Clays and Clay Minerals, Vol. 32, No. 2, 131–138, 1984.

SURFACE POTENTIALS DERIVED FROM CO-ION EXCLUSION MEASUREMENTS ON HOMOIONIC MONTMORILLONITE AND ILLITE

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Abstract—Simple equations are presented which allow double-layer potentials of clays to be derived from co-ion exclusion measurements in monovalent and divalent electrolyte solutions. These equations have been used to re-interpret earlier results for illite and montmorillonite. The potentials derived follow the lyotropic series for the various homoionic modification of each clay. We have demonstrated that the Schofield equation, which assumes high double-layer potentials, cannot be applied to co-ion exclusion in clay systems. Re-analysis of earlier measurements has shown that for a given homoionic clay the potentials are almost independent of concentration over the range 0.3 to 0.003 molar. Thus, clay surfaces appear to behave more like constant-potential than constant-charge surfaces.

Key Words—Co-ion exclusion, Double-layer potential, Illite, Montmorillonite, Surface charge.

INTRODUCTION

Edwards and Quirk (1962, 1965a, 1965b, 1965c) presented information on co-ion (chloride) exclusion from negatively charged, well-characterized homoionic clays in the presence of alkali and alkaline earth counterions. Because illite is a nonexpanding, mica-like phyllosilicate, only an external double layer around the platelet can contribute to co-ion exclusion. On the other hand, montmorillonite is an expanding phyllosilicate in alkali metal ion solutions and hence exhibits a very large surface area corresponding to 10-Å thick, elementary silicate sheets. Surface area determinations by nitrogen adsorption for montmorillonite give a gross underestimate of the area exposed to solution, whereas for the illite clays the areas should be similar. In this paper equations are presented that permit double layer potentials for the clay-solution interface to be calculated from negative adsorption (co-ion exclusion) results, provided the area of the interface is known. Using these equations, previously reported experimental results on ion-exclusion from clay minerals have been re-analyzed to determine their surface potentials in a range of electrolyte solutions.

THEORETICAL BACKGROUND

The number (N) of negative ions (chloride) excluded per unit area of negatively charged surface is given by:

$$N = \int_0^\infty [C(R) - C(x)]\, dx, \qquad (1)$$

where C(R) is the reservoir chloride concentration and C(x) is the corresponding concentration at a distance x from the flat charged surface. Using the Boltzmann distribution the concentration of negative ions at x is related to the mean electrostatic potential, $\psi(x) < 0$, at the same point by $C(x) = C(R)\exp\{q\psi(x)/kT\}$. N can be converted to the equivalent volume per gram of clay (V^{ex}) from which chloride ions are completely excluded (for a diagrammatic explanation, see Figure 1); thus,

$$V^{ex} = \frac{N}{C(R)} \cdot A = A\int_0^\infty \left[1 - \exp\left\{\frac{q\psi(x)}{kT}\right\}\right] dx, \qquad (2)$$

where A is the solid-solution interfacial area per gram of clay. Eq. (2) is a general relation for an electrolyte containing monovalent anions which are excluded from a negative surface.

To determine the integral in Eq. (2) for monovalent electrolytes the Gouy-Chapman theory for the potential distribution can be used. Rearrangement of Eq. (2) gives:

$$V^{ex} = A\int_{y=y_d}^{y=0} (1 - e^y)\left(\frac{dx}{dy}\right) dy, \qquad (3)$$

where $y = q\psi(x)/kT$ and y_d is the corresponding value at the Stern layer surface, from which the diffuse double layer originates. Using the general Poisson-Boltzmann equation,

$$\frac{d^2\psi(x)}{dX^2} = -\frac{4\pi q}{\epsilon}\Sigma_i C_i^B z_i \cdot \exp(-qz_i\psi(x)/kT), \qquad (4)$$

the value of dy/dx that is required for solution of Eq.

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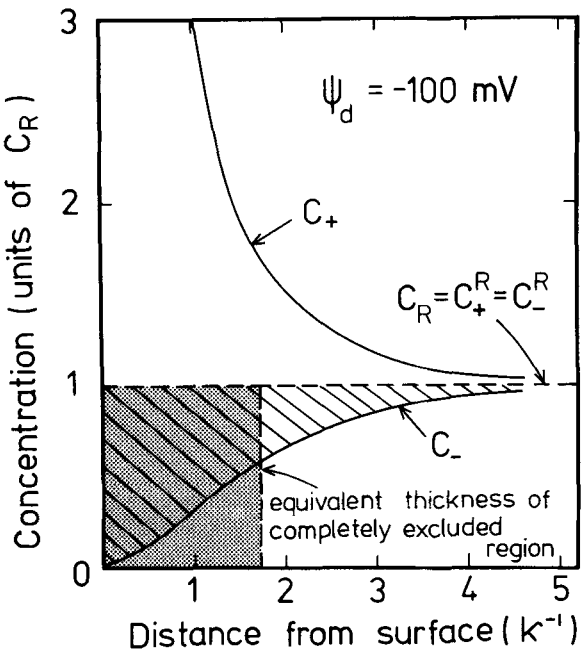

Figure 1. Concentrations of positively charged counterions C_+ and negatively charged co-ions C_- as a function of distance from a planar surface of double layer potential −100 mV. The dashed area corresponds to the total deficit of co-ions near the surface compared with the bulk concentration and is equivalent to a layer of thickness $1.7\kappa^{-1}$ from which the ions are completely excluded (shaded area). This layer thickness multiplied by the area per gram of surface gives the volume excluded per gram of material V^{ex}. C_R is the reservoir concentration.

(3) can easily be obtained. For a monovalent electrolyte,

$$dy/dx = +\sqrt{2}\kappa(\cosh y - 1)^{1/2}, \qquad (5)$$

where

$$\kappa = \left\{\frac{4\pi q^2}{\epsilon kT}\Sigma_i C_i^R z_i^2\right\}^{1/2} \qquad (6)$$

is the inverse Debye length.

Thus, by combining Eqs. (3) and (5),

$$V^{ex} = -\frac{A}{\kappa}\int_{y_d}^{0}\left[\frac{(1 - e^y)}{2\sinh(y/2)}\right]dy \qquad (7)$$

which can now be integrated to give

$$V^{ex} = (2A/\kappa)(1 - e^{y_d/2}), \qquad y_d < 0, \qquad (8)$$

from which, knowing the area of the interface and the volume of exclusion, the double layer potential ($\psi_d = y_d kt/q$) can be obtained for a given concentration of monovalent electrolyte. A similar derivation for divalent electrolytes gives:

$$V^{ex} = \frac{A\sqrt{3}}{\kappa}\left[\sqrt{3} - (1 + 2e^{y_d/2})^{1/2}\right]. \qquad (9)$$

Table 1. Surface potentials obtained from chloride exclusion measurements on illite clays for a range of monovalent cations as counterions.

Ion	$A_M{}^1 = V^{ex}\kappa/2$	$A_M/A_{N_2} = 1 - \exp(y_d/2)$	ψ_d (mV)
Li	80	0.73	−65
Na	70	0.64	−51
K	35	0.32	−19
NH_4	22	0.20	−11
Rb	10	0.091	−5
Cs	0	—	0

[1] A_M is the slope of the line obtained by plotting V^{ex} against $2/\kappa$ (see Figure 2) and corresponds to the area of the solid-solution interface *only* for very high diffuse layer potential. For low potentials (<200 mV) the ratio of A_M to the true area of the solid (e.g., the N_2 adsorption area, A_{N_2}) gives the double-layer potential via the relationship: $A_M/A_{N_2} = 1 - \exp(y_d/2)$. The true surface area A_{N_2} is the B.E.T. surface area derived from the nitrogen adsorption isotherm. A value of 110 m^2/g has been used here, although the values determined by Edwards and Quirk (1965a) vary slightly from this value (±5) for the different ions.

It should be mentioned here that Grahame (1947) derived a relationship for the fraction of the double-layer charge accounted for by each ion in monovalent electrolyte from which the excluded volume can be calculated.

ANALYSIS OF CO-ION EXCLUSION MEASUREMENTS ON CLAY MINERALS

From Eq. (8) it follows that the excluded volume of chloride ions will depend upon the area exposed, the electrolyte concentration, and the double-layer potential. In earlier applications of this equation to a variety of systems it was assumed that the double layer potential is very large and negative. Under these conditions Eq. (8) becomes

$$V^{ex} = 2A/\kappa. \qquad (10)$$

Table 2. Surface potentials obtained from chloride exclusion measurements on montmorillonite clays for a range of monovalent cations as counterions.

Ion	$A_M{}^1 = V^{ex}\kappa/2$	$A_M/A_C = 1 - \exp(y_d/2)$	ψ_d (mV)
Li	625	0.83	−90
Na	560	0.75	−69
K	436	0.58	−44
NH_4	256	0.34	−21
Cs	156	0.21	−12

[1] A_M is the slope of the line obtained by plotting V^{ex} against $2/\kappa$ (see Figure 2). The ratio of this value to the exposed solid-solution interface A_C gives the diffuse layer potential via the relation: $A_M/A_C = 1 - \exp(y_d/2)$. A_C has a value of 750 m^2/g, calculated from the unit-cell weight and a and b crystallographic parameters for montmorillonite dispersed into its elementary silicate sheets with approximate dimensions of 2000 × 2000 × 10 Å. On drying, the elementary sheets condense and prevent the accurate determination of surface area from nitrogen adsorption.

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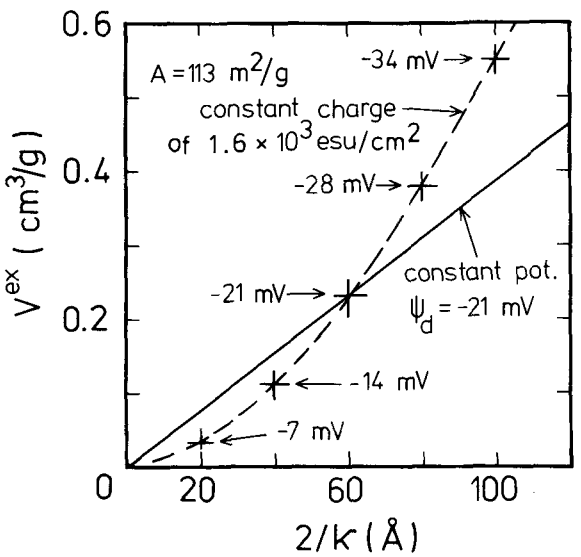

Figure 2. Volume exclusion V^{ex} of monovalent negative ions as a function of electrolyte concentration (as $2\kappa^{-1}$) for the case of constant low potential −21 mV and the corresponding case of constant charge (fitted at $2\kappa^{-1}$ = 60 Å). The linear curve corresponds to that experimentally observed by Edwards and Quirk (1965a) for K-illite. The variation in potential for the constant charge case, which is expected for a simple ion-exchange surface, is also shown. The discrepency between the two cases is quite marked for low potentials (cf. Figure 3).

Thus, a plot of V^{ex} against $2/\kappa$ will yield a straight line with the interfacial area as the slope. It now seems clear that for clay minerals the double-layer potentials are not large; in fact, electrophoretic mobility measurements on montmorillonite (Callaghan and Ottewill, 1974) and potentials obtained from double-layer interactions between muscovite mica (Pashley, 1981) indicate that clay systems typically have surface potentials less than 100 mV. For this range of surface potentials Eq. (10) is not valid and Eq. (8) must be used. As mentioned above, illite has an interfacial area in solution which will be close to the nitrogen adsorption value, whereas montmorillonite is completely expandable, and the area can be calculated from crystallographic parameters. Thus, in both cases the interfacial area, A, is known, and, hence, surface potentials from co-ion exclusion measurements can be obtained. Volume exclusion results for an illite and a montmorillonite clay were presented by Edwards and Quirk (1965a, 1965b) who found that for both clays, V^{ex} was a linear function of $2/\kappa$. From Eq. (8) it is clear that this relationship exists only if the diffuse layer potential does not vary with concentration. The calculated potentials, using the linear slopes given by Edwards and Quirk (1965a, 1965b) for the illite and montmorillonite samples are given in Tables 1 and 2 for a range of monovalent counterions.

The surface potentials obtained for different cations at a fixed concentration are consistent with an ion-binding or ion-exchange model of the clay-solution interface; i.e., the less hydrated cations have higher adsorption densities on the clay surface and give rise to a potential of lower magnitude because the negative sites on the silicate surface are neutralized by cation adsorption. Note that the net diffuse layer charge has been assumed to be given by the sum of the negative lattice charge of the clay and the density of adsorbed cations. The diffuse double layer (Gouy layer) is considered to begin from a plane just outside the layer of adsorbed ions (Stern layer) with a diffuse double-layer potential ψ_d. The surface potentials of montmorillonite are consistently greater than those of illite.

That the apparent potentials of the clay systems are all more or less independent of electrolyte concentration is unexpected; indeed, for an ion-exchange surface the magnitude of the surface potential should fall rapidly, with an increase in bulk concentration of ions that can adsorb into the Stern layer. For most clays a wide range of cations can be adsorbed or ion exchanged onto the exposed basal plane. Ion adsorption should occur according to the surface reaction (see Healy and White, 1978)

$$S^- + M^+ \rightleftharpoons SM,$$

with dissociation constant,

$$K_M = [S^-][M^+]_s/[SM]. \qquad (11)$$

$[S^-]$ and $[SM]$ are the dissociated and filled surface site densities, respectively, and $[M^+]_s$ is the concentration of M^+ ions in solution immediately adjacent to the clay surface which is given by the Boltzmann relation:

$$[M^+]_s = [M^+]_B e^{-q\psi_d RT}, \qquad (\psi_d < 0), \qquad (12)$$

where $[M^+]_B$ is the bulk concentration of M^+ ions. This simple ion-exchange model predicts that the double-layer charge should remain roughly constant and that the potential must therefore fall rapidly with increase in concentration of the adsorbing ion. A comparison of the constant charge and potential cases is shown in Figures 2 and 3. For a low potential (e.g., K-illite) the difference is marked, whereas at higher potentials (e.g., Na-montmorillonite) the nonlinear constant charge curve is close to the constant potential result. Low potential measurements have a larger error because of the much lower volume excluded; the difference between the constant charge and potential results may be somewhat difficult to ascertain. Because the original data of Edwards and Quirk were presented as linear curves we have re-analyzed the results in terms of a constant potential. It must be realized, however, that to obtain an exactly linear relation, cations adsorbed at the clay surface must desorb as the bulk concentration increases, a situation which does not conform with existing models of ion-exchange adsorption into the

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Stern layer. That this is the case can be seen from the relation between diffuse layer charge σ_d and potential ψ_d, derived using Gouy-Chapman theory:

$$\sigma_d = -\frac{\epsilon kT}{2\pi zq}\kappa \sinh[y_d/2]. \quad (13)$$

Clearly, if the diffuse layer potential is held constant the charge must increase with increase in electrolyte concentration and hence cations must de-sorb from the Stern layer.

Co-ion exclusion measurements on Ca-illite clay (Edwards and Quirk, 1965c) also show a linear relationship consistent with a constant surface potential over a concentration range of about 0.001 M to 0.3 M. These results can be analyzed using Eq. (9). The potentials obtained from these results are low, about −10 mV for Ca, presumably due to the greater electrostatic attraction of divalent counterions to the negatively charged clay surface. The observation that the apparent potential is again independent of electrolyte concentration presents similar problems of interpretation.

The observation of constant potential suggests that the experimental procedures used in determining co-ion exclusion volumes on powdered clay minerals should be re-examined. For a correct interpretation, of the experimental observations, the double layers around each clay platelet must not significantly overlap. Because of the importance of this assumption, it is necessary to discuss to what extent the co-ion exclusion measurements could possibly be affected by particle interaction or even particle *condensation* into a primary minimum.

PARTICLE INTERACTION

Edwards and Quirk (1965a) demonstrated that for Li- and Cs-illite suspensions, the average particle separations for concentrations between 0.5 M and 0.003 M are at least an order of magnitude greater than κ^{-1}, the Debye-Huckel characteristic length, and that at these distances the effects of interaction on co-ion exclusion can be neglected. The average particle separation was given by twice the "film thickness" obtained by dividing the volume of entrained solution by the nitrogen surface area. For Na-montmorillonite prepared in a manner similar to that used by Edwards and Quirk (1965b) for co-ion exclusion measurements but with the addition of Calgon (to preclude the possibility of positive sites), Norrish and Rausell-Colom (1963) obtained the following empirical relationship, using X-ray powder diffraction:

$$d = 21.2C^{-1/2} + 21 \quad \text{and}$$
$$d = 7\kappa^{-1} + 21, \quad (14)$$

where d is the "average" distance in Å (κ^{-1} in Å) between montmorillonite sheets. This value is, in fact, the distance of the first maximum in the plot of W(R), the probability of finding a sheet at a distance R from any one sheet, vs. distance R. C is the concentration of monovalent electrolyte in mole/liter. Norrish (1954) noted that for high concentrations when the distribution is relatively sharp, the value of d probably represents the average and most stable position of one sheet relative to another. For more dilute solutions, he noted that considerable error exists in determining the position or distance of the maximum, and therefore doubted whether the maximum represents either the average or the most stable interlayer spacing. Thus, the plate separation should depend on the history of the material.

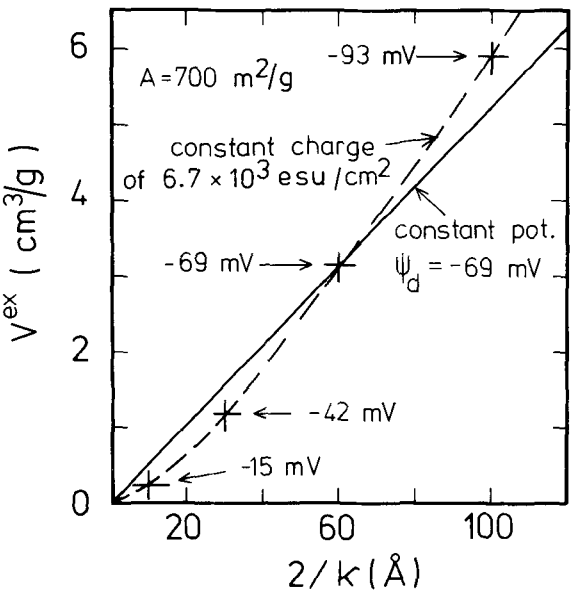

Figure 3. Volume exclusion V^{ex} of monovalent negative ions as a function of electrolyte concentration (as $2\kappa^{-1}$) for the case of constant potential (−69 mV) and the corresponding case of constant charge (fitted at $2\kappa^{-1}$ = 60 Å). The linear curve corresponds to that experimentally observed by Edwards and Quirk (1965b) for Na-montmorillonite. The constant charge curve is expected from the single ion-exchange model of the clay surface. The difference between the two cases is not large for reasonably high potentials (cf. Figure 2).

Norrish's (1954) results on K-montmorillonite are relevant in that when the montmorillonite was expanded with dilute solutions of NaCl and then replaced with KCl, spacings similar to those of Na-montmorillonite were obtained. Montmorillonite in 0.2 M KCl and NH_4Cl gave large spacings together with 15-Å spacings. In lower concentrations of KCl and NH_4Cl, montmorillonite gave large spacings only. Edwards and Quirk (1965b) reported that the "average particle separation" for K- and NH_4-montmorillonite is greater than $8\kappa^{-1}$.

Given the circumstances outlined above, the Li-, Na-, K-, and NH_4-montmorillonites of Edwards and Quirk (1965b) most likely existed in suspension as elementary

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silicate sheets or if aligned were separated by distances approaching $8\kappa^{-1}$; hence, from the point of view of chloride exclusion the particles can be regarded as weakly interacting clay sheets.

This conclusion is reinforced by examination of the experimental details of the work reported by Edwards and Quirk. Norrish and Rausell-Colom (1963) worked with oriented flakes which had been dried prior to wetting. The oriented flakes have a high degree of order as indicated by a nitrogen surface area of 5 m^2/g reported by Greene-Kelly (1964) as compared with values of 40–50 m^2/g for dried powders obtained by Aylmore and Quirk (1962). Norrish and Rausell-Colom referred to friction or "internal" load within the gel restricting swelling. By contrast Edwards and Quirk's starting material was powdered Wyoming bentonite (Na^+ being the dominant ion) which was dispersed in distilled water. After particles $>2\ \mu m$ equivalent spherical diameter were separated, the clay was converted into various ionic forms by washing with 1 M or 0.1 M chloride solutions, and the excess salt was them removed by dialysis. The clay was *never dried,* and the electrolyte was added to the suspension in varying amounts for negative adsorption measurements.

Edwards and Quirk's results (1962) for Na-montmorillonite were obtained by separating the clay (3% suspension) from the equilibrium solution by dialysis. The slope obtained from co-ion exclusion measurements of 560 m^2/g agrees closely with those of Bolt and Wakentin (1958) (see Figure 1, Edwards and Quirk, 1962). Recently, Schramm and Kwak (1982), using a dialysis technique and a 2% clay suspension of Belle Fourche montmorillonite, found a slope of their co-ion exclusion plot of 570 m^2/g.

PARTICLE CONDENSATION

We now consider whether particle condensation into a primary minimum has influenced the reported co-ion exclusion results. Cebula *et al.* (1978) examined 1% suspensions of homoionic montmorillonites using neutron diffraction. For Li-montmorillonite they reported that the particle thickness, H, is 10.3 Å, indicating that the Li-montmorillonite system is dispersed to give elementary silicate sheets. By contrast, as the counter ion was changed to Na, through K to Cs, a marked change in the small angle scattering pattern took place. They concluded that the upper limit for the particle thickness of Cs-montmorillonite is 40 Å. Such measurements have some limitations, however, it seems reasonable to conclude that Cs-montmorillonite in the suspensions of Cebula *et al.* (1978) consisted of particles or quasi-crystals (Aylmore and Quirk, 1971) which were three elementary silicate layers thick.

Fitzsimmons *et al.* (1970) were able to prepare Ca-montmorillonite in elementary silicate sheets; however, the system was metastable, and even in the absence of electrolyte the plates, with shaking, condensed to form quasi-crystals 50 Å thick, or thicker, depending on the method of treatment of the original suspension following the preparation of the single plate material. This condensation gave a material with internal and exteral surfaces; the internal surface was limited in its expansion to give a d(001) of 19 Å. Sodium and other monovalent ion clays did not behave in this manner except when dried, although it is expected that Cs-montmorillonite would behave similarly to Ca-montmorillonite and therefore have a strong tendency to condense into a primary minimum.

Some parallel condensation of the Ca-illite particles to form domains may exist (Aylmore and Quirk, 1962). This phenomenon is unlikely even for Cs-illite inasmuch as Greene *et al.* (1978) were not able to obtain evidence for domain formation in Ca-illite suspensions. It thus appears that pre-drying of these clays is necessary for domain formation. Furthermore, it should be emphasised that unlike the 10-Å elementary sheets of montmorillonites, the plate-shaped illite crystals will average about 70 Å thick and have irregular or stepped surfaces.

Condensation should remove the internal area from co-ion exclusion and an effect that should increase with electrolyte concentration. Under these conditions one would expect from Eq. (8) an even more nonlinear relationship between V^{ex} and κ^{-1}. Hence, it is evident that condensation into a primary minimum cannot be invoked to explain the observed linear behavior or the decreased magnitude of the slopes of co-ion exclusion plots with increasing ion size in the alkali metal series.

DISCUSSION

Schofield's (1947) equation for co-ion exclusion provides a basis for obtaining the surface area of a material over a range of concentrations when the surface potential is high ($\geq$200 mV). For lower potentials the slope of the co-ion exclusion plot (V^{ex} vs. $1/\kappa$), which has the dimensions of an area per unit mass, is less than the actual surface area of the material. It has been shown here (Eq. (8)) that provided the surface area of the clay is known the ratio of the slope of the co-ion exclusion plot to the actual surface area provides a basis for obtaining the diffuse double-layer potential, i.e., the potential at the boundary of the Stern and Gouy layers.

The results of Edwards and Quirk (1962, 1965a, 1965b, 1965c) have been re-examined in terms of this treatment, and the most significant feature to emerge is that for the various homoionic modifications of montmorillonite and illite the potentials are roughly constant over a concentration range 0.5–0.003 M. These data indicate that a constant potential model is more appropriate when considering the distribution of ions at the clay/solution interface. From simple ion-exchange or site-binding models, however, the surface potential should be a strong function of electrolyte concentration. This discrepancy remains a serious prob-

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lem in the interpretation of these experiments. Using the site-binding model, it is possible to explain a constant potential by assuming that co-ions can also be specifically adsorbed in the Stern layer on the face of the platelets. There is no experimental evidence, however, to support this suggestion (see, e.g., Bolt and Wakentin, 1958). We have also noticed that the co-ion exclusion results show no variation with pH in the range 4.5–9.0 indicating the absence of positive sites (Edwards, 1964).

The observation of an apparent constant potential with concentration is difficult to understand even apart from the site-binding model. For example, the diffuse layer charge σ_d calculated using Eq. (13) for the potential obtained from co-ion exclusion measurements on Na-montmorillonite in 10^{-3} M NaCl (−69 mV, see Figure 3) is about 2×10^3 esu/cm^2. If the value at the same potential but at the much higher concentration of 0.3 M is calculated, a corresponding charge of about 4×10^4 esu/cm^2 is obtained, a value that is greater than the lattice charge of the clay! From Gouy-Chapman theory one would expect that the potential must fall at high salt concentrations; however, some residual excluded volume is likely in the clay due to internal area which would cause the linear exclusion curve to pass through the ordinate at a finite exclusion value. Inasmuch as the potential should fall in this region, these two effects may compensate each other to produce curves which indicate constant potential behavior even at high salt concentration, as has been reported (see, e.g., Edwards and Quirk, 1962; Posner and Quirk, 1964).

The potentials for illite follow the lyotropic series for Li to Rb with Li-illite having a surface potential of −65 mV and Rb-illite a potential of −5 mV over the concentration range 0.5 M to about 0.01M in the alkali metal chloride solutions (Table 1). The results reported by Edwards and Quirk (1965a) for Cs-illite, unlike those for other ions, show considerable scatter. Because these data are close to the abscissa, the authors reported a slope of zero which indicates a zero surface potential. The points for Cs-illite, however, lie below those for Rb-illite; hence, the magnitude of the potential for the Cs-clay must be less than −5 mV.

The diffuse layer potentials for the homoionic modifications of montmorillonite in Table 2 also follow the lyotropic series and vary from −90 mV for Li-montmorillonite to −21 mV for NH_4-montmorillonite, with a value of −12 mV for Cs-montmorillonite being subject to some qualification below. From X-ray powder diffraction evidence discussed above it seems reasonable to assume that for Li-, Na-, K-, and NH_4-montmorillonite the weak diffuse-layer interaction has no effect on the results and that condensation into quasi-crystals is not involved under the circumstances of the experiments being discussed. It is noted that the various ionic modifications of montmorillonite, with a surface density of charge 3.5×10^4 esu/cm^2, have a greater negative potential than the corresponding illite which has a surface density of charge of 6×10^4 esu/cm^2.

As mentioned above there are serious difficulties with other methods of determining the surface potential of clays, hence there are few results with which potentials derived from co-ion exclusion can be compared. Those that are available seem to agree tolerably well with the values reported here, especially with respect to the relative constancy over a range of concentrations. For example, Callaghan and Ottewill (1974) reported electrophoretic mobility measurements for Na-montmorillonite (Wyoming) which provide almost constant potential values varying from −50 mV to −44 mV, respectively, over the concentration range 10^{-1} to 10^{-4} M NaCl.

Using electrophoretic mobility measurements, P. F. Low (quoted by Friend and Hunter, 1970) reported zeta-potentials for Na-montmorillonite (Wyoming) of −30, −35, and −30 mV at concentrations of 10^{-2}, 10^{-3}, and 10^{-4} M NaCl, respectively, with one value of −45 mV in the vicinity of 10^{-2} M NaCl. More recently, Low (1981), on the basis of electrophoretic measurements for 34 different Na-montmorillonites in 10^{-4} M NaCl, reported zeta-potential values in the range −48 to −73 mV; the value reported for Na-montmorillonite (Wyoming) is −67 mV which compares with the value of the double-layer potential reported here of −69 mV for Na-montmorillonite from the same source. Such close agreement, however, may be fortuitous because the same potentials are expected only if the plane of shear in electrophoresis measurements corresponded to the boundary of the Stern and Gouy part of the double layer at the particle interface. Furthermore, a series of significant assumptions must be made to use the Smoluchowski equation to convert electrophoretic mobilities to zeta-potentials. In addition, it is evident that clay preparation and storage must play a significant role so that in future experiments considerable care should be taken to define and monitor conditions of preparation, including storage.

Pashley (1981) reported double-layer electric potentials derived from measuring the double-layer force as a function of separation between freshly cleaved muscovite surfaces in the form of crossed cylinders. At 10^{-2} M in chloride solutions he obtained the following potential values: −110 mV (Li^+), −70 mV (Na^+), −55 mV (K^+), and −50 mV (Cs^+, extrapolated). The electric potential values however varied with concentration but not in any regular or consistent fashion although Pashley provided an ion exchange model to account for the main features of the variation. It is significant, however, that the surface potentials obtained by this method are appreciably less than −200 mV.

The Cs-montmorillonite diffuse-layer potential of −12 mV reported in Table 2 needs further consider-

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ation. If, instead of using 750 m^2/g as the reference surface area, it is assumed that 3 elementary montmorillonite (10 Å thick) sheets are condensed (Cebula *et al.,* 1978), the reference area becomes 250 m^2/g and the surface potential calculated is −49 mV. This value is out of harmony with the lyotropic series: e.g., K-montmorillonite has a potential of −44 mV. It is also relevant that high precision was not claimed for the neutron scattering technique used by Cebula *et al.* (1978) to arrive at the average number of elementary silicate sheets per particle or quasi-crystal. It should be noted that the nitrogen surface area for the Cs-montmorillonite is 146 m^2/g which indicates an average number of elementary silicate sheets per quasi-crystal of about 5 after drying so that prior to drying, less condensation than this would be expected.

Notwithstanding what has been advanced about condensation for Cs-montmorillonite, the fact remains that even if it is necessary to consider "internal" and "external" surfaces, the co-ion exclusion volumes arising from the double layers on the "external" surface are linearly related to κ^{-1}, indicating an almost constant surface potential. For Ca-montmorillonite it is clear from the intercept of 0.3 ml/g on the ordinate of the co-ion exclusion plot that the value of 750 m^2/g must be partitioned into "internal" and "external" surface area (Edwards and Quirk, 1965c). If it is assumed that each quasi crystal contains an average of three elementary silicate sheets, the reference area is 250 m^2/g. Using the co-ion exclusion plot slope of 114 m^2/g in Eq. (9) leads to a diffuse layer potential of −18 mV. If 250 m^2/g were the reference area, condensation of elementary silicate sheets to give thicker particles on drying must be considerable inasmuch as the nitrogen surface area is 40 m^2/g. In comparison, Ca-illite has a co-ion exclusion plot slope of 16 m^2/g which corresponds to a potential of −5 mV for a nitrogen surface area of 110 m^2/g.

CONCLUSIONS

Co-ion exclusion measurements provide an alternative method for the determination of double-layer potentials for particles of irregular shape for which interpretation of electrophoretic mobility measurements is difficult. Using the Gouy-Chapman theory, earlier co-ion exclusion measurements on illite and montmorillonite clay minerals have been re-interpreted in terms of the behavior of the surface potentials for a wide range of counterions. These results indicate that the less hydrated monovalent ions (i.e., NH_4^+, Cs^+, Rb^+) bind more strongly to the clay surface and therefore produce low double-layer potentials, whereas the more hydrated ions (i.e., Li^+, Na^+) bind less and give higher potentials. Divalent alkaline earth ions also produce very low potentials on illite and montmorillonite presumably due to a stronger electrostatic attraction. In all samples studied the surface-potential is roughly independent of electrolyte concentration over a range of about 10^{-3} M to 0.05 M, and any reduction of surface area due to condensation cannot explain the observed behavior of constant potential.

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https://doi.org/10.1346/CCMN.1984.0320207 Published online by Cambridge University Press

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(Received 2 December 1982; accepted 18 May 1983)

Резюме—Представлены простые уравнения, при помощи которых можно получить величины потенциалов двойного слоя для глин из измерений, исключая ионы одинакового знака в одно- и двувалентных электролитических растворах. Эти уравнения использовались для ре-интерпретации ранних результатов для иллита и монтмориллонита. Полученные потенциалы следуют лиотропные серии для разных одноионных модификации каждой глины. Показано, что уравнение Шефельда, которое принимает высобкие потенциалы двойного слоя, не может применятся к исключениям ионов одинакового знака в системах глин. Уточнения ранних измерений показали, что для данной одноионной глины потенциалы почти независят от концентрации в диапазоне 0,3 до 0,003 моля. Таким образом представляется, что поверхности глин ведут себя скорее как поверхности постоянного потенциала, чем постоянного заряда. [E.G.]

Resümee—Es wurden einfache Gleichungen angegeben, mit deren Hilfe man die Doppelschichtpotentiale von Tonen aus "Co-ion exclusion measurements" in ein- und zweiwertigen Elektrolytlösungen ableiten kann. Diese Gleichungen wurden benutzt, um frühere Ergebnisse für Illit und Montmorillonit neu zu interpretieren. Die abgeleiteten Potentiale folgten der lyotropen Serie für verschiedene homoionische Modifikationen jedes einzelnen Tons. Es wurde gezeigt, daß die Schofield-Gleichung, die hohe Doppelschichtpotentiale voraussetzt, bei der "Co-ion exclusion" in Tonsystemen nicht angewandt werden kann. Eine erneute Analyse früherer Messungen hat gezeigt, daß die Potentiale für einen bestimmten homoionischen Ton über den Bereich von 0,3 bis 0,003 molar nahezu unabhängig von der Konzentration sind. Das heißt, daß Tonoberflächen sich eher wie Oberflächen mit konstantem Potential zu verhalten scheinen und weniger wie Oberflächen mit konstanter Ladung. [U.W.]

Résumé—On presente de simples équations qui permettent de dériver des potentiels à couches doubles d'argiles à partir de mesures d'exclusion de co-ions dans des solutions électrolytes monovalentes et divalentes. Ces équations ont été utilisées pour ré-interpréter des résultats précédants pour l'illite et la montmorillonite. Les potentiels derivés suivent la série lyotropique pour les modifications homoioniques variées de chaque argile. On a demontré que l'équation de Schofield, qui suppose des potentials élevés à couches doubles, ne peut être appliquée à l'exclusion de co-ions dans des systèmes argileux. La ré-analyse de measures précédantes a montré que pour une argile homoionique donnée, les potentiels sont presqu'indépendants de la concentration sur l'étendue 0,3 à 0,003 molaire. Les surfaces d'argiles semblent ainsi se comporter plus comme des surfaces à potential constant que comme surfaces à charge constante. [D.J.]

https://doi.org/10.1346/CCMN.1984.0320207 Published online by Cambridge University Press