

Effects of Permanent Charge on the Electrical Double-Layer Properties of Clays and Oxides¹

W. B. KLEIJN AND J. D. OSTER²

ABSTRACT

Two complimentary models which describe the surface chemistry of, respectively, clay minerals and oxides submersed in an aqueous solution are presented. Both models incorporate isomorphous-substitution charge, specific adsorption of counter ions at the inner Helmholtz plane, and a diffuse double layer outside the outer Helmholtz plane. In addition, one of the models allows for adsorption of potential-determining ions at the surface plane, which is located inward of the inner Helmholtz plane. General algorithms to solve surface chemistry models are given and methods to determine the associated empirical parameters are discussed. With the model which includes adsorption of potential-determining ions, it is shown that isomorphous substitution may be of great importance to the adsorption properties of oxides. Based on published data for NaCl/Al₂O₃ and KCl/SiO₂, computations are made which show that changes in the charge density of the potential-determining ions adsorbed at the surface plane tend to be equal in magnitude but opposite in sign to changes in the isomorphous-substitution charge density (σ_o). However, this cancellation is not perfect, and especially for KCl/SiO₂ systems, the counter-ion exchange capacity and its pH dependency and the zeta potential are strongly dependent on σ_o . The dependence on σ_o is particularly strong in the region where σ_o is small ($-0.04 < \sigma_o < 0.02$ C/m²). This implies that small amounts of isomorphous substitution may have a dramatic effect on the physico-chemical properties of oxides. The ion-adsorption behavior of montmorillonite cannot be explained with our generalized model for oxide surfaces. Thus, our calculations confirm the long-standing view that the basal planes of clay minerals do not adsorb H⁺ and OH⁻ as potential-determining ions.

Additional Index Words: diffuse double layer, potential-determining ions, Stern layer.

Kleijn, W. B., and J. D. Oster. 1983. Effects of permanent charge on the electrical double-layer properties of clays and oxides. *Soil Sci. Soc. Am. J.* 47:821-827.

CLAY MINERALS AND OXIDES adsorb anions and cations when immersed in an aqueous solution. Both exhibit pH-dependent charge and, therefore, pH-dependent adsorption capacities.

In addition to a pH-dependent charge at their edges, clay minerals also have a charged base plane which results from isomorphous substitution within the crystal structure. This charge is known to have a large effect on the surface chemistry of clays. Similar structural impurities can exist in oxides (e.g., Parks, 1965, p. 187). Models for ion adsorption on the basal planes of clay minerals are based on the internal charge of the clay crystal. For crystalline oxides, several different site-binding models have been developed which describe the material balance in ion-exchange experiments and zeta potential over a large range in ionic strength (Wright and Hunter, 1973; Yates et al., 1974; Bowden et al., 1977). However, these

models have not incorporated structural impurities, neglecting experimental observations (Parks, 1965). Here we present two models wherein isomorphous-substitution charge is taken into account and we use these models to compare the surface properties of clay minerals and oxides.

One model is based on the so-called "triple-layer model," introduced by Yates et al. (1974). This model, like that of Bowden et al. (1977), incorporates specific adsorption of potential-determining ions and counter ions in two separate planes near the solid surface and a diffuse double layer outside forementioned planes. Potential-determining ions adsorb significantly closer to the mineral surface than any other ions and they are usually limited to one or two ion species. Specific adsorption of counter ions is physically located further outward of the mineral surface and is not limited to one or two ion species. Of the existing models for the physico-chemical properties of oxide surfaces, the triple-layer model has been shown to be most accurate (Westall and Hohl, 1980). Thus we selected this model as the starting point of our generalized model. However, the triple-layer model does not allow for the specific adsorption of counter ions if the adsorption of potential-determining ions does not occur. Therefore a second model has to be introduced for surfaces which do not adsorb potential-determining ions. This second model is a modified Stern model (Stern, 1924). It is our opinion that together these models provide a fairly complete description of mineral surfaces present in soils.

Using the models we show that the presence of isomorphous substitution may be of great importance to the physico-chemical properties of oxides. Further, a general algorithm to solve surface chemistry models is presented and procedures to evaluate the empirical parameters of the model are also discussed.

THEORY

Several features and assumptions are common to both models. Their "geometries" are identical (Fig. 1). The isomorphous-substitution charge is located in the structure of the mineral. The effect of the isomorphous-substitution charge is approximated by a uniform electrical field. This is a good approximation since it follows from standard electrostatic theory that the discontinuity of the dielectric constant at the interface will make the electric potential along the interface more uniform. Thus, the distance from the isomorphous-substitution charge to

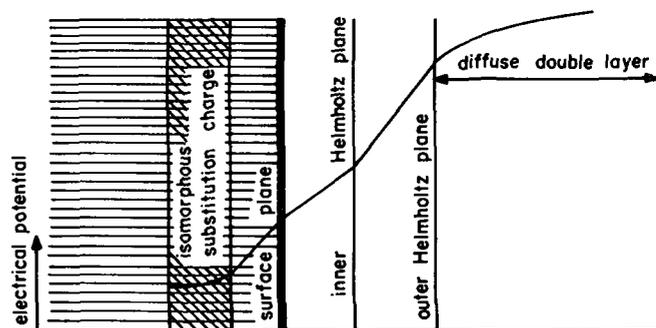


Fig. 1—Schematic picture of the oxide/aqueous interface.

¹ Contribution from the U.S. Salinity Laboratory, USDA-ARS, 4500 Glenwood Drive, Riverside, CA 92501, and the Dep. of Soil and Environmental Sciences, Riverside, CA 92521. Received 19 Nov. 1981. Approved 23 Feb. 1983.

² Research Fellow, Dep. of Physical Chemistry, Univ. of Melbourne, Parkville, Victoria, 3052; and Soil and Water Specialist, Univ. of California Cooperative Extension, Dep. of Soil and Environmental Sciences, Riverside, CA 92521. This work was supported, in part, by the United States-Israel Agriculture Research and Development Fund (BARD).

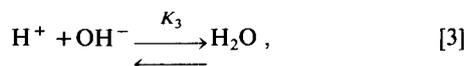
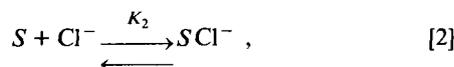
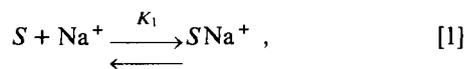
the solid/liquid interface is not essential to any of our calculations. Going from the solid to the liquid phase, three planes are distinguished (see Fig. 1): the surface plane, the inner Helmholtz plane, and the outer Helmholtz plane. Potential-determining ions adsorb at the surface plane in one model, while the other model does not include the adsorption of potential-determining ions. Specific adsorption of counter ions can occur at the inner Helmholtz plane in both models. The outer Helmholtz plane represents the innermost boundary of the diffuse double layer. Beyond this boundary, the ion distribution is governed by nonspecific Coulombic interactions. In both models, the outer Helmholtz plane is also assumed to be the plane of shear, beyond which viscous flow occurs. Movement of water molecules and ions located inward of this plane is assumed to be diffusive only; the net flux with respect to the solid would be zero.

The Bowden model (Bowden et al., 1977) has a geometry similar to the one just described, but it combines the inner and outer Helmholtz planes in a single plane. The triple-layer model (Davis et al., 1978) has the geometry presented here, but, like the Bowden model, it lacks a provision for the isomorphous-substitution charge.

To alleviate the mathematical complexity of the models, some simplifying assumptions are made: (i) The discrete charges located in a particular plane (e.g., the specifically adsorbed ions in the inner Helmholtz plane) are approximated by a uniform, planar charge density. Thus discreteness of charge effects have been ignored. This effect is hard to quantify for oxide surfaces because of the complexity of their surface structure (Yates et al., 1974). (ii) The diffuse double layer is approximated with the theory of Gouy (1910). (iii) The nonelectrostatic part of the adsorption energy of an ion is assumed to be independent of the density of the adsorbed species. For a rigorous treatment of these assumptions see Healy and White (1978). An implicit assumption of both models is that near-uniform density configurations of the interface species are far more likely to occur than nonuniform configurations. Also ion activities and concentrations are assumed to be equal. With these approximations, it is possible to define a one-dimensional, macroscopic potential function for the interface region which is essential to the models. Of this potential function only the potential at the shear plane (the outer Helmholtz plane), the zeta potential, is experimentally observable.

Model A

The first model, A, describes an interface that does not adsorb potential-determining ions. It will be shown that this model is applicable to the basal planes of clay minerals. Using the example of a mineral immersed in a sodium chloride solution, the following equilibria are essential:



where S is the surface site. The sites available for specific adsorption at the inner Helmholtz plane are assumed to be associated with the charges due to isomorphous substitution, σ_o :

$$(S) = \sigma_o / F , \quad [4]$$

where F is the Faraday constant, and the round brackets indicate concentrations. Writing the potential at the inner Helmholtz plane as ψ_{β} , the mass action equations become

$$(\text{SNa}^+) = K_1(S)(\text{Na}^+) \exp(-q\psi_{\beta}/kT) , \quad [5]$$

$$(\text{SCl}^-) = K_2(S)(\text{Cl}^-) \exp(+q\psi_{\beta}/kT) , \quad [6]$$

$$1 = K_3(\text{OH}^-)(\text{H}^+) , \quad [7]$$

where K_1 , K_2 , and K_3 are stability constants, q is the protonic charge, and kT is the thermal energy. The Boltzmann-distribution factors in Eq. [5] and Eq. [6] describe the effect of the electric potential on the equilibria. For a careful derivation of equations similar to Eq. [5] and Eq. [6], see Healy and White (1978).

The magnitude of the charge density in the inner Helmholtz plane, σ_{β} , is a function of the concentration of the different interface species:

$$\sigma_{\beta} = F \{ (\text{SNa}^+) - (\text{SCl}^-) \} . \quad [8]$$

Similarly, the charge located in the diffuse double layer is a function of the species concentration. From the Poisson-Boltzmann equation and Gauss' law, the following equation can be derived for the diffuse double-layer charge, σ_d :

$$\sigma_d = \left\{ \sum_i 2N_{av} \epsilon_w \epsilon_o k T c_i \left[\exp\left(\frac{-z_i q \psi_d}{kT}\right) - 1 \right] \right\} , \quad [9]$$

where N_{av} is Avogadro's number, ϵ_o is the permittivity of vacuum (SI units are used), ϵ_w is the dielectric constant of the solution, c_i is the concentration of ion species i , z_i is the valence of ion species i , and ψ_d is the zeta potential. Note that Eq. [9] is general and does not require a symmetrical electrolyte.

The interface potentials, ψ_d and ψ_{β} , and the diffuse double-layer charge σ_d can be related according to Gauss' law:

$$\psi_{\beta} = \psi_d - \sigma_d / C_{\beta d} , \quad [10]$$

where $C_{\beta d}$ is the capacitance of the region between the inner and outer Helmholtz plane. In the model of Stern (Stern, 1924), $C_{\beta d}$ is infinite. For the planar case, which applies here, the capacitance is a function of the thickness, d , and the dielectric constant of the region. In case of a well-defined, constant, dielectric constant, $\epsilon_{\beta d}$, this relation is

$$C_{\beta d} = \epsilon_{\beta d} \epsilon_o / d . \quad [11]$$

The total charge over the interface must be equal to zero:

$$\sigma_o + \sigma_{\beta} + \sigma_d = 0 . \quad [12]$$

Further, the bulk solution will satisfy the electroneutrality equation:

$$(\text{Na}^+) - (\text{Cl}^-) + (\text{H}^+) - (\text{OH}^-) = 0 . \quad [13]$$

Since the model contains eight equations (Eq. [5]–[10], [12], [13]), the equations describing model A (in the case of the simple sodium chloride example can be solved if 3 of the 11 variables (S , Na^+ , Cl^- , H^+ , OH^- , SNa^+ , SCl^- , σ_{β} , σ_d , ψ_{β} , and ψ_d) are specified if $C_{\beta d}$, K_1 , K_2 , and K_3 are known constants).

Yates et al. (1974) and Davis et al. (1978) found that a capacitance of 0.2 F/m² for the outer zone of the triple-layer model (located between the two Helmholtz planes) best described experimental data. The same value is a good estimate of the compact-layer capacitance on Hg and AgI (Davis et al., 1978). Thus, it appears that 0.2 F/m² is a reasonable estimate for $C_{\beta d}$ of model A.

Experimental curves of the zeta potential as a function of ionic strength can be used to obtain optimum values for the stability constants of model A. Often, specific adsorption of either anions or cations is negligible (a positive isomorphous-substitution charge suppresses cation adsorption and vice versa). For this case, fitting the remaining stability constant is straightforward. If the stability constant of one surface-ion complex is

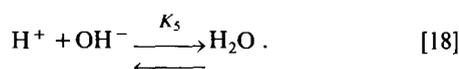
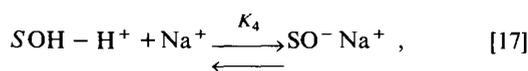
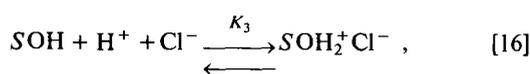
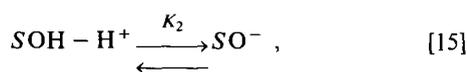
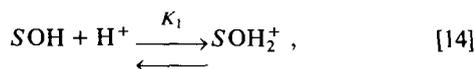
known, data of exchange of this ion with a second ion will provide a value for the stability constant of the surface complex of the second ion.

Model B

In contrast to model A, model B allows for the adsorption of H^+ and OH^- as potential-determining ions at the surface plane as is the case on oxide surfaces. The potential-determining ions are adsorbed by amphoteric surface groups. The density of these groups, or sites, must be derived from experimental data.

In model B, the specifically adsorbed counter ions, located in the inner Helmholtz plane, are assumed to form complexes with charged groups (of opposite sign) in the surface plane. This pairwise bonding of the counter ions with charged surface groups is a unique feature of the triple-layer model and model B. In contrast, the Bowden model has a fixed number of adsorption sites in the inner Helmholtz plane (which is combined with the outer Helmholtz plane).

Considering an example with components sodium chloride, hydrochloric acid, water and the surface group, SOH, the appropriate equilibria for model B are



With these equilibria, it is possible to relate the density of the interface species to the bulk solution concentrations of the components:

$$(SOH_2^+) = K_1(SOH)(H^+) \exp(-q\psi_s/kT) , \quad [19]$$

$$(SO^-) = K_2(SOH)/[(H^+) \exp(-q\psi_s/kT)] , \quad [20]$$

$$(SOH_2^+ Cl^-) = K_3(SOH)(Cl^-) \exp(+q\psi_\beta/kT) (H^+) \exp(-q\psi_s/kT) , \quad [21]$$

$$(SO^- Na^+) = K_4(SOH)(Na^+) \exp(-q\psi_\beta/kT) [(H^+) \exp(-q\psi_s/kT)] , \quad [22]$$

where ψ_s is the potential in the surface plane. Further we have

$$1 = K_5(H^+)(OH^-) . \quad [23]$$

The magnitudes of the charge densities in the surface plane, σ^s , and inner Helmholtz plane, σ_β , are functions of the concentrations of the different interface-species concentrations:

$$\sigma_s = F[(SOH_2^+) - (SO^-) + (SOH_2^+ Cl^-) - (SO^- Na^+)] , \quad [24]$$

$$\sigma_\beta = F[-(SOH_2^+ Cl^-) + (SO^- Na^+)] . \quad [25]$$

The value for σ_d is given by Eq [9]. The total charge over the

interface must be zero:

$$\sigma_o + \sigma_s + \sigma_\beta + \sigma_d = 0 . \quad [26]$$

Equation [10] relates the potentials at the inner and outer Helmholtz planes of model B. In addition, the surface plane potential is related to the inner Helmholtz plane potential in an identical manner:

$$\psi_s = \psi_\beta - (\sigma_\beta + \sigma_d)/C_s , \quad [27]$$

where C_s is the capacity of the region between the surface plane and the inner Helmholtz plane. For model B, the electroneutrality eq. [13] also applies.

The equations describing model B can be solved if four of the fifteen variables (SOH , SOH_2^+ , SO^- , $SOH_2^+ Cl^-$, $SO^- Na^+$, H^+ , OH^- , Na^+ , Cl^- , ψ_d , ψ_s , ψ_β , σ_s , σ_β , σ_d) are specified since 11 equations are given ([9], [13], [19]–[27]).

For model B, evaluation of the isomorphous-substitution charge is not straightforward. The isomorphous-substitution charge, σ_o , will be equal to the surface plane charge for the case that the inner Helmholtz plane and diffuse layer do not contain a net charge:

$$\sigma_o = \sigma_s \quad (\sigma_\beta = \sigma_d = 0) . \quad [28]$$

To obtain a system with no inner Helmholtz plane charge it is helpful to use ions that do not tend to form ion pairs in aqueous solutions. The pH value for which $\sigma_d = 0$ can then be found from the crossover point of pH titration curves of different ionic strength. For a system where no specific adsorption occurs in the inner Helmholtz plane the crossover point or point of zero salt effect (PZSE) (Sposito, 1981) should not vary with ionic strength.

Hypothetical pH titration curves are shown in Fig. 2 for a mineral at two different ionic strengths. The plateaus of the curves indicate when the amphoteric sites are saturated with H^+ (A, A') and when they are depleted of H^+ (B, B'). As required by Eq. [14] and Eq. [15], the amount of H^+ added per unit surface between the plateaus will be twice the total amphoteric site density, SO_t . At the midlevel between the plateaus there is no net surface plane charge, while at the PZSE indicated by the crossover of the titration curves, the surface plane charge equals the isomorphous-substitution charge. Therefore, the amount of H^+ added between the PZSE and the midlevel corresponds to the isomorphous substitution charge in faraday units, σ_o/F (see Fig. 2).

It must be recognized that the above determination of the isomorphous substitution charge assumes that only amphoteric sites are present. If more direct methods, such as chemical analysis, can be employed they will probably lead to more accurate results.

Evaluation of the stability constants, K_i , of the interface species of model B can be done similarly to the method devised by Davis et al. (1978) for the triple-layer model. To calculate K_i , let us assume that experimental data are available for systems in which SOH_2^+ is the only dominant interface species besides SOH. In other words, for this consideration concentra-

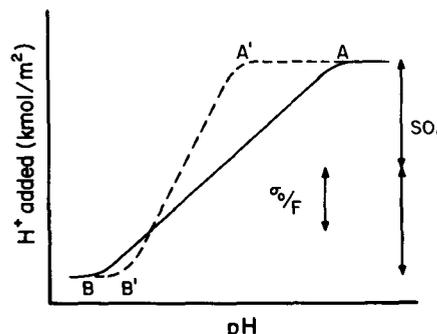


Fig. 2—The determination of σ_o in model B.

tions of other charged interface species are assumed to be negligible. Based on these assumptions Eq. [19] can be written as

$$pK_1 = pQ_1 - q\psi_s/kT \quad [29]$$

with

$$pQ_1 = -pH - \log\left\{\frac{\alpha}{1-\alpha}\right\} \quad [30]$$

and

$$\alpha = \sigma_s/[FN] \approx (\text{SOH}_2^+)/N \quad [31]$$

where N is the total number of amphoteric surface sites. Plotting pQ_1 as a function of σ_s gives a linear relationship. When $\sigma_s = -\sigma_o$, ψ_s will vanish. Therefore, from the experimental relationship of pQ_1 and σ_s , pK_1 can be found, either through linear extrapolation or linear interpolation. A similar procedure can be used to find K_2 from experimental data for which SO^- is the only dominant interface species besides SOH . To calculate K_3 , data are needed for which $\text{SOH}_2^+\text{Cl}^-$ is the only dominant interface species besides SOH . Equation [21] then becomes

$$pK_3 = pQ_3 + q(\psi_\beta - \psi_s)/kT \quad [32]$$

with

$$pQ_3 = -pH + \log(\text{Cl}^-) - \log\left[\frac{\alpha}{1-\alpha}\right] \quad [33]$$

and

$$\alpha = \sigma_s/[FN] \approx (\text{SOH}_2^+\text{Cl}^-)/N \quad [34]$$

At the point where $\sigma_s = -\sigma_o$, in the linear relationship between pQ_3 and σ_s , ψ_β will be equal to ψ_s , and the last term in Eq. [32] will be equal to zero. There, pK_3 will equal pQ_3 . Again, σ_s can be calculated from the pH-titration curves. K_4 can be found in a similar manner.

Clearly, for positive σ_s , SOH , SOH_2^+ , and $\text{SOH}_2^+\text{Cl}^-$ will dominate at the interface. Similarly, SOH , SO^- , and SO^-Na^+ dominate at negative σ_s . At high electrolyte concentrations, $\text{SOH}_2^+\text{Cl}^-$ and SO^-Na^+ are likely to be more abundant than SOH_2^+ and SO^- , these roles being reversed at low concentrations. If an interface species is dominant for a certain range of ionic strength and pH, then the experimental values found for its stability constant will not vary within this range. Some interface species will not be dominant for any range of ionic range, and their stability constants cannot be determined empirically with the methods described above. For many purposes, it is satisfactory to set the stability constant of such a species equal to a small arbitrary value. Illustrations of the above procedures for the case that $\sigma_s = 0$ (triple-layer model) can be found in Davis et al. (1978). For the effect of variation of the adjustable parameters at $\sigma_s = 0$, see Yates et al. (1974).

DISCUSSION OF COMPUTER ALGORITHMS

Two similar computer programs were written to solve the two models. They can be obtained from the authors by written request. To allow for easy adaptation to complex systems, a systematic setup was used. Table 1 demonstrates the setup using the sodium chloride example for model A. A set of microcomponents is defined. The microcomponents are the fundamental variables of the models. Via the mass-action equations, all species can be expressed in terms of the microcomponents which include the Boltzmann factors. The mass action equations are defined by the stoichiometric matrix $A(i,j)$ and the stability constants $K(i)$ (equation I). The charge densities σ_d , σ_β , σ_o can be expressed in species concentrations with the equations II, III, IV.

The "fundamental" equations which need to be solved are the "irregular" equations V, VI, VII, and the "reg-

Table 1—Mathematical description of Model A using a sodium chloride solution.

| Definitions | | | | | | | |
|---|----------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Microcomponent | $\exp \frac{\psi_{\beta q}}{kT}$ | Cl ⁻ | Na ⁺ | H ⁺ | S | | |
| Free concentration | $X(1)$ | $X(2)$ | $X(3)$ | $X(4)$ | $X(5)$ | | |
| Total concentration | -- | $T(2)$ | $T(3)$ | $T(4)$ | $T(5)$ | | |
| Species Concentration | SNa ⁻ | SCL ⁻ | S | OH ⁻ | OH ⁺ | Na ⁺ | Cl ⁻ |
| | $C(1)$ | $C(2)$ | $C(3)$ | $C(4)$ | $C(5)$ | $C(6)$ | $C(7)$ |
| The auxiliary equations | | | | | | | |
| Mass action equations | | | | | | | |
| $\ln[C(i)] = \ln[K(i)] + \sum_{j=1}^5 A(i,j)\ln[X(j)] \quad i = 1-7$ I | | | | | | | |
| with | | | | | | | |
| $A = \begin{matrix} & \begin{matrix} 1 & 0 & 1 & 0 & 1 \\ -1 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{matrix} \end{matrix}$ | | | | | | | |
| Layer charges | | | | | | | |
| $\sigma_o = FC(3)$ II | | | | | | | |
| $\sigma_\beta = F[C(1) - C(2)]$ III | | | | | | | |
| $\sigma_d = \sum_i 2 N_{av} \epsilon_o \epsilon_w kT C(i) \left[\exp\left(-\frac{z(i)q\psi_d}{kT}\right) - 1 \right]$ IV | | | | | | | |
| The irregular equations | | | | | | | |
| $0 = \psi_d - \psi_\beta - \sigma_d/C_{\beta d}$ V | | | | | | | |
| $0 = \sigma_o + \sigma_\beta + \sigma_d$ VI | | | | | | | |
| $0 = C(5) + C(6) - C(4) - C(7)$ VII | | | | | | | |
| The regular equations | | | | | | | |
| $0 = T(j) - \sum_{i=1}^7 A(i,j)C(i) \quad j = 1-5$ VIII | | | | | | | |

ular" equations VIII. The irregular equations represent Eq. [10], [12], and [13]. The regular equations VIII are the mass-balance equations for the microcomponents (except the Boltzmann factor), $T(j)$ being the total concentration of microcomponent j . The number of regular equations increases with the number of microcomponents, while the number of irregular equations for model A is always equal to three.

With the auxiliary equations I through IV, the fundamental equations V through VIII can be solved for the variables $X(j)$ and $T(j)$. Note that $T(1)$ is nonexistent. In general, for a system with n microcomponents, $n+2$ regular and irregular equations can be written. There are $2n-1$ variables [n X variables and $(n-1)T$ variables]. Thus, the system can be solved if $n-3$ variables are known. In this discussion, the zeta potential, ψ_d , is considered to be a constant. The computer program solving model A uses the zeta potential and the total [$T(j)$], or free [$X(j)$] concentrations, of $n-3$ microcomponents as input. The Boltzmann factor cannot be used as input.

The computer program solving model B uses a similar setup. Here, two Boltzmann factors are included. There are four irregular equations ([10], [13], [26], [27]) and a variable number of regular equations. For a similar aqueous solution, model B will have one more microcomponent than model A (the Boltzmann factor of the surface plane). For model B, m microcomponents result in a system of $m+1$ regular and irregular equations and

Table 2—Empirical parameters for model B.

| | KCl/SiO ₂ | NaCl/γAl ₂ O ₃ |
|---------------------------------------|----------------------|--------------------------------------|
| pK ₁ | 1.2 | -5.7 |
| pK ₂ | 7.2 | 11.5 |
| pK ₃ | 6.7 | 9.2 |
| pK ₄ | 0.7 | -7.9 |
| C ₁ (F/m ²) | 1.25 | 1.10 |
| C ₂ (F/m ²) | 0.2 | 0.2 |
| Site density (sites/nm ²) | 5 | 8 |

$2m-2$ variables, needing $m-3$ known variables to be solved. As input, the computer program uses the zeta potential and $m-3$ free or total concentrations of the microcomponents (the Boltzmann factors excluded). Thus, for a similar solution, model B needs one more input variable than model A.

The fundamental equations are solved with a multi-dimensional Newton-Raphson method. A modification was made to prevent the concentrations from becoming negative during the iterative treatment. The Newton-Raphson method requires continuously increasing or decreasing functions for convergence. This prevents a free choice of input variables. Thus, the zeta potential was used as input instead of the preferred isomorphous-substitution charge.

MODEL CALCULATIONS

Model B allows for the adsorption of potential-determining ions at the solid/liquid interface. For oxides, these ions are mainly H⁺ and OH⁻. For the case of zero isomorphous-substitution charge, the model is identical to the triple-layer model introduced by Yates et al. (1974). Davis et al. (1978) and Davis and Leckie (1978) published empirical parameters for the triple-layer model for several oxide/-solution interfaces. Although these data were obtained for minerals assuming isomorphous substitution is zero, they can be used for our model B as well. While this assumption may be incorrect (the actual isomorphous-substitution charge density on oxide samples has never been evaluated), the data of Davis et al. (1978) make it possible to evaluate the effect of the isomorphous-substitution charge on the surface chemistry of clay minerals and oxides in aqueous solutions. Table 2 gives data for the KCl/SiO₂ and NaCl/Al₂O₃ interfaces derived from the data of Davis et al. (1978). The behavior of these interfaces is similar to interfaces where other monovalent counter ions are present, as can be seen from comparison of the titration curves of SiO₂ with KCl, NaCl, LiCl, and CaCl solutions (Tadros and Lyklema, 1968; Abendroth, 1970). Figure 3 shows the surface-plane charge density, σ_s , as a function of the isomorphous-substitution charge density, σ_o , for several pH values. Changes in σ_s tend to be equal in magnitude but opposite of sign to σ_o for NaCl/Al₂O₃ (Fig. 3a), whereas for KCl/SiO₂ (Fig. 3b) a small deviation from similar behavior is found around $\psi_o = 0$. Therefore, the titration curves, which relate ψ_o with the pH, should be virtually independent of σ_o for Al₂O₃ while a slight dependency should be found in SiO₂ in the region around $\sigma_o = 0$.

Variation of σ_o does have a large effect on the diffuse-layer charge, σ_d , and on specific adsorption in the inner Helmholtz plane. Figure 4 shows the sum of the inner-Helmholtz-plane charge density, σ_b , and σ_d , which is equal

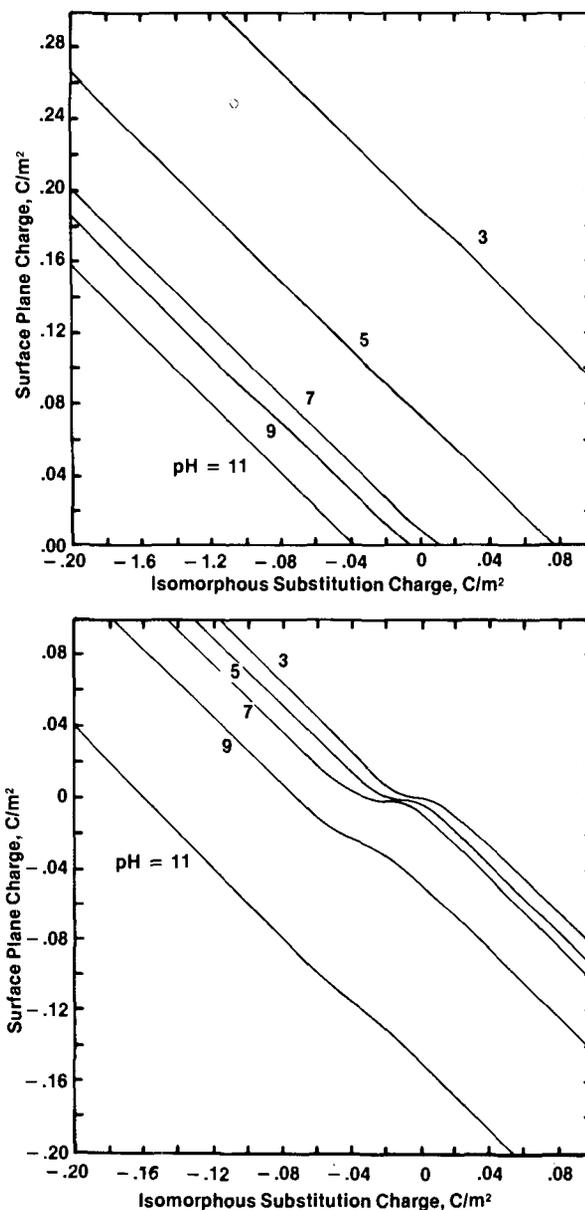


Fig. 3—The surface-plane charge density as a function of the isomorphous-substitution charge density at several values of the pH for the NaCl/γAl₂O₃ interface (top) and KCl/SiO₂ interface (bottom).

to the counter-ion exchange capacity, as a function of σ_o for the KCl/SiO₂ interface. Similar to the surface plane charge density, the counter-ion exchange capacity experience, its strongest dependency on σ_o in the region near $\sigma_o = 0$. This means that small amounts of isomorphous substitution will have large effects on these parameters. For the NaCl/Al₂O₃ case the counter-ion exchange capacity is not as strongly dependent upon σ_o . In both cases, the counter-ion exchange capacity is generally not equal in magnitude to σ_s , as the triple-layer model would predict.

Since the value of σ_d is dependent upon σ_o , it is to be expected that the zeta potential varies with σ_o . This effect is shown in Fig. 5 for the KCl/SiO₂ case. The zeta potential vs. pH function is found to be strongly dependent upon the value of σ_o , again in the region around $\sigma_o = 0$.

From the above discussion it becomes clear that the previously neglected isomorphous-substitution charges will

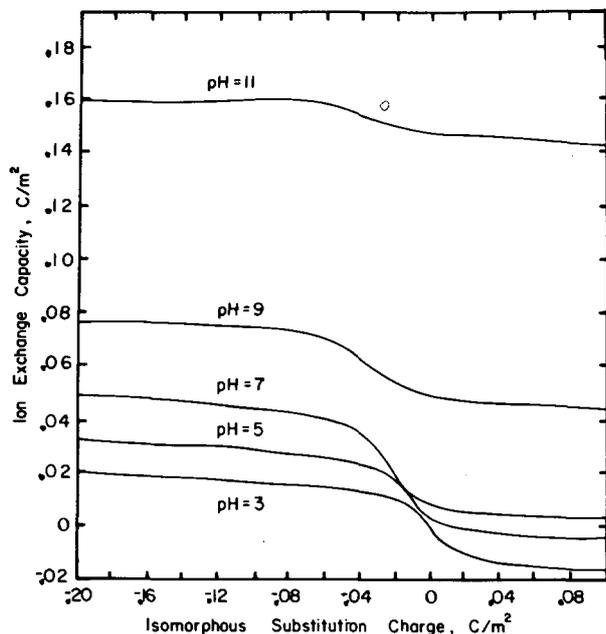


Fig. 4—The sum of the diffuse double-layer charge density and the inner-Helmholtz-plane charge density, ion exchange capacity, as a function of the isomorphous-substitution charge density for the KCl/SiO₂ interface.

influence the adsorption properties of oxides. A small isomorphous-substitution charge density may have a dramatic effect on the physico-chemical properties of the oxides. Thus it will be difficult to detect isomorphous-substitution in minerals with a low surface/volume ratio such as oxides from chemical analysis, especially for low charge densities. For example, a surface area of 10 000 m²/kg and an isomorphous-substitution charge density of 0.01 C/m² means that there is only 1 mmol of charge/kg [(10 000 m²/kg)(0.01 C/m²)/96.5 C/mmol charge]. Our results indicate, however, that the determination of isomorphous-substitution charge density, even if it is very small, is essential to describe ion adsorption on oxide surfaces correctly.

At neutral pH values, for a σ_0 of -0.12 C/m², as present in montmorillonite, model B predicts that σ_0 for Al₂O₃ and SiO₂ are 0.13 C/m² and 0.08 C/m² (see Fig. 3). Thus, H⁺ should make up a large fraction of the counter ions of montmorillonite at neutral pH if model B is valid for its basal-plane surfaces. The counter-ion composition of clay minerals can be calculated from the total chemical analysis of the clay mineral (Gast, 1977). Although H⁺ is not considered in the chemical analysis, the amount of adsorbed H⁺ can be determined from the charge balance, since the quantities of all the other ions are known. The analytical data published by Grim (1968) show that only a very small fraction of the adsorbed ions is H⁺, contradicting the predictions by model B. This confirms the long-standing view that the basal-plane surface of montmorillonite does not adsorb H⁺ and OH⁻ as potential-determining ions. A similar analysis is not possible for kaolinite since its edge charges dominate its adsorption behavior. However, from the above results, it can be expected that both its basal planes, which are cleavage planes do not adsorb H⁺ and OH⁻ as potential-determining ions.

Since the surfaces of other clay minerals are similar to those of montmorillonite and kaolinite, it is concluded

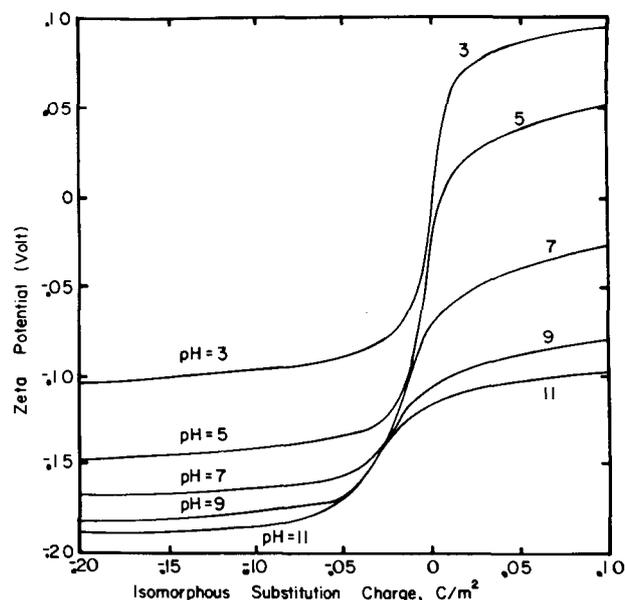


Fig. 5—The zeta potential as a function of the isomorphous-substitution charge density for the KCl/SiO₂ interface.

that the adsorption and desorption of H⁺ and OH⁻ as potential-determining ions at the basal planes of clay minerals is negligible. Consequently, model B and/or the triple-layer model are not applicable to the basal planes of clay minerals. In a future paper we will show that model A can be used to model the coagulation and zeta potentials of clay minerals.

DISCUSSION

The two models described in this paper are intended to be complementary in the description of the chemistry of the interfaces of clay minerals and oxides with an aqueous solution. Since isomorphous substitution is of great importance to the physico-chemical properties of clay minerals we included it also in the description of oxide surfaces (model B). Model calculations using experimental data obtained for Al₂O₃ and SiO₂ show that the physico-chemical properties of oxides are strongly influenced by even moderate amounts of isomorphous substitution. When applying model B (which is intended for oxides only) to clay minerals the amount of potential-determining ion adsorption is unreasonable. Model A, which does not include the adsorption of potential-determining ions is concluded to be the proper model for the basal planes of clay minerals. Both models allow for the specific adsorption of counter ions and incorporate a diffuse (Gouy) layer to provide for nonspecific adsorption. A finite capacitance is expected to account for the finite size of the ions and part of the discrete charge effect. For similar reasons a finite capacitance is present between the surface plane (where the potential-determining ions adsorb) and the inner Helmholtz plane in model B.

Where model A is applicable, a linear relation between isomorphous-substitution charge and ion-exchange capacity exists. Neither the pH or the ionic strength will affect this relationship. Generally, the pH will not influence the electric potentials of surface, inner, and outer Helmholtz planes. The ionic strength does affect these potentials and will determine the distribution of adsorbed

electrolyte ions over the diffuse double layer and the inner Helmholtz plane.

Model B does not reduce to model A for the limiting cases of very small values of the stability constants K_1 and K_2 (Eq. [14] and [15] and/or a zero number of adsorption sites for potential-determining ions. For this case, specific adsorption of counter ions at the inner Helmholtz plane could not occur; according to model B specific adsorption is associated with charged surface groups (SO^- and SOH_2^+ , Eq. [16] and [17]). The basal planes of clay minerals do not have such charged surface groups, or if they do their number is small. Consequently the mechanism of specific adsorption of counter ions on the basal planes of clay minerals is different from that on oxides. For a given clay mineral the number of adsorption sites in the inner Helmholtz plane has been taken to be fixed, said number being related to the isomorphous substitution charge by Eq. [4].

The Bowden model (Bowden, 1977), like model B and the triple-layer model, is intended to describe the surfaces of oxides. It includes the adsorption of potential-determining ions at the surface plane and the specific adsorption of counter ions in a Helmholtz plane. There is zero capacitance between inner and outer Helmholtz plane, merging them into a single plane. The number of adsorption sites in the Helmholtz plane is assumed to be fixed for a certain mineral, but is not related to other model parameters. Thus, in contrast with the model, A and B and the triple-layer model this number of adsorption sites is a fitting parameter in the Bowden model.

The Bowden model (Bowden, 1977), like model B and the triple-layer model, is intended to describe the surfaces of oxides. It includes the adsorption of potential-determining ions at the surface plane and the specific adsorption of counter ions in a Helmholtz plane. There is zero capacitance between inner and outer Helmholtz plane, merging them into a single plane. The number of adsorption sites in the Helmholtz plane is assumed to be fixed for a certain mineral, but is not related to other model parameters. Thus, in contrast with the models, A and B and the triple-layer model this number of adsorption sites is a fitting parameter in the Bowden model. The Bowden model gives a fair agreement with experimental data (Bowden et al., 1977). It is likely that this agreement could be enhanced by the adoption of separate inner and outer Helmholtz planes. Then, however, the Bowden model would have one more adjustable variable than the triple-layer model; normally both models have an equal number of adjustable variables. face groups (SOH , SOH_2^+ , SO^-) decreases.

Several authors have suggested that for oxide-type surfaces the relationship between ion-exchange capacity and pH is straightforward and follows from the combination of the Gouy theory for the diffuse double layer and the Nernst equation, using H^+ and OH^- as potential-determining ions (Parker et al., 1979; Uehura and Gillmann, 1980). However, such a theory is incorrect on two ac-

counts: (i) specific adsorption in the inner Helmholtz plane is ignored, and (ii) the Nernst equation is not valid for oxides (Berube and de Bruyn, 1968). The Nernst equation assumes that the chemical potential of the potential-determining ions, which are adsorbed at the surface plane, is independent of the composition of the electrolyte solution. In reality, the chemical potential of the adsorbed potential-determining ions must be a function of the concentrations of the interface species. In addition, as indicated by Model B, the ion-exchange capacity and the distribution of the adsorbed counter ions over the diffuse layer and the inner Helmholtz plane are functions of both the pH and the ionic strength in the bulk solution.

ACKNOWLEDGMENTS

We gratefully acknowledge the encouragement and advice provided by Drs. Garrison Sposito and Dirk Stigter.

REFERENCES

1. Abendroth, R.P. 1970. Behavior of pyrogenic silica in simple electrolytes. *J. Colloid Sci.* 34:591-596.
2. Berube, Y.G., and P.L. de Bruyn. 1968. Adsorption at the rutile-solution interface. I. Thermodynamic and experimental study. *J. Colloid Interface Sci.* 27:305-318.
3. Bowden, J.W., A.M. Posner, and J.P. Quirk. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical-charge development and titration curves. *Aust. J. Soil Res.* 15:121-136.
4. Davis, J.A., R.O. James, and J.O. Leckie. 1978. Surface ionisation and complexation at the oxide water interface. I. Computation of electrical double layer properties in simple electrolytes. *J. Colloid Interface Sci.* 63:480-499.
5. Davis, J.A., and J.O. Leckie. 1978. Surface ionisation and complexation at the oxide/water interface. II. Surface properties of amorphous iron, oxyhydroxide and adsorption of metal ions. *J. Colloid Interface Sci.* 67:90-107.
6. Gast, R.G. 1977. Surface and colloid chemistry. p. 27-74. In J.B. Dixon and S.B. Weed (ed.) *Minerals in soil environment*. Soil Sci. Soc. of Am., Madison, Wis.
7. Gouy, E. 1910. Sur la constitution de la charge électrique a la surface d'un électrolyte. *Ann. Phys. (Paris) Serie 4*, 9:457-468.
8. Grim, R.E. 1968. *Clay mineralogy*. McGraw-Hill, New York.
9. Healy, T.W., and L.R. White. 1978. Ionizable surface group models of aqueous interfaces. *Adv. Colloid Interface Sci.* 9:303-345.
10. Parker, J.C., L.W. Zelazny, S. Sampath, and G.W. Harris. 1979. A critical evaluation of the extension of the zero point of charge theory (ZPC) to soil systems. *Soil Sci. Soc. Am. J.* 43:668-674.
11. Parks, G.A. 1965. The isoelectric point of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.* 65:177-198.
12. Sposito, G. 1981. The operational definition of the zero point of charge in soils. *Soil Sci. Soc. Am. J.* 45:292-297.
13. Stern, O. 1924. Zur Theorie der elektrolytischen Doppelschicht. *Z. Electrochem.* 30:508-516.
14. Tadros, Th., and F.J. Lyklema. 1968. Adsorption of potential-determining ions at the silica-aqueous electrolyte interface and the role of some cations. *J. Electrochem.* 17:267-275.
15. Uehara, G., and G.P. Gillman. 1980. Charge characteristics of soils with variable and permanent charge minerals: I. theory. *Soil Sci. Soc. Am. J.* 44:250-252.
16. Westall, J., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Adv. Colloid Interface Sci.* 12:265-294.
17. Wright, H.J.L., and R.J. Hunter. 1973. Adsorption at solid-liquid interfaces. II. Models of the electrical double layer at the oxide-solution interface. *Aust. J. Chem.* 26:1191-1206.
18. Yates, D.E., S. Levine, and T.W. Healy. 1974. Site-binding model of the electrical double layer at the oxide/water interface. *J. Chem. Soc. Faraday Trans. 1* 70:1807-1819.