows 2\ \mathrm{exch}(+) + \mathrm{salt}(++)$$

in which one distinguishes four components which are reacting in pair to deliver the other pair, one finds for two equivalents of exchanger, at equilibrium:

$$\triangle G_{P,T} = 0 = 2\mu(+)_{a} + \mu(++)_{o} - \mu(++)_{a} - 2\mu(+)_{o}$$

in which the subscripts, o and a, of the chemical potentials indicate the salt and the exchanger, respectively.

Making use of the fact that four different components were recognized, one may introduce convenient standard states for each of these, thus defining the activities of the components, a_a and a_o, respectively, according to $\mu = \mu^\circ + RT \ln a$. This then yields:

$$\triangle G^\circ_{P,T} = 2\ \mu^\circ(+)_a - \mu^\circ(++)_a - 2\ \mu^\circ(+)_o + \mu^\circ(++)_o$$

$$= -RT \ln \frac{(a_a{}^+)^2}{a_a{}^{++}} \frac{a_o{}^{++}}{(a_o{}^+)^2} = -RT \ln \mathbf{K} \qquad (4)$$

The standard Gibbs free energy of exchange is thus defined in terms of the equilibrium values of the activities of reactants and products, its value clearly depending upon the standard states chosen for the different components. As such equation 4 is a pure formality, which does not involve any questionable assumption, but cannot be applied without further specifications (cf. Babcock, 1963, p. 499).

In order to render this equation applicable to the interpretation of experimental data on the exchange equilibrium between cations and e.g. clays, Gaines and Thomas (1953) selected the following standard states. For the exchanger they chose the homoionic state, in equilibrium with the solvent at unit activity (in effect amounting to homoionic exchanger in equilibrium with an infinitely dilute solution of the salt of the cation), whereas for the salts the conventional standard state in solution was accepted (amounting to an ideal solution of the salt at unit molarity). In doing so, $\triangle G^\circ$ represents the change in Gibbs free energy if 2 moles of exch(+), in homoionic form in equilibrium with an infinitely dilute solution of salt(+), are reacted reversibly with 1 mole of salt(++) (at unit activity) to form 1 mole of exch(++) and 2 moles of salt(+), both in their respective standard states. By this (arbitrary) choice of the standard state of the exchanger, $\triangle G^\circ$ becomes a measure of the relative affinity between the exchanger and the two cations concerned, and thus lends itself to a comparison between different cation pairs (and the same exchanger) or between different exchangers (and the same cation pair).

Applying the above choice of standard states it must then be attempted to relate the value of **K** to experimentally measurable quantities. Gaines and Thomas introduce to this purpose activity coefficients applying to the exchanger, which are defined as:

$$a_a{}^+ = f^+N^+ \text{ and } a_a{}^{++} = f^{++}N^{++} \qquad (5)$$

thus coupling the activity of the exchanger with a particular cation to the equivalent fraction adsorbed of the latter. As no assumptions about the functional relationships between f and N are made, no arbitrary element is introduced at this stage. One introduces furthermore an experimentally accessible 'corrected selectivity coefficient', K_N, as[1]:

$$K_N = \frac{(N^+)^2}{N^{++}} \frac{a_o{}^{++}}{(a_o{}^+)^2} \qquad (6)$$

i.e. a selectivity coefficient based on equivalent fractions adsorbed and activities in solution (assuming that the activity coefficients on solution may be calculated from

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[1] The ratio $a_o{}^{++}/(a_o{}^+)^2$ in equation 6 and following equations, referring to the salts in solution, may also be considered as the ratio of the cation activities in solution, as follows from dividing numerator and denominator by $(a^-)^2$.

the measured concentrations in solution). Accordingly the quantity **K** sought is now defined as:

$$\ln \mathrm{K} = \ln K_N + 2 \ln f^{+} - \ln f^{++} \tag{7}$$

Applying the Gibbs-Duhem equation to the exchanger, along a pathway running from the standard state of e.g. exch(+) (at unit activity of the solvent) to the homoionic clay at finite electrolyte concentration, from there at constant electrolyte concentration to the homoionic exch(++) and on to the standard state of exch(++), Gaines and Thomas showed that for the particular system considered:

$$\ln \mathbf{K} = 1 + \int_{0}^{1} \ln K_N \, dN^{+} + \int n_s \, d \ln a_s \tag{8}$$

in which the last integral indicates the change in Gibbs' free energy of the solvent adsorbed per unit exchanger, relative to RT ($\int n_s \, d\mu_s$, with n_s = moles of water adsorbed per 2 equivalents of exchanger) when moving along the specified pathway. The latter integral is rather difficult to determine, but Gaines and Thomas are of the opinion that this term is usually negligible in comparison to the other terms (Gaines and Thomas, 1955).

Accordingly, aside from the latter, probably reasonable, assumption, one may obtain the value of **K** pertaining to the combination of a particular exchanger with a given cation-pair from experimental data without invoking any particular model theory. At the same time one may calculate the values of f^{+} and f^{++} for any equilibrium situation by part integration of the Gibbs–Duhem equation (Gaines and Thomas, 1953).

Although the above approach appears practically free from arbitrary assumptions and model considerations, it should be realized that it constitutes only a standardized method of presentation of experimental data. It allows a comparison between different systems, but does not permit an actual prediction of the exchange behavior of a particular system, i.e. outside of situations which were analyzed experimentally beforehand. An exception to this statement is the prediction of the value of **K** for a certain ion pair, of which the **K** values with respect to a common third cation were determined experimentally. Then the equality:

$$\mathbf{K}_{1-2} = \frac{\mathbf{K}_{1-3}}{\mathbf{K}_{2-3}}$$

should hold, as was proven to be true in certain cases (Lewis and Thomas, 1963; Martin and Laudelout, 1963).

If for a given system the tabulated values of **K**, f^{+} and f^{++} are available, one may calculate the amounts adsorbed from the solution composition, and vice versa. As this calculation amounts to a reconstitution of K_N from the tabulated data, it is understandable that for the purpose of practical applications the soil scientist often does not go beyond experimental determination of K_N as a function of the solution composition, limiting himself to the range of practical interest. It is also clear that, if extrapolation from measured data to unknown systems is required, the introduction of certain models — thus limiting the applicability of the ensuing relations to the validity of the inherent assumptions — cannot be avoided.

Exchange equations derived from model considerations

Monolayer models

In these models the exchanger-cations are considered to be present in a homogeneous phase, their relative concentrations being independent of their position in (or on) the exchanger. Leaving exchange materials capable of 'internal' adsorption out of consideration (as e.g. exchange resins), this situation is for layer silicates with external adsorption best visualized as the existence of a monolayer of exchangeable cations on the surface of the exchanger. Because the anions should be effectively excluded from such a monolayer, it appears likely that the activities of the two forms of the exchanger recognized, i.e. exch(+) and exch(++), are largely determined by their respective equivalent or mole fractions.

The oldest forms of exchange equations based on this approach are those of Kerr (1928) and Vanselow (1932). The first of these is of minor interest as it is limited to homovalent exchange, the second one is still being used at present. Vanselow, visualizing the monolayer as an ideal two-dimensional solid solution, assumes the activities of the two exchanger components to be proportional to their respective mole fractions, thus yielding for the standard states selected in equation 6 and 8 :

$$\mathrm{K_V} = \frac{(M^+)^2}{M^{++}} \, \frac{a_o^{++}}{(a_o^{+})^2} = \text{constant} \tag{9}$$

Clearly the above equation defines in general another corrected fractional selectivity coefficient, K_M , which in contrast to K_N above is expressed in mole fractions of the adsorbed species. Vanselow's model then suggests that this coefficient should be a constant, $\mathrm{K_V}$. The relationship between $\mathrm{K_V}$ and the thermodynamic exchange constant $\mathbf{K}$ is found by substituting $K_M = 4K_N/(1 + N^+)$ into equation 8 (omitting the last term), which gives:

$$1 + \int_0^1 \ln K_N \, dN^+ = \int_0^1 \ln K_M \, dN^+ \tag{10}$$

So the assumptions of Vanselow, in conjunction with the standard states chosen in equation 8, indicate that the thermodynamic exchange constant should equal:

$$\ln \mathbf{K} = \int_0^1 \ln \mathrm{K_V} \, dN^+ = \ln \mathrm{K_V} \tag{11}$$

Obviously this result follows also directly from the substitution of mole fractions for the activities of the exchanger components into equation 4.

A more refined approach was introduced by Davis (Davis, 1950; Davis and Rible, 1950) and applied to exchange on soil clays by Krishnamoorthy and Overstreet (1950). Davis c.s. considered the probability of placement of cations with different valence on a regular array of negative point-charges as supposed to be present on the exchanger surface. Although Davis indicates that his treatment should apply to a 'monolayer' in the widest sense of the word, i.e. each surface-charge being accompanied by one countercharge only in the adsorbed layer, it appears that other assumptions inherent in the treatment, as e.g. absence of anions, probability of placement being based on a regular array of the positions available for the ions, are warranted only if one considers a monolayer in a narrow sense, i.e. a localized monolayer. Applying the above principle, Davis c.s. show that the distribution of the cations on the surface should be governed by the relationship:

$$(M^+)^2 \,/\, \left\{M^{++}\,(q^+M^+ + q^{++}M^{++})\right\} = \text{constant} \times (a_a^+)^2 \,/\, a_a^{++} \qquad (12)$$

in which the mole fractions, $M_i = m_i \,/ \Sigma m_i$, have been substituted for the number of moles, m_i, adsorbed by the exchanger. The values of q in this equation depend on the assumed number of nearest neighbors, n, of the adsorbed ions (interactions with other neighbors being neglected in the treatment), according to the relation $q_i = (n\,z_i - 2\,z_i + 2)/n$, with z_i = valence. For the mono-divalent case one thus finds: $q^+ = 1$ and $q^{++} = 2(n-1)/n$.
Substituting equation 12 into equation 4 then yields a distribution equation of the type:

$$\mathrm{K_D} = \frac{(M^+)^2}{(M^{++})\left\{M^+ + \dfrac{2(n-1)}{n}M^{++}\right\}}\;\frac{a_o^{++}}{(a_o^+)^2} = \text{constant} \qquad (13)$$

It is interesting to note, as pointed out by Davis, that for $n = 2$ (i.e. linear array of surface charges), this gives:

$$\mathrm{K_D}\,(n=2) = \frac{(M^+)^2}{(M^{++})\,(M^+ + M^{++})}\;\frac{a_o^{++}}{(a_o^+)^2} \quad (= K_M) \qquad (13a)$$

$$= \text{constant}\ (= \mathrm{K_V})$$

the exchange equation thus reverting to Vanselow's equation 9.
If, on the other hand, n is taken to be a rather large number (which might be of interest as an approximation to the situation arising in a diffuse cloud of counterions) one finds:

$$\mathrm{K_D}\,(n \longrightarrow \infty) = \frac{(M^+)^2}{(M^{++})\,(M^+ + 2\,M^{++})}\;\frac{a_o^{++}}{(a_o^+)^2} \quad (= 2\,K_N) \qquad (13b)$$

$$= \text{constant}\ (= 2\,\mathrm{K_E})$$

in which the constant $\mathrm{K_E}$, introduced by Eriksson (1952), replaces the coefficient K_N. Krishnamoorthy and Overstreet employed Davis' equation with $n = 4$ (square array of surface charges), yielding:

$$\mathrm{K_D}\,(n=4) = \frac{(M^+)^2}{(M^{++})\,(M^+ + \frac{3}{2}M^{++})}\;\frac{a_o^{++}}{(a_o^+)^2} \qquad (13c)$$

$$= \text{constant}\ (= \mathrm{K_{DKO}})$$

Bloksma (1956) pointed out, that in calculating the number of modes of occupation of sites adjacent to an occupied site, the above authors oversimplified the picture.

Selecting a hexagonal array of surface charges one finds for a divalent ion 8 adjacent sites, of which 2 sites give a value of q^{++} equal to 4/3 rather than 5/3 according to Davis. Accordingly equation 13 could be written for the hexagonal array as:

$$\mathrm{K_D}\ (n = 6) = \frac{(M^+)^2}{(M^{++})\ (M^+ + 1.6\ M^{++})} \frac{a_o{}^{++}}{(a_o{}^+)^2} = \text{constant} \tag{13d}$$

Taken together, the equations 13a–d could be considered as distribution equations, relating the occupation of the exchange sites in terms of adjusted mole fractions to the ratio of the activities of the salts (or cations) in the equilibrium solution via a constant which must be determined empirically. This constant, which might be termed a distribution constant, is not necessarily equal to the thermodynamic exchange constant, $\mathbf{K}$, as defined in equation 8, even if the term $\int n_s \text{ d ln } a_s$ is neglected. In that case one finds in accordance with equation 10:

$$\begin{aligned} \ln \mathbf{K} &= 1 + \int_o^1 \ln K_N \, \mathrm{d}N^+ = \int_o^1 \ln K_M \, \mathrm{d}N^+ \\ &= \int_o^1 \ln \mathrm{K_D} \, \mathrm{d}N^+ + \int_o^1 \ln \left\{ M^+ + \frac{2(n-1)}{n} M^{++} \right\} \mathrm{d}N^+ \\ &= \ln \mathrm{K_D} + (n-1) \ln \left\{ n/(n-1) \right\} - \ln 2 \end{aligned} \tag{14}$$

Again, for $n = 2$, one finds $\ln \mathbf{K} = \ln \mathrm{K_D} = \ln \mathrm{K_V}$, as then $\mathrm{K_D} = \mathrm{K_V}$ $(= K_M)$ $=$ constant. Alternatively, for $n \longrightarrow \infty$, equation 14 gives $\ln \mathbf{K} = \ln \mathrm{K_D} + 1 - \ln 2 = \ln \mathrm{K_E} + 1$ as then $\mathrm{K_D} = 2\ \mathrm{K_E}$ $(= 2\ K_N) =$ constant.

The distribution 'constant' $\mathrm{K_D}$ should thus lie between K_M and $2\ K_N$, its value depending on the number chosen for n (between two and infinity), its actual constancy probably depending on the nature of the exchange material and the spatial arrangement of the adsorbed cations. It is of interest to note that various authors (Bower, 1959; Bower and Hatcher, 1962; Kerr, 1928; Krishnamoorthy and Overstreet, 1950; Lagerwerff and Bolt, 1959; Magistad, 1944; Pratt and Grover, 1964; Pratt et al., 1962; Turner, 1965; Vanselow, 1932) have made different claims as to the constancy of the various forms of $\mathrm{K_D}$, viz. $\mathrm{K_V}$, $\mathrm{K_E}$ and $\mathrm{K_{DKO}}$. It appears safe to conclude from these data that for layer silicates and the common ions Na, K, Ca and Mg, one may expect that often acceptable constancy is obtained with one of the forms of $\mathrm{K_D}$. Inasfar as a constant value of any one of these allows one to describe the entire exchange equilibrium with one parameter, one might actually consider to adjust n for the particular system studied, thus specifying the exchange parameters $\mathrm{K_D}$ and n. Application of equation 14 then also allows the calculation of $\triangle G^\circ$ if needed. On the other hand, if the required range and accuracy of prediction are limited, one might prefer to use $\mathrm{K_V}$ or $\mathrm{K_E}$. Certainly $\mathrm{K_E}$ is more convenient to handle than $\mathrm{K_{DKO}}$, the composition of the exchanger usually being given in terms of equivalent percentages or fractions of the cations present.

Although its derivation appears to be a bit strained, it seems worthwhile to mention here the exchange equation of Gapon (1933) which may be written as:

$$\frac{N^+}{N^{++}} \frac{\sqrt{a_o{}^{++}}}{a_o{}^+} = \text{constant} = \mathrm{K_G} \tag{15}$$

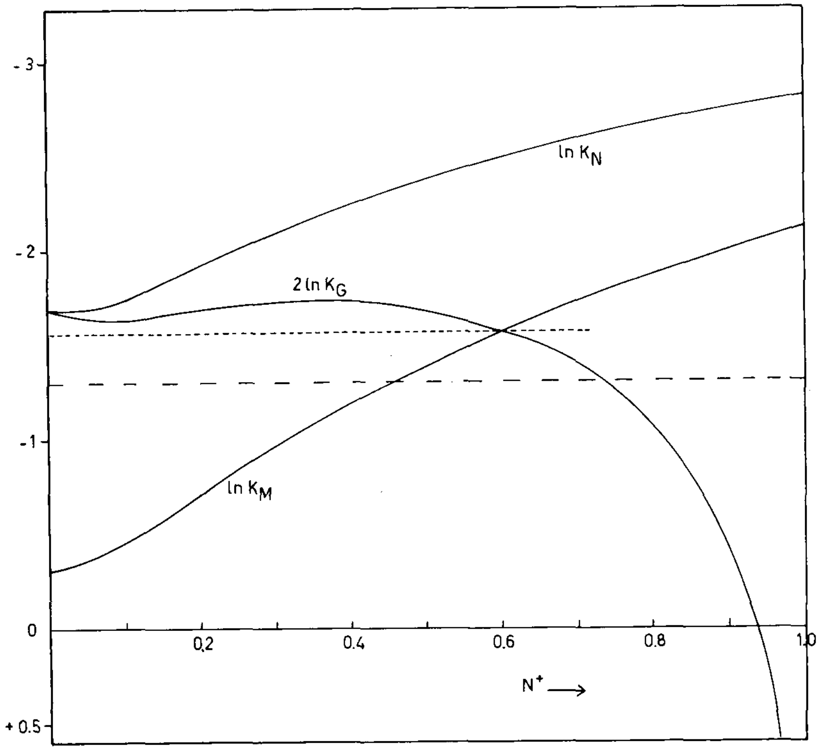

Fig. 1 *Values of* $\ln K_M$ *(*$= \ln K_V$*),* $\ln K_N$ *and* $2 \ln K_G$ *as a function of* N^+ *calculated according to the Gouy theory (equation 23) for* $\Gamma = 3.16 \times 10^{-7}$ *meq./cm²,* *at* 10^{-2} *N total electrolyte. Dashed line:* $\ln K$ *according to equation 8. Dotted line:* $2 \ln K_G$ *as used by U.S. Salinity Laboratory.*

Comparing with the selectivity coefficients defined above, one finds:

$$K_G^{\,2} = \frac{K_N}{(1-N^+)} = \frac{(1+N^+)}{4(1-N^+)} K_M$$

Obviously, for $N^+ \longrightarrow 0$, constancy of the above three exchange parameters should be roughly similar. In fact, over a limited range of N^+ values (which are of paramount importance for the characterization of alkali soils) K_G may be as dependable a characteristic as is K_E, K_{DKO} or K_V. Moreover the estimation of the percentage exchangeable Na-ions on soils is in practice more conveniently done with the Gapon equation. Its dependability for this purpose has been substantiated by numerous data published by the U.S. Salinity Laboratory[2]. It should be mentioned, however, that the usage of the Gapon equation in the range above 50% exchangeable Na-ions appears not warranted (cf. also Fig. 1). It may finally be pointed out that for a con-

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[2] Cf. USDA, Agriculture Handbook No. 60, Washington 1954.

stant value of K_G over the entire range of N^+ (however unlikely) one would find the exchange constant as $\ln K = 2 \ln K_G$.

Finally the use of the Langmuir adsorption equation should be mentioned. Application of this equation to cation exchange in soils was initiated by Vageler (1932). The original Langmuir equation is found directly from the application of the Mass Law to an idealized adsorption equilibrium between a surface and a single adsorbate, equating the product of rate constant in forward direction, concentration of adsorbate and number of free places available on the adsorbent, with that of the rate constant in backward direction and the number of places already occupied by the adsorbate. Vageler's equation appears to be an erroneous attempt to restate the Langmuir equation in terms of amounts of the cation added to the system rather than its concentration at equilibrium. It may be shown that only when the ratio of the rate constants is close to unity such a restatement is acceptable. In all other cases it appears to be unsound.

Aside from Vageler's equation, the original Langmuir equation is in its simplest form useless for cation exchange, as it does not take into consideration the competition between the cationic species. One may, however, introduce this competition effect into the Langmuir equation rather simply by using Kerr's and Gapon's equations as a starting point. For the homovalent and heterovalent exchange equilibrium one finds, respectively (assuming ideal behavior in solution):

$$\frac{N^+}{N^{++}} = K_G \frac{c_o{}^+}{\sqrt{c_o{}^{++}}} \quad \text{and} \quad \frac{N_1}{N_2} = K_K \frac{c_{o1}}{c_{o2}}$$

For biionic systems this gives:

$$\frac{N^+}{N^+ + N^{++}} = \frac{c_o{}^+}{c_o{}^+ + \sqrt{c_o{}^{++}}/K_G} \quad \text{and} \quad \frac{N_1}{N_1 + N_2} = \frac{c_{o1}}{c_{o1} + c_{o2}/K_K}$$

For a monovalent cation i, in competition with cation j (mono- or divalent) these may be generalized in terms of a Langmuir equation, as:

$$N_i = \frac{c_{oi}}{c_{oi} + f(c_{oj})}$$

In this equation the constant appearing in the denominator of the classical Langmuir equation has been replaced by a term which is a function of the concentration and valence of the competing ion. Seen in this light a Langmuir formulation of cation-exchange is certainly not in conflict with the simplest types of exchange equations given above; at the same time it contributes nothing new.

Three-dimensional models

In the previous section the exchangeable cations were visualized to be situated in a condensed layer on the exchanger surface, enabling one to recognize the exchanger as a discrete component. In doing so the nature of the binding forces between ions and exchanger was left out of consideration, except for the fact that a fixed value of the exchange capacity was introduced. It is obvious, however, that electrostatic forces play an important role in determining the distribution of ions of different valence between solution and exchanger. The simplest way to introduce the effects of the electrostatic potential on the distribution of ions is the application of the Donnan equation to a system consisting of two phases, one phase having acquired an electric potential with respect to the other phase as a result of the presence of 'constrained' charges in it. Although the original Donnan equation was derived for two phases separated by a membrane (impermeable to the 'constrained' charges, but permeable to ions and solvent), this system does not lend itself for a direct application to the exchange equilibrium on layer silicates, as this would imply that the cationic composition of the exchanger would vary grossly if a clay suspension were diluted with its own equilibrium solution (cf. also Babcock, 1963, p. 458). For soils and clays it thus appears necessary to limit the phase with constrained charge to a zone adjacent to the exchanger surface. This model might be termed the 'micro Donnan system', and has been used extensively by Mattson (1942), Mattson and Wiklander (1940) and Wiklander (1955). Working out this model it appears that the standard states chosen for the exchanger components recognized in the thermodynamic treatment are now impractical in view of the recognition here of two solution phases over which cations are distributed. In fact it seems logical to use similar standard states for the two cations present in both phases, which upon introduction into equation 4 gives:

$$\triangle G^{\circ}_{P,T} = 0$$

or:

$$\frac{(a_m{+})^2}{a_m{++}} \; \frac{a_o{++}}{(a_o{+})^2} = \mathrm{K} = 1 \qquad (16)$$

in which a_m now indicates the activities of the cations in the 'micellar' phase, which have no relation to the activities of the exchanger components used in the previous sections. By itself this equation is of no interest, as the difference in affinity of the exchanger for the two ions considered has disappeared from it. One may attempt to reintroduce this aspect by relating a_m to the amount adsorbed. In doing so one may first establish that the ratio of the micellar activities of the salts may be identified with the micellar activity ratio of the cations, the activities of the accompanying anions canceling each other. Next one may, as a first approximation, assume that the ions in both phases behave ideally, their concentration distribution being governed solely by the difference in electric potential between the phases. Such an attempt, although incorrect, nevertheless serves the purpose of showing very clearly the inherent weakness of the approach based on the Donnan equilibrium when applied to layer silicates.

Introducing the concept of ideal behavior, equation 16 becomes:

$$\frac{(c_m{+})^2}{c_m{++}} \; \frac{c_o{++}}{(c_o{+})^2} = 1 \qquad (16a)$$

in which c_o indicates the concentration in the equilibrium solution, in moles per liter. The concentration in the micellar phase may now be related to the amount 'adsorbed' of the cations by the introduction of the micellar volume, V_m, in ml per meq. of exchanger. Thus if the electric potential difference between the phases is sufficiently large to warrant neglect of the anions present in the micellar phase, one finds:

$$N^{+} = V_m\, c_m{}^{+} \quad \text{and} \quad N^{++} = 2\, V_m\, c_m{}^{++} \tag{17}$$

Introduced into equation 16a this gives an exchange equation of the type:

$$\frac{(N^{+})^2}{N^{++}}\;\frac{c_o{}^{++}}{(c_o{}^{+})^2} = \frac{V_m}{2} \tag{18}$$

Thus for ideal behavior in solution, and a homogeneous phase potential, the exchange equation based on the Donnan equilibrium becomes identical with equation 6, with the understanding that K_N is now identified as half the micellar volume (which volume determines the mean micellar concentration and is thus directly related to difference in electric potential between the two phases). For resinous exchangers this may be sensible, as the micellar volume could be regarded as the volume of the liquid phase inside the resin beads. For layer silicates equation 18 seems of little help, as no a priori information is available on the magnitude, nor on the constancy of the micellar volume. Although one could replace V_m by d^{+}/Γ, in which d^{+} indicates the thickness of the layer of cation accumulation and Γ the surface density of charge in meq./cm^2, this is of little help as again d^{+} is neither known nor necessarily constant. Admitting finally that the behavior of the ions in both phases is certainly not ideal, the Donnan model leads to the conclusion that K_N as defined in equation 6 should also be related to micellar activity coefficients according to:

$$K_N = \frac{f_m{}^{++}}{(f_m{}^{+})^2}\;\frac{d^{+}}{2\Gamma} \tag{19}$$

This seems a useless equation as no information is available on either f_m or d^{+}.

The situation is different for the resinous exchangers; V_m being probably accessible for measurement, one could thus obtain the functional relationship between the ratio of the micellar activity coefficients and the exchanger composition.

A further consideration indicates, moreover, that the presence of a homogeneous micellar phase on a layer silicate is hardly, if ever, a realistic picture of the situation. Cations present in the vicinity of a charged planar surface will acquire a diffuse concentration distribution, unless adsorption forces other than electrostatic forces or steric factors effectively condense them into a monolayer. In the latter case the approach of Davis appears to be more enlightning, as it allows for the consideration of effects other than electrostatic. At the same time it must be admitted that for a monolayer the value of d^{+} could perhaps be estimated, giving the order of magnitude of K_N to be expected (cf. Bolt, 1955).

If, however, this condensation into a monolayer has not taken place one may describe the accumulation of cations in a much more detailed fashion by making use of the Gouy theory of the electric double layer formed on planar, charged surfaces. This approach was introduced by Eriksson (1952) following the works of Schofield (1947, 1952) in this field. Later this model was worked out in more detail by Bolt (1955), Lagerwerff and Bolt (1959), Bolt and Page (1965).

Admittedly the assumption of ideal behavior of the ions in the double layer and the assumed absence of forces other than electrostatic ones severely limit the applicability of the ensuing equations for predictive purposes. On the other hand the model allows the calculation of the actual value of the selectivity coefficient K_N inasfar as it is determined by electrostatic forces. Thus it serves as a normalized treatment allowing one to evaluate non-electrostatic effects influencing the cation adsorption by comparison of calculated and measured values of K_N.

Starting with equation 16a above one may specify the (varying) concentration in the double layer as:

$$c^{+} = c_{o}^{+} . \mathrm{e}^{-e\psi/kT} \quad ; \quad c^{++} = c_{o}^{++} \, \mathrm{e}^{-2e\psi/kT} \tag{20}$$

in which $\psi = \mathrm{f}(x)$ is the electric potential in the double layer, varying with the distance to the surface, x. The amount of cations present in the double layer is then found as:

$$\begin{aligned} N^{+} &= \frac{1}{\Gamma} \int_{o}^{d} (c^{+} - c^{-}) \, \mathrm{d}x = \frac{c_{o}^{+}}{\Gamma} \int_{o}^{d} (u - 1/u) \, \mathrm{d}x \\ N^{++} &= \frac{2}{\Gamma} \int_{o}^{d} (c^{++} - c^{=}) \, \mathrm{d}x = \frac{2 \, c_{o}^{++}}{\Gamma} \int_{o}^{d} (u^{2} - 1/u^{2}) \, \mathrm{d}x \end{aligned} \tag{21}$$

in which $u = \mathrm{e}^{-e\psi/kT}$; Γ = charge density of the surface in meq./cm². For ease of notation the system is assumed to contain a mixture of symmetric salts rather than two salts with a common anion (cf. Bolt and Page, 1965). The ensuing expression of K_N then reads:

$$\begin{aligned} K_N &= \frac{(N^{+})^{2}}{\mathrm{N}^{++}} \, \frac{c_{o}^{++}}{(c_{o}^{+})^{2}} \\ &= \frac{1}{2\,\Gamma} \, \frac{\left\{ \int_{o}^{d} (u - 1/u) \mathrm{d}x \right\}^{2}}{\int_{o}^{d} (u^{2} - 1/u^{2}) \mathrm{d}x} \end{aligned} \tag{22}$$

Equation 22 obviously reverts to equation 18 if u is considered to be constant, $1/u$ is neglected, and d is identified with d^{+}. This equation also indicates the fundamental error made when applying the equation 18, based on the Donnan formulation, to systems in which the electric potential of the 'micellar' phase is gradually decreasing to zero with increasing distance from the charged surface. As was pointed out already by Davis (1942, 1945) such application implies equating the sum of the squares of the Boltzmann factors, u, for consecutive layers, with the square of the sum of these factors.

Double layer theory provides the means to carry out the above integrations. Taking freely expanded diffuse double layers one finds for the symmetric salts above an expression of the type:

$$K_N = \frac{\left\{ \arg\sinh \left(\Gamma \sqrt{\beta} / \sqrt{r^{2} + 8N_{o}} \right) \right\}^{2}}{\Gamma \left\{ \beta\Gamma - r\sqrt{\beta} \arg\sinh \left(\Gamma \sqrt{\beta} / \sqrt{r^{2} + 8N_{o}} \right) \right\}} \tag{23}$$

in which $\beta \approx 10^{15}$ cm/meq., $r = c_o^+ / \sqrt{c_o^{++}}$, $N_o = c_o^+ + 2\, c_o^{++}$ (total concentration in the equilibrium solution).

Equation 23 represents a distribution equation of the type introduced in equation 13, except that it does *not* contain a constant to be determined experimentally. The computed values of K_N may thus be compared with experimental data. Extensive experimentation on Na-Ca-soils and clays (Bolt, 1955; Bower, 1959; Bower and Hatcher, 1962; Lagerwerff and Bolt, 1959; Pratt and Grover, 1964) indicated that for these systems, especially illitic clays, the agreement is remarkably good, considering the neglect of both specific adsorption forces and activity corrections. At the same time other ion pairs indicate considerable deviations; nevertheless equation 23 appears to be the only one which allows a computation of the electrostatically induced distribution of cations on clays under idealized conditions. It is of interest to note that when comparing the values of K_V, K_N and K_G, as computed from equation 23 together with the corresponding relations between the different coefficients, K_G appears to be the best 'constant' in the range of N^+ from $0 \longrightarrow 0.4$ at electrolyte levels around 10^{-2} N, (cf. Fig. 1). Beyond that range the other coefficients remain constant better than K_G.

Equation 23 may also be used to obtain an estimate of ln K, and thus of the Coulombic energy component of $\triangle G°$ for heterovalent exchange. Integrating graphically the curves obtained for ln K_N from equation 23 at different electrolyte concentrations and extrapolating to vanishing electrolyte level one finds $\triangle G°/RT = -1.08$ for $\Gamma = 10^{-7}$ meq./cm^2 and $\triangle G°/RT = +1.22$ for $\Gamma = 3.2 \times 10^{-7}$ meq./cm^2. Comparison of these figures with experimental data requires information over the full range of mixed heterovalent compositions at different electrolyte levels. Recently such data were produced by van Bladel and Laudelout (1967).

Combined models

As was pointed out before, the distribution equation derived from the Gouy theory does not allow for preference factors aside from the valence effect. Application of the model to homovalent exchange is thus without interest, as it leads to the conclusion that the ratio of adsorbed ions should equal the concentration ratio in solution. In this respect also the approach used by Davis offers no direct perspectives, as this distribution equation does not contain any parameters that could be related to properties of the ion other than its valence. At the same time, once the monolayer model is accepted, one could perhaps assume that in this layer a 'constant' preference would exist for one ion with respect to the other. In the diffuse layer model any preference for a particular ion would necessarily vary with the location in this layer, gradually changing from a certain value close to the surface to unity in the equilibrium solution. Heald et al. (1964) have taken this into consideration by dividing the adsorbed layer into two regions. In the part close to the surface, which could be named a Stern layer, a preference factor is admitted, whereas the remainder (Gouy layer) is assumed to be sensitive only to valence of the ion. The preference constant for the Stern layer is then introduced as a formation constant for an ion-surface pairing reaction, which yields for the amount of the ion adsorbed in the Stern layer, A_S(i), in meq. per cm^2 exchanger surface:

$$A_S(\mathrm{i}) = k_\mathrm{i}\, c_G(\mathrm{i})\, \Gamma_G \qquad (24)$$

in which k_i = pair formation constant; c_G (i) = concentration of the ion at the boundary between Stern and Gouy layer; Γ_G = counterionic charge present in the

Gouy layer, which signifies the number of free places in the Stern layer. It is interesting to note that equation 24 also follows directly from the application of the Boltzman equation to the Stern layer, as was done by Stern in his original approach. One then finds:

$$c_S(i) = \frac{g_S}{g_o} c_o(i)\ e^{-ze\psi_S/kT}\ e^{-\varphi_i/kT} \tag{25}$$

in which g indicates a statistical weight factor which is taken proportional to the number of available positions for the ion in the Stern layer and in the equilibrium solution, respectively, and z is valence. The electric potential in the Stern layer equals ψ_S, and the non-Coulombic adsorption potential of the ion i in this layer is indicated with φ_i. Introducing the concentration of the ion at the boundary between Stern and Gouy layer as $c_G = c_o\ e^{-ze\psi_G/kT}$ equation 25 may be written as:

$$c_S(i) = \frac{g_S}{g_o} c_G(i)\ e^{-\triangle E_S/kT} \tag{25a}$$

with $\triangle E_S = z_i\ e\ (\psi_S - \psi_G) + \varphi_i$, which potential difference is a constant for a particular ion species. As furthermore g_o may be taken as a constant, while g_S is proportional to Γ_G, multiplication of both sides of equation 25a with the thickness of the Stern layer, δ_S, yields again:

$$A_S(i) = \delta_S c_S(i) = k_i c_G(i)\ \Gamma_G$$

Applying the above to a homoionic system one finds:

$$c_G(i)/\Sigma c_G(i) = c_o(i)/\Sigma c_o(i)$$

no preference factors being considered in the Gouy layer. Standard double layer theory allows the total concentration at the boundary between Gouy and Stern layer to be related to the total countercharge present in this layer according to (cf. Bolt and Page, 1965):

$$\frac{\beta \Gamma_G^2}{4} \approx \Sigma\ c_G(i)$$

Introduced into equation 24 this gives:

$$A_S(i) = k_i \frac{\beta}{4} \Gamma_G^3\ c_o(i)/\Sigma\ c_o(i) \tag{26}$$

Applying this treatment to a system containing two species of monovalent cations, indicating the equivalent fraction adsorbed by N, this gives:

$$N(1) = \left\{ A_S(1) + A_G(1) \right\} / \Gamma$$

$$N(2) = \left\{ A_S(2) + A_G(2) \right\} / \Gamma$$

$$N(1) + N(2) = 1$$

Using equation 26, with $a = \Gamma_G/\Gamma$ one finds the 'conservation' equation:

$$\frac{\beta\Gamma^2}{4}\left\{k_1c_o(1)/\Sigma c_o + k_2c_o(2)/\Sigma c_o\right\} a^3 + a - 1 = 0 \tag{27}$$

Recombination of the above equations yields:

$$N(1) = 1 - k\,\frac{c_o(2)}{c_o(1)}\,N(1) + a\left\{-1 + \frac{1 + k\,c_o(2)/c_o(1)}{1 + c_o(2)/c_o(1)}\right\} \tag{28}$$

in which $k = k_2/k_1$.

A plot of $N(1)$ against $\{c_o(2)/c_o(1)\}N(1)$ now yields an estimate of k as the slope of the line at $N(1) \longrightarrow 1$. This estimate of k then allows evaluation of a from the difference between the observed curve and the tangent at $N(1) = 1$. Finally substitution of a and k into equation 27 should yield the absolute values of k_1 and k_2.

The corresponding exchange equation would read:

$$\frac{N(1)}{N(2)} = \frac{k_1a^2\,\beta\Gamma^2/4 + 1}{k_2a^2\,\beta\Gamma^2/4 + 1}\;\frac{c_o(1)}{c_o(2)} \tag{29}$$

with $a = \mathrm{f}\left\{k_1, k_2, c_o(1), c_o(2)\right\}$, according to equation 27.

The first ratio on the right-hand side of equation 29 represents the selectivity coefficient $K_{1,2}$ of the monovalent exchange reaction considered.

The application of the suggested treatment to experimental data (in order to derive appropriate values of k_1 and k_2) is involved and thus liable to yield only approximate values of the parameters concerned. Especially the estimation of k from the limiting slope in the range of complete saturation, where the accuracy of the experimental data is relatively low, seems difficult. In turn this will render the calculations of a over the entire range of compositions of the exchanger rather uncertain. A curve fitting procedure may thus be necessary in order to obtain satisfactory numerical values for k_1 and k_2.

At the same time the above approach provides an interesting link between the monolayer model and the diffuse layer model. Obviously, in the absence of a significant contribution of the assumed non-specific diffuse layer, the plot suggested by equation 28 yields a straight line. The exchange equation 29 then becomes identical with the Kerr equation (k_1a^3 and k_2a^3 remain finite for vanishing a; cf. also equation 28). It would be of interest to investigate whether Na-Li-clay systems (which should have a significant diffuse layer) would obey equation 28 with a constant value of k.

The extension of this approach to the mono-divalent case has not been done as yet. Mathematical difficulties appear to be considerable, although these could be surmounted with a computer. Heald c.s. limited their attempt to working out the equation, assuming that in the presence of divalent ions the contribution of the diffuse layer would be negligible. In addition the pair formation for divalent ions was visualized as a relation between the ion and two independent free sites, leading to the appearance of $(\Gamma_G)^2$ in the corresponding equation 24. This is hardly of interest as then the resulting equation becomes identical with Vanselow's equation, the exchange constant K_V now being identified as the ratio $(k_1)^2/k_2$, with k_1 and k_2 indicating the (unknown) pair formation constants for mono- and divalent cations.

Aside from the above semi-empirical approach (i.e. deriving preference parameters from a comparison between experimental data and an equation based on a generalized model) one might also attempt to estimate the magnitude of these parameters from a theoretical analysis of the forces acting on cations in close proximity of the exchanger surface. Such an approach was recently published by Shainberg and Kemper (1966). The difficulty in such calculations is the fact that one must estimate the difference in energy between hydrated cations situated at a distance equal to the radius of the hydrated form, and the (partially) dehydrated cations situated at shorter distance. As pointed out by the above authors, this difference in energy comprises several terms as e.g. the energy associated with the formation of the hydration shell on the cations, the change in Coulombic energy upon close approach to the charged surface, plus at least the charge-dipole interaction between water molecules and the charged surface. Most of these terms can only be estimated roughly, yielding values around 4 kcal./mole according to Shainberg c.s. The calculated difference in energy between the two positions of the cation then falls in the range from + ½ kcal./mole for Li to — ½ kcal./mol for K. As suggested by the authors the uncertainty about the actual values of this small difference between the much larger single terms may be a less serious limitation when this treatment is used to compare two different ionic species.

In a following paper on the subject, Shainberg and Kemper (1967) attempt to incorporate these computations into an exchange equation, following an approach very similar to that of Heald c.s.

Obviously the change in potential of an ion when it is transferred from the boundary layer to the Stern layer, as calculated according to the procedure described above, may be identified with the quantity $\triangle E_S$ appearing in equation 25a. Not mentioning the weight factor g of this equation, the authors back-calculate k_i from an equation of this type as:

$$k_i = \frac{\delta_S \, e^{-\triangle E_{S(i)}/kT}}{\Gamma_G} \tag{30}$$

Next the values of k_i obtained for the homoionic forms of the clay with different cation species are incorporated into an equation similar to equation 29 above, yielding a selectivity coefficient for the homovalent exchange reaction written as (cf. Shainberg and Kemper, 1967; equation 18):

$$K_{SK} = \frac{k_1 c_G + 1}{k_2 c_G + 1} \tag{31}$$

in which c_G indicates again the total concentration of cations in the boundary layer. Although superficially identical with the selectivity coefficient defined with equation 29, the selectivity coefficient of Shainberg–Kemper, K_{SK} , differs from the latter as a result of two suppositions made by the authors in working out equation 31.

In the first place the parameters k_1 and k_2 as defined in equation 30 will vary with the changing value of Γ_G when going from one homoionic 'endpoint' to the other endpoint through the mixed compositions in between. The equation 30 is thus in conflict with the concept of a pair formation 'constant' as used by the authors in the earlier part of their paper. They circumvent this difficulty by using the values of k_1 and k_2 pertaining to the homoionic endpoints of the system, but then violate their equation describing the pair formation reaction. In the second place the authors define the total concentration in the boundary layer, c_G, for mixed systems as the weighed mean of the particular values found for the homoionic 'endpoints' of the exchange reaction. Of these two suppositions, the second one (although mathematically convenient) is unnecessary and also unwarranted, because the double-layer theory, as used by the authors for calculating the value of c_G in the homoionic systems, also supplies the relationship valid for mixed systems, i.e.:

$$c_G = \beta \Gamma_G^2/4 = a^2 \beta \Gamma^2/4 \tag{32}$$

in which again $a = \Gamma_G/\Gamma$. The first supposition, which is unwarranted in the present context, could be repaired by the introduction of a weight factor proportional to Γ_G in the formulation for the Stern layer, which would cancel this factor in equation 30.

The ensuing equation for k_i would then contain the proportionality constant between g_S and Γ_G which must be evaluated if k_i is to be expressed in terms of $\triangle E_S$. Turning to the original literature on the subject (Stern, 1924, cf. also Grahame, 1947) one finds that the number of ions per cm² of the Stern layer, n_S, is related to the number of ions per cm³ equilibrium solution, n_o, via the expression:

$$n_S/(z_S - n_S) = e^{-W/kT} \, n_o/(z_o - n_o) \tag{33}$$

in which z indicates the maximum number of positions available to the ions and $(z - n)$ the number of 'free' positions; W is the difference in potential of an ion in the Stern layer relative to an ion in solution. The value of z_o is then taken equal to the number of solvent molecules per cm³, whereas z_S equals the solvent molecules present per cm² of the Stern layer, i.e. $z_S = \delta_S z_o$. Unless extreme crowding is expected n_S and n_o are usually negligible in comparison to z_S and z_o (cf. Grahame, 1947). Although this condition is approximately fulfilled in clay systems (distances between the clay charges are of the order of 10 — 15 Å), the present model used for the calculation of the Stern potential of the ion is based on the contention that Stern ions must be situated in close vicinity of the clay charges. The 'free' positions in the Stern layer could thus not exceed the number of water molecules present in the fraction of the Stern layer opposite to non-paired surface charges, or:

$$(z_S - n_S) = z_o \delta_S \Gamma_G/\Gamma \tag{34}$$

Expressing the amounts present in milliequivalents and introducing c_G, this gives:

$$A_S = c_G e^{-\triangle E_S/kT} \delta_S \Gamma_G/\Gamma \tag{35}$$

The pair-formation constant then equals:

$$k_i = \frac{\delta_S e^{-\triangle E_S/kT}}{\Gamma} \tag{36}$$

and is now invariant with composition in mixed systems in accordance with the chosen model. Although one might contend that the 'free' fraction of the Stern layer is even smaller than Γ_G/Γ, any further reduction of k_i would be independent of the mixing ratio of the adsorbed ions. Because of the uncertainty about the precise value to be taken for δ_S (cf. the relevant comment in Shainberg and Kemper, 1967) it would seem satisfactory to maintain Γ_G/Γ in the equations, remembering that δ_S should be an 'effective' thickness of the Stern layer, which could certainly not exceed the diameter of the ions in the Stern layer. When comparing the above derivations with the one used by Shainberg c.s., it would seem that the pair-formation constants as calculated by the latter authors should at least be reduced with a factor Γ_G/Γ.

The difference between the approach of Shainberg c.s. and that of Heald c.s. is also reflected in the calculation of $\Gamma_G/\Gamma = a$, i.e. the fraction of the surface charge balanced by hydrated ions. As worked out by the former authors for homoionic systems, the relationship used may be written as:

$$pa^2 + a - 1 = 0 \qquad (37a)$$

$$\text{with } p = \frac{\beta\Gamma'^2}{4}\,\delta_S\,\frac{e^{-\Delta E_S/kT}}{\Gamma}$$

$$= \frac{\beta\Gamma'^2}{4}\,ka \ (= \text{constant})$$

In contrast the comparable equation of Heald c.s. reads:

$$p'a^3 + a - 1 = 0 \qquad (37b)$$

$$\text{with } p' = \frac{\beta\Gamma'^2}{4}\,k'$$

It should be noted that upon introduction of equation 36 into 37b p' will equal p, whereas k' differs from k. Accordingly the values of a, calculated by Shainberg c.s. will deviate from the ones found when applying the pair-formation concept in a consistent manner according to equation 36.

Notwithstanding the above criticism the contribution of Shainberg c.s. is of great interest as an effort to estimate the magnitude of the pair-formation constants on the basis of physical properties of the ions, which could rather easily be amended to become consistent with the semi-empirical approach of Heald c.s. Although, as pointed out by Shainberg and Kemper (1967) in the discussion section of their paper, the uncertainty about the actual values of physical parameters to be used remains considerable, the proposed treatment presents an important step forward in the process of gaining understanding about the nature of the cation exchange equilibrium in clay systems. A further comparison of the values of the selectivity coefficients for homoionic exchange as suggested by Shainberg and Kemper and those obtained with the equations amended as suggested above with e.g. the experimental data presented by Martin and Laudelout (1963) would be of great interest. Also the extension of this treatment to heterovalent exchange would appear a worthwhile goal.

Concluding remarks

In Table 1 the equations for heterovalent exchange as discussed are summarized. As is customary, the exchange reaction involving clays has been formulated as an exchange between ions adsorbed by the clay and ions in solution. Accordingly the activities, a_o, refer to the cationic activities in solution. As was mentioned before, the 'reduced activity ratio', $a_o^{+} / \sqrt{a_o^{++}}$, appearing in these equations — usually in the form of its square — may also be interpreted as the reduced activity ratio of the salts present in the equilibrium solution.

With the exception of the equation derived from diffuse double-layer theory, all model equations contain an empirical selectivity coefficient, which is expected to be constant. Inasfar as this contention may be proved to be satisfactorily obeyed for any

Table 1 Equations for mono-divalent cation exchange

General:

$$\ln \mathbf{K} = 1 + \int_{o}^{1} \ln K_N \, dN^+ \left(= \int_{o}^{1} \ln K_M \, dN^+ \right) = \frac{-\Delta G^\circ}{RT}$$

$$\text{with } K_N = \frac{(N^+)^2}{N^{++}} \frac{a_o^{++}}{(a_o^+)^2} \quad \text{and} \quad K_M = \frac{4\,K_N}{1+N^+}$$

Equations based on model considerations

Monolayer models

Vanselow:

$$K_V = \frac{(M^+)^2}{M^{++}} \frac{a_o^{++}}{(a_o^+)^2} \qquad (= \text{constant})$$

Davis:

$$K_D = \frac{(M^+)^2}{(M^{++}) \left\{ M^+ + 2\left(\frac{n-1}{n}\right) M^{++} \right\}} \frac{a_o^{++}}{(a_o^+)^2} \qquad (= \text{constant})$$

with $n = 4$:

$$K_{DKO} = \frac{(M^+)^2}{(M^{++})(M^+ + 1\tfrac{1}{2}\,M^{++})} \frac{a_o^{++}}{(a_o^+)^2} \qquad (= \text{constant})$$

with $n = \infty$:

$$K_E = \frac{(M^+)^2}{(M^{++})(M^+ + 2M^{++})} \frac{a_o^{++}}{(a_o^+)^2} \qquad (= \text{constant})$$

$$= \frac{(N^+)^2}{N^{++}} \frac{a_o^{++}}{(a_o^+)^2}$$

Gapon:

$$K_G^{\,2} = \left(\frac{N^+}{N^{++}} \frac{\sqrt{a_o^{++}}}{a_o^+} \right)^2 = \frac{K_N}{(1-N^+)} \qquad (= \text{constant})$$

Three-dimensional models

Donnan:

$$K_N \left(= \frac{(N^+)^2}{N^{++}} \frac{a_o^{++}}{(a_o^+)^2} \right) = \frac{f_m^{++}}{(f_m^+)^2} \frac{d^+}{2\Gamma}$$

with f_m = micellar activity coefficient

$$\frac{d^+}{\Gamma} = V_m = \text{micellar volume (in cm}^3\text{/meq.)}$$

Diffuse double layer:
(assuming ideal behavior)

$$K_N = \frac{\left\{ \arg\sinh\left(\Gamma \sqrt{\beta} / \sqrt{r^2 + 8\,N_o}\right) \right\}^2}{\Gamma \left\{ \beta\Gamma - r\sqrt{\beta} \arg\sinh\left(\Gamma \sqrt{\beta} / \sqrt{r^2 + 8\,N_o}\right) \right\}}$$

with Γ = surface-charge density (meq./cm²)

$$r = \frac{c_o^+}{\sqrt{c_o^{++}}}$$

one of these equations (i.e. within the required degree of accuracy) the application of that equation allows one to characterize the particular exchanger–ion combinations in terms of a single parameter. As the models underlying the different equations are still rather simple, there appears to be no reason to expect that any one of the selectivity coefficients will be truly constant over a wide range of conditions. However, since practical interest in exchange behavior of soil materials is often limited to fairly rough predictions for a particular system over a particular range of compositions, one should perhaps select to this purpose the coefficient which fulfills best the condition of constancy under these circumstances. If the ease of application plays a role it seems that K_G is perhaps best suited for the above rough predictions.

In a more detailed study of the exchange behavior of soil materials the monolayer-model equations do not offer much perspective for interpretative usage. One should then rather use the method of presentation as suggested by Gaines and Thomas. Experimental data can then be summarized in terms of a plot relating the K_N- and f-values to the exchanger composition, provided the complete range of compositions from $N = 0$ to $N = 1$ has been covered. The value of K may then be obtained from graphical intergration over $\ln K_N$. When interpreting the values of K and f thus derived for systems involving mono- and divalent cations, the computed values of K_N, as derived from the double-layer theory for ideal behavior, should serve as a standard for comparison. Such comparison would allow evaluation of the relative importance of electrostatic (Coulombic) versus specific energy of adsorption of the ions. The most promising model for the description of adsorption on external surfaces appears to be a Stern–Gouy approach along the lines as used for the homovalent case by Heald et al. (1964) and further advanced by Shainberg and Kemper (1967). Extension of this model to heterovalent exchange will increase its complexity considerably, as both the fraction of the divalent ions in the Gouy layer and that in the Stern layer will depend on the valence. In the Stern layer the statistical weight factor would also have to be corrected for the valence of the ion: possibly Davis' model could serve as a guide line for calculation. The use of an electronic computer appears to be necessary for the work-out of such a model.

A final remark should be made on the assumed reversibility of the exchange reaction. There is evidence that certain exchange reactions are incompletely reversible. The obvious example of such a system is the adsorption of potassium by certain clay minerals. There steric factors influence the relative affinity of the clay for different cations, which necessitates the recognition of a range of sites with different relative affinity (Bolt et al., 1963; van Schouwenburg and Schuffelen, 1963). The fact that often the cationic composition in turn influences these steric factors (by a varying degree of collapse of the crystal lattice) suggests a considerable degree of hysteresis in exchange reactions involving interlattice sites. Evidence has been presented indicating that in these collapsing systems (e.g. vermiculite) one might even expect a type of phase separation, certain interlayer spaces being filled preferentially with one cationic species, others with the competing ion (Coleman and Le Roux, 1965). Till this moment no model theories have been advanced to describe such systems.

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