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pH-INDEPENDENT AND pH-DEPENDENT SURFACE CHARGES ON KAOLINITE

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Abstract—Model cation-exchange curves are presented for an idealized kaolinite surface where the charge on the surface (1) has its origin in cation substitution in the structure, and hence, is pH independent; and (2) is produced by protonation/deprotonation reactions of oxide-like sites, and hence, depends on the acid and base strengths of the surface sites, as well as the ionic strength. Two pH-independent situations are considered: one where the exchanging ions have no selectivity for the surface and are all in the diffuse layer; and one where selectivity exists for one ion and where that ion is partly in a Langmuir-Stern layer and partly in the diffuse layer. If one of the exchanging ions is a proton, the shape of the curves and their position on the pH scale depend on ionic strength and ionic selectivity.

The model curves are compared with data for actual kaolinites. Under most conditions exchangeable Al is released from the structure, and the shape of the charging curves becomes similar to that of an oxide-like surface. However, if titration is carried out rapidly, or account is taken of the presence of Al, the proton binding curves are similar in shape to those expected for sites resulting from cation substitution in the structure of kaolinite, either near the surface or at the edge of the crystal.

Key Words—Cation substitution, Ion selectivity, Kaolinite, pH, Protonation/deprotonation, Surface charge.

INTRODUCTION

Cation substitutions in the lattice of kaolinite have been difficult to prove. Unlike other clay minerals small deviations from stoichiometry in kaolinite are impossible to detect by direct chemical analysis. Also, kaolin samples are seldom, if ever, free from mineralogical impurities. Evidence for cation substitution in the lattice is usually sought by studying the relationship between pH and charge (cation adsorption) (e.g., Samson, 1953; Schofield and Samson, 1953, 1954; Weiss, 1959; Ferris and Jepson, 1975; Bolland *et al.*, 1976). In this paper model surface charge-pH curves are presented for pH-independent and pH-dependent charge on idealized kaolinite and compared with those of actual samples.

pH-INDEPENDENT CHARGE

Kaolinite consists of successive silico-alumina (7 Å) units held together by hydrogen bonding to form 'stacks' (Grim, 1953; Marshall, 1964). Because counterions between individual silico-alumina units are not known, charges due to cation substitution within kaolinite 'stacks' must be balanced by counterions at the external surface of the 'stacks,' generally on the basal surfaces or near the edges (Weiss and Russow, 1963; Follet, 1965) rather than uniformly distributed throughout the 'stacks.' In either case, a large distance in electrostatic terms exists between the counterions at the surface of the clay and the seat of the replacement charge. Thus, by analogy with oxy-acids (Pauling, 1960), counterions should be held at the surface by relatively weak electrostatic forces and should be readily replaced by other counterions. The counterions that balance charges due to cation substitution should thus behave similarly to strong electrolytes in that they are completely ionized in water but are restricted in position by an electrical potential at the surface. In the acid form the clay should have titration characteristics similar to those of strong acids. Hence, the sites on clays produced by cation substitution in the structure have been called strong acid sites (Pauling, 1960) and have been shown to have such character through titration curves (Harward and Coleman, 1954).

Model with no selectivity

In this model it is assumed that only pH-independent charge is present on the clay and that counterions are held at the surface by coulombic forces only, there being no selectivity. Homovalent cation exchange, therefore, results in no change in the distribution of electrical potential at the surface. The surface charge density is then:

$$-(\sigma_p) = N_S \qquad (1)$$

where σ_p is the charge density of the clay (eq/cm²), and N_s is the density of charged sites on the clay surface (eq/cm²). If only one cation species (C^+) other than H^+ is present, as the pH of the medium is changed, C^+ and H^+ exchange through the reaction:

$$C^+_s + H^+ \rightleftharpoons H^+_s + C^+$$

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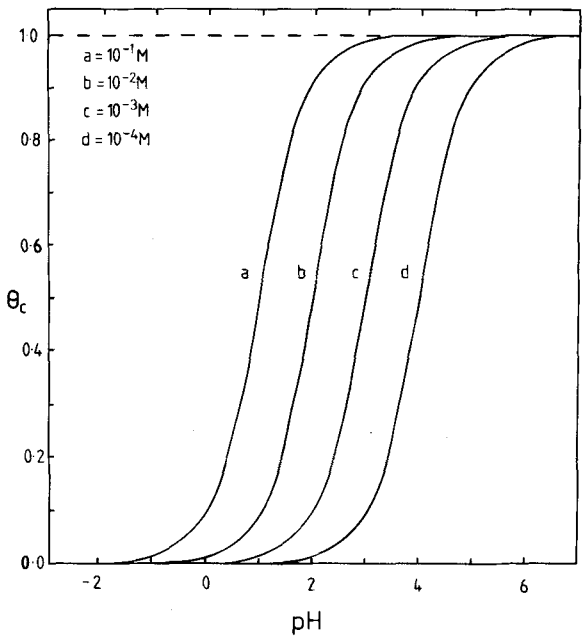


Figure 1. Model curves describing the fractional exchange, θ_c, between C^+ and H^+ balancing a pH-independent charge on a kaolinite surface in aqueous suspension when the surface charge has no selectivity for H^+ or C^+. a, b, c, and d are model curves for different concentrations of C^+ as a function of pH.

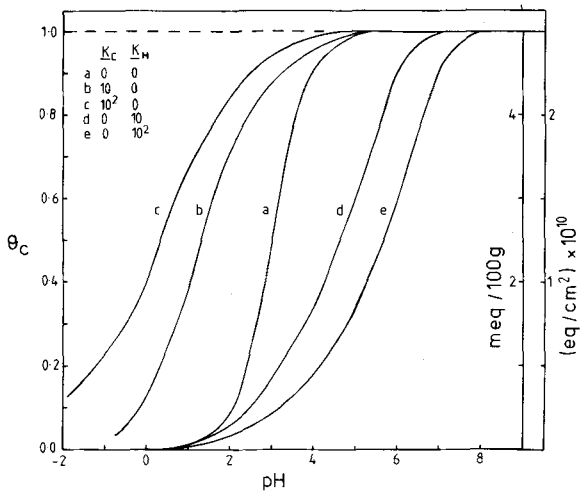


Figure 2. Model curves describing the competition between C^+ and H^+ balancing the pH-independent negative charge on the surface of kaolinite in aqueous suspension when the surface had different selectivities for H^+ and C^+. The concentration of C^+ is 10^{-3} M; the surface area of the kaolinite is put at 20 m²/g; and the surface charge is put at 5 meq/100 g. K_C and K_H are the binding constants for C^+ and H^+, respectively (liter/mole).

where C^+_s and H^+_s are the cations balancing the cation substitution charge of the clay, and C^+ and H^+ are the cations in bulk solution. In all of the following discussions, it is assumed that the solution to clay ratio is so large that there is no detectable pH change as a result of the removal of H^+ from the exchange complex. The fraction of charged sites balanced by C^+ in competition with H^+ (θ_c) in dilute clay suspensions is given by:

$$\theta_c = C_c/(C_c + C_H) \qquad (2)$$

where C_c and C_H are the concentrations of C^+ and H^+ in solution at equilibrium. In this situation all counterions, i.e., C^+_s and H^+_s, will be in the diffuse layer. The base saturation, θ_c, is plotted in Figure 1 for four concentrations of C^+ (curves a, b, c, and d). Because neither C^+ nor H^+ is selectively adsorbed, the four curves are symmetrical and displaced from one another by one pH unit for every ten-fold change in C_c. C^+ and H^+ are present on the clay in direct proportion to their relative concentrations in solution.

Model with selectivity

In this model, on general surface-chemistry grounds, negative charge due to cation substitution on kaolinite is expected to display different selectivities for different countercations, e.g., Na^+, K^+, or Cs^+. Again, only charge due to cation substitution in the lattice is assumed to be present on the kaolinite surface. C^+ is given a binding constant K_c so that surface potential cannot be assumed to be constant and independent of the relative concentrations of the adsorbed cations. The first plane of the diffuse layer (called the inner plane) is defined as the plane that contains the selected ion. This is an oversimplification because there are undoubtedly many different planes of adsorption. C^+ can exist in the inner plane and in the diffuse layer, whilst H^+ can only exist in the diffuse layer. The charge density on the inner plane ($\sigma_{I.P.}$) can be described by a Langmuir-Stern equation:

$$\sigma_{I.P.} = \frac{K_c N_s C_c \exp - (\psi_d ZF/RT)}{1 + K_c C_c \exp - (\psi_d ZF/RT)} \qquad (3)$$

where K_c is the binding constant or selectivity of the surface for cation C^+; ψ_d is the potential in the inner plane, assumed to be the first plane of the diffuse layer; F/RT has its usual physico-chemical meaning; and Z is the valency, including sign, of C^+ which is unity in this case. σ_d is given by Gouy-Chapman theory by:

$$\sigma_d = -1.22 \times 10^{-10}(C_c + C_H)^{\frac{1}{2}} \sinh(0.0195|Z|\psi_d) \qquad (4)$$

where ψ_d is in millivolts and C in mole/liter. Electrical neutrality requires that:

$$-\sigma_p = (\sigma_{I.P.} + \sigma_d) \qquad (5)$$

The total C^+ adsorbed for a given pH value is given by:

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$$\text{Total } C^+ \text{ Bound} = \sigma_{\text{I.P.}} + (\sigma_{\text{Diffuse}} \times C_c)/(C_c + C_H) \quad (6)$$

$$\text{and} \quad \theta_c = (\text{Total } C^+ \text{ Bound})/N_s \quad (7)$$

Test values of K_c = 10 and 100 liter/mole were arbitrarily used to obtain Figure 2. Arbitrary values were assigned to ψ_d in Eq. (3) and $\sigma_{\text{I.P.}}$ evaluated. σ_d was then derived from Eq. (5), C_H from Eq. (4), and θ_c from Eqs. (6) and (7). The results are presented in Figure 2.

At sufficiently high pH values the surface will be effectively uncharged for all finite values of K_c because C^+ will be situated in the inner plane balancing the whole surface charge. As the pH is lowered, the surface will become charged due to the exchange of C^+ for H^+ and because H^+ can exist only in the diffuse layer in this model. The increasing development of the diffuse layer potential (ψ_d) makes it increasingly difficult to remove C^+ from the surface, resulting in a broadening of the curves at low pH values. As the value of K_c increases, a lower pH is required to replace C^+ by H^+ and hence the displacement of the curves along the pH scale. At high pH all curves converge because ψ_d tends to zero.

The other extreme model to be examined gives a finite binding constant ($K_H > 0$) to H^+ (K_H) so that H^+ adsorbs in both the inner plane and the diffuse layer, while C^+ adsorbs only in the diffuse layer (viz. K_C = 0). Then:

$$\sigma_{\text{I.P.}} = \frac{K_H N_S C_H \exp - (\psi_d ZF/RT)}{1 + K_H C_H \exp - (\psi_d ZF/RT)} \quad (8)$$

and

$$\sigma_d = -1.22 \times 10^{-10}(C_H + C_C)^{\frac{1}{2}} \sinh(0.0195|Z|\psi_d) \quad (9)$$

To make the mathematics simpler, C_H was omitted in Eq. (9) thus:

$$\sigma_d = -1.22 \times 10^{-10} C_C^{\frac{1}{2}} \sinh(0.0195|Z|\psi_d) \quad (10)$$

The effect of this simplification is to make θ_c lower than it should be below pH 3.5. Test values of K_H = 10 and 100 liter/mole were used, and the other parameters were given the same values as those used in Figure 1. The equations were solved in a similar fashion, and the results plotted in Figure 2 (curves d and e). At sufficiently low pH values the surface will be uncharged for all finite values of K_H because H^+ will be situated in the inner plane balancing charge. All curves, including K_H and K_c equal zero, then coincide because no effect of the charge is discernible. C^+ will exchange with H^+, and a diffuse layer charge will develop because C^+ cannot exist in the inner plane in this model. The development of an increasing diffuse layer potential ψ_d with replacement of the surface H^+ makes it increasingly difficult to remove further H^+ from the surface—hence the broadening of the curves as the pH increases. The higher the value of K_H, the more the curves become displaced along the pH scale because a lower concentration of H^+ relative to C^+ is needed to replace H^+_s by C^+. The similarity of shapes of the curves at high pH values stems from the fact that curves all have about the same charge.

If the values of K_H and K_c are both very large no diffuse layers will develop, and the θ_c vs. pH curves will be identical in shape to Figure 1, although their position on the pH scale will be determined by the ratio K_H/K_c. The real situation will be between the extreme models given here.

pH-DEPENDENT CHARGE

Kaolinite can be considered a combination of two oxides, silica and gibbsite. The surface charge on oxides in aqueous solution in the presence of indifferent ions only (Bowden *et al.*, 1977) is pH dependent because of protonation and deprotonation reactions at exposed oxygen, hydroxyl, or water molecules (Hingston *et al.*, 1972).

In the model now presented, the two separate types of sites due to silica and alumina on kaolinite are neglected and treated as a single oxide. The mathematical complexities of treating this case with two types of site are formidable at the present time and as it will be seen are not necessary for the present purposes of comparison. Some recognition of the influence of silica is made by placing the isoelectric point IEP (Parks, 1967) at pH 3.5. The surface charge on kaolinite is assumed to result only from the adsorption of H^+ and OH^- (potential determining ions or PDIs). The only other ions assumed to be present are indifferent ions which adsorb to balance the excess charge developed by the adsorption of the PDIs.

The surface charge density (σ_s) due to adsorption is given by (Bowden *et al.*, 1977)

$$\sigma_s = \frac{N_s[K_H(C_H)\exp(-F\psi_s/RT) - K_{OH}(C_{OH})\exp(F\psi_s/RT)]}{1 + [K_H(C_H)\exp(-F\psi_s/RT) + K_{OH}(C_{OH})\exp(F\psi_s/RT)]} \quad (11)$$

where C_H and C_{OH} (mole/liter) are the solution concentrations of H^+ and OH^- (activity coefficients assumed to be unity), respectively. K_H K_{OH} are the binding constants of H^+ and OH^-, respectively (liters/mole).

σ_s is also given by:

$$\sigma_s = G(\psi_s - \psi_d) \quad (12)$$

$$G = \epsilon/4\pi d \quad (13)$$

where G is the electrical capacitance of the region between the surface plane of the PDIs and the inner plane, ϵ is the electrical permittivity of this region, and d is the distance between the planes. The expression for σ_d is

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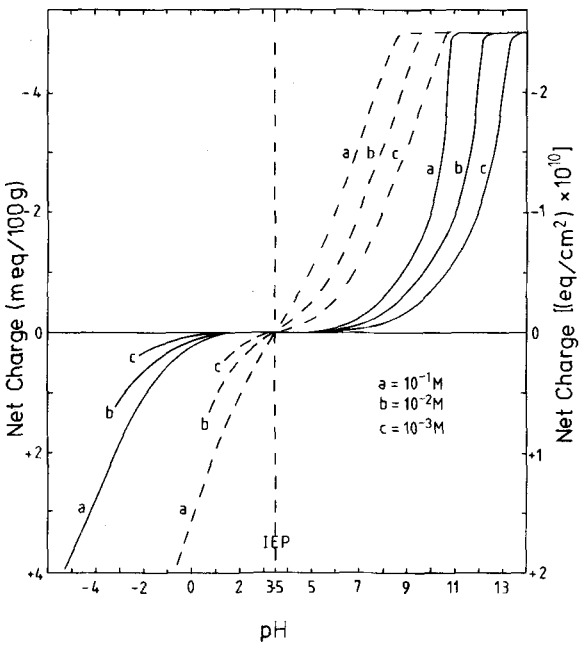


Figure 3. Model net charge curves plotted as a function of pH for three ionic strengths (a, b, and c) for a kaolinite with a pH-dependent charged surface. Solid line = weak electrolyte type sites with $K_H = 10^{-1}$ and $K_{OH} = 10^{6}$; dashed line = strong electrolyte type sites with $K_H = 10^{5}$ and $K_{OH} = 10^{12}$. For both models the surface area of the kaolinite is assumed to be 20 m^2/g; N_s is put equal to 5 meq/100 g; G is 2×10^{-12} eq/mV cm^2; IEP is positioned at pH 3.5.

the same as that used in Eq. (10) above, and for electrical neutrality:

$$\sigma_s + \sigma_d = 0 \tag{14}$$

Values assigned to the various parameters are given in the legend to Figure 3. Values were given to K_H and K_{OH}, various values were assigned to ψ_d and C in Eq. (10), and σ_d was evaluated. Thus, σ_s was calculated from Eq. (14) and then ψ_s from Eq. (12). C_H was then determined from Eq. (11), and σ_s was plotted as a function of pH for different values of C and extreme values of K_H and K_{OH} (Figure 3). Figure 3 shows that K_H and K_{OH} determine the shape of the pH-dependent charge (Bowden *et al.*, 1977). If the surface charge on kaolinite is assumed to be pH dependent, three extreme situations are possible.

(1) When K_H and/or K_{OH} is small, a large proportion of the sites will be in the neutral form near the IEP until the pH is sufficiently far away from the IEP of the surface, whereupon the number of charged sites will increase markedly. The surface sites thus have weak base and/or acid character showing little tendency to gain or lose a proton until extremes of pH. This behavior is given by the charging curves of silica on the alkaline side of the IEP (Tadros and Lyklema, 1968). An example of a model oxide with an IEP at 3.5 for 3 different concentrations of indifferent electrolyte is given in Figure 3 (solid lines).

If kaolinite behaved as an oxide with a very small K_{OH}, it would show little cation adsorption on the alkaline side of pH 3.5 until pH >7. For example, in a 10^{-3} M electrolyte, it would charge over a pH range of 3.5–13 (cf. Figure 1 for a kaolinite possessing only pH-independent charge: in 10^{-3} M electrolyte the clay would adsorb cations over a pH range 0.5–5.5, and have a significant charge above pH 2.0.)

If K_H is zero and K_{OH} is very large, Eq. (11) becomes:

$$\sigma_s = N_s$$

The base saturation curve is then given by Eq. (2) because surface potential does not change with a change in composition if there is no selectivity for one cation over the other. It would thus not be possible to distinguish this situation from those due to cation substitution in the lattice.

(2) When K_H and K_{OH} are very large most of the sites are in the charged form at all pHs, with very few of the neutral sites being present. In this situation two protons are added in effect in one step to each site during titration so that a site passes directly from positive to negative and vice versa. Eq. (11) then becomes:

$$\sigma_s = \frac{N_s[K_H(C_H)\exp(-F\psi_s/RT) - K_{OH}(C_{OH})\exp(F\psi_s/RT)]}{[K_H(C_H)\exp(-F\psi_s/RT) + K_{OH}(C_{OH})\exp(F\psi_s/RT)]} \tag{15}$$

or equivalently,

$$\sigma_s = \frac{N_s[R(C_H)^2\exp(-2F\psi_s/RT) - 1]}{[R(C_H)^2\exp(-2F\psi_s/RT) + 1]} \tag{16}$$

where R is K_H/K_wK_{OH} ($K_w = 10^{-14}$), and the IEP will be given by ½ log R. The sites with these characteristics behave like strong electrolytes and are strong acid/base sites, but their charging curves will be influenced by the changing net charge on the surface affecting the value of ψ_s as it is titrated. The net adsorption curves resulting from an oxide site with large K_H and K_{OH} will thus change over a larger pH range than the corresponding curves for pH-independent charge sites. An example of a model surface possessing only pH-dependent charge with large K_H and K_{OH} is given in Figure 3 (dashed lines). It can be seen that the surface charge develops rapidly as the pH rises above the IEP (3.5). Thus, in 10^{-3} M electrolyte, charging occurs over the pH range 3.5 to 11. Compare this to the 10^{-3} M curve in Figure 1 for a surface possessing only pH-independent charge where the cation adsorption range is pH 0.5 to 5.5 and the weak acid and base site described under (1) above where the range is 3.5 to 13 (Figure 3).

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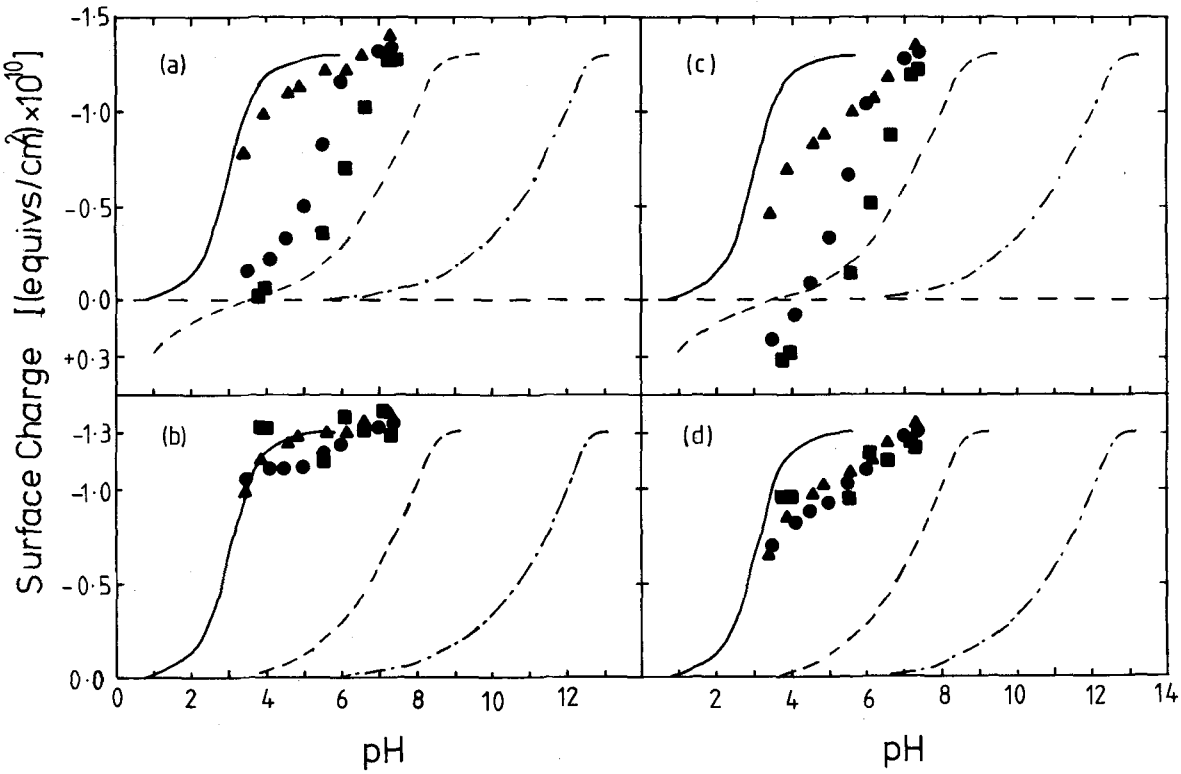


Figure 4. Comparison of model curves for negative and net surface charge with data for Cornish clay. Solid line = exchange between C^+ and H^+ balancing a pH-independent charge on a kaolinite surface when $C^+ = 10^{-3}$ M and $N_s = 1.3 \times 10^{-10}$ eq/cm²; dashed line = net charge for a strong electrolyte type site when ionic strength is 10^{-3} M; $K_H = 10^5$, and $K_{OH} = 10^{12}$ liter/mole; $N_s = 1.3 \times 10^{-10}$ eq/cm²; $G = 2 \times 10^{-12}$ eq/mV cm²; IEP positioned at pH 3.5; dot–dashed line = model net charge curve for a weak electrolyte type site when the ionic strength is 10^{-3} M; $K_H = 10^{-1}$ and $K_{OH} = 10^6$ liter/mole; $N_s = 1.3 \times 10^{-10}$ eq/cm²; $G = 2 \times 10^{-12}$ eq/mV cm²; IEP positioned at pH 3.5. The experimental points are negative, and the net charge was measured on the Cornish clay as a function of the pH of the 4th equilibration solution when the clay was equilibrated with either 10^{-3} M $NaNO_3$ or KNO_3 and extracted with 0.1 M $BaCl_2$ (pH 3) at 0°C, as described by Bolland *et al.* (1976). Solid:solution ratio 0.5 g in 10 ml. ▲ = 4 hour equilibration at 0°C with 10^{-3} M $NaNO_3$; ● = 48 hour equilibration at 20°–25°C with 10^{-3} M KNO_3; ■ = 48 hour equilibration at 20°–25°C with 10^{-3} M $NaNO_3$; (a) Na^+ or K^+ adsorption; (b) ($Na^+ + Al^{3+}$) or ($K^+ + Al^{3+}$) adsorption; (c) ($Na^+ + NO_3^-$) or ($K^+ - NO_3^-$) adsorption; (d) [($Na^+ + Al^{3+}$) $- NO_3^-$[or [($K^+ + Al^{3+}$) $- NO_3^+$] adsorption.

EVIDENCE FOR pH-INDEPENDENT CHARGES ON KAOLINITES

Bolland *et al.* (1976) measured the positive, negative, and net surface charge of several natural kaolinites as a function of the pH and ionic strength of the IR aqueous suspensions, using different index cations and periods of equilibration. The negative surface charge and net charge as measured by exchangeable K^+ and Na^+ were found to be pH dependent in the pH range 3.5–7.0 when the equilibration period was greater than 4 hr. However, when the equilibration period was short and temperatures low (4 hr at 0°C) the amount of exchangeable Al and dissolution of Al from the kaolinites was found to be small, and the negative charge was largely independent of pH in the range 3.5 to about 8.5 (Bolland, 1975; Bolland *et al.*, 1976). A similar result is obtained when due allowance is made for exchangeable Al release under other conditions (Bolland, 1975; Bolland *et al.*, 1976). In Figure 4, the negative and net surface charge measured on Cornish kaolinite clay are compared to model curves presented in this paper. Some properties of the clay have been given previously, together with the experimental procedures used to measure the surface charge (Bolland *et al.*, 1976). The results presented here for the Cornish clay have hitherto not been published, and are similar to those obtained for the other kaolinites studied (Bolland, 1975). In Figure 4a, the negative charge as measured by adsorption of either Na^+ or K^+ is compared to the model curves. When the equilibration time was 48 hr, as measured by Na^+ or K^+ adsorption, the negative surface charge more closely resembles the model charge curve for amphoteric, strong electrolyte, oxide surface-sites (dashed curve in Figure 4a). However, when the equilibration procedure was done at 0°C for 4 hr, as measured by Na^+ adsorption, the negative charge on

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the clay more closely resembles the solid curve in Figure 4a for charge due to cation substitution. In Figure 4b the exchangeable Al is added to the index cation to calculate the negative surface charge as described by Bolland *et al.* (1976). In all three cases the experimental data more closely resemble the solid curve in Figure 4b for charge due to cation substitution than the others. The negative surface charge on the kaolinites studied are thus concluded to be largely pH independent and likely to be due to cation substitution.

In Figure 4c the net surface charge measured on the kaolinite (obtained by subtracting NO_3^- adsorption from either Na^+ or K^+ adsorption) are compared to the model curves. When the equilibration period was long, the experimental points for the net charge resemble the model curve for strong electrolyte oxide type sites (dashed line in Figure 4c). In the case of the shorter equilibration at low temperatures, though the experimental data more closely resemble the model curve for isomorphous substitution (solid curve in Figure 4c), the experimental data show some pH dependency. This is because the positive charge on the kaolinite surfaces was pH dependent, increasing with decreasing pH values and increasing ionic strength of the aqueous medium (Bolland, 1975; Bolland *et al.*, 1976). Thus, as the pH of the aqueous kaolinite suspension decreases, though the negative charge may be constant, the positive charge increases, and the resultant net charge curve tends to become pH dependent and decreases with pH.

CONCLUSIONS

A comparison of the variation of surface charge as a function of pH with studies of the charge of several natural kaolinites reported here and elsewhere (Bolland *et al.*, 1976) in the pH range 3.5 to about 8.5 suggests the charge is likely due to cation substitution in the lattice.

Unless due consideration is given to Al dissolution, the negative surface charge on the kaolinites can be mistakenly attributed to a pH-dependent, oxide-like charge on the kaolinite surface. The amount of Al that balances negative surface charge is minimized by equilibrating as rapidly as possible at low temperatures and by using Cs^+ as the index cation (Bolland, 1975), thus minimizing the problem of assigning charge to the Al that balances the negative surface charge.

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Резюме—Модельные кривые катионного обмена представлены для идеалиризированной каолинитовой поверхности, когда заряд на поверхности (1) вызывается катионной подстановкой в структуре и в этом случае является pH независимым; и (2) получен в результате реакции протонации/депротонации окисо-подобных узлов, и тогда зависит от силы кислоты и основания поверхностных узлов, а также от ионной силы. Рассматриваются pH независимые случаи: первый, когда обменные ионы не имеют селективности по отношению к поверхности и все они находятся в диффузионном слое; и другой, когда имеется селективность для одного иона и когда этот ион находится частично в слое Лангумира-Стерна и частично в диффузионном слое. Эсли один из обменивающихся ионов является протоном, тогда форма кривых и их место на pH шкале зависит от ионной силы и ионной селективности.

Модельные кривые сравниваются с данными для натуральных каолинитов. В предварительных условиях обменный Al освобождается из структуры и зарядовые кривые становятся похожими по форме на кривые, которые имеются для окисо-подобной поверхности. Однако, если титрование проводится быстро или берется во внимание присутствие Al, кривые протоновой связи являются похожими по форме на те, которые ожидаются для узлов, получаемых путем катионной подстановки в структуре каолинита или поблизости или на гране кристалла. [E.C.]

Resümee—Es wurden Modelle von Kationenaustauschkurven für eine idealisierte Kaolinitoberfläche dargestellt, wobei die Beladung an der Oberfläche (1) von der Kationensubstitution in der Struktur herrührt, daher pH-unabhängig ist und (2) durch Protonierungs/Deprotonierungs-Reaktionen der Oxid-artigen Seiten hervorgerufen wird. Sie hängt daher von der Säure- und Basenstärke der Oberflächen sowie von der Ionenstärke ab. Zwei pH-unabhängige Situationen werden betrachtet: Bei einer haben die austauschenden Ionen keine Selektivität gegenüber der Oberfläche und sind alle in einer diffusen Lage angeordnet. Bei der anderen Situation existiert eine Selektivität für ein Ion, wobei dieses Ion zum Teil in einer Langmuir-Stern-Lage und z.T. in der diffusen Lage angeordnet ist. Wenn eines der austauschenden Ionen ein Proton ist, hängt die Kurvenform und ihre Lage auf der pH-Skala von der Ionenstärke und der Ionenselektivität ab.

Die Modellkurven werden mit Daten für reale Kaolinite vergleichen. Unter den meisten Bedingungen wird austauschbares Al aus der Struktur entfernt, und die Form der Beladungskurven wird ähnlich der einer Oxid-ähnlichen Oberfläche. Titriert man jedoch schnell oder berücksichtigt man das Vorhandensein von Al, dann sind die Protonenbindungskurven in der Form ähnlich jenen, die man für Lagen erwartet, die bei der Kationensubstitution in der Struktur von Kaolinit entweder in der Nähe der Oberfläche oder an den Kanten des Kristalls entstehen. [U.W.]

Résumé—Des courbes types d'échange de cations sont presentées pour une surface de kaolinite idealisée où la charge sur la surface (1) doit son origine à une substitution de cations dans la structure et par conséquent est indépendante du pH; et (2) est produite par les réactions de protonation/déprotonation des sites semblables aux oxides, et par conséquent, dépend des forces acides et de base sur les sites de surface, ainsi que de la force ionique. Deux situations indépendantes du pH sont considerées: l'une où les ions échangeants n'ont pas de sélectivité pour la surface et sont tous dans la couche diffuse; et l'une où la sélectivité existe pour un ion et où cet ion est partiellement dans une couche Langmuir-Stern et partiellement dans la couche diffuse. Si l'un des ions échangeants est un proton, la forme des courbes et leur position sur l'echelle de pH dépendent de la force ionique et de la sélectivité ionique.

Les courbes types sont comparées aux données pour des kaolinites reels. Sous la plupart des conditions, Al échangeable est relaché de la structure, et la forme des courbes de charges devient semblable à celle d'une surface semblable aux oxides. Si, cependant, la titration est faite rapidement, ou si l'on tient compte de la présence d'Al, les courbes de liaison de protons ont une forme semblable à celle à laquelle on s'attend pour des sites résultant de substitution de cations dans la structure de kaolinite, soit près de la surface, soit au bord du crystal. [D.J.]

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