

A Critical Assessment of Surface Adsorption Models

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ABSTRACT

The theory on variable ionization energy of surface sites is criticized based on inconsistencies of traditional potentiometric titration data (singular reference curve methods) with electrophoretic mobility (EM) data, and on the nature of dissolution of the solid phase. The mathematical consequences of including the Boltzmann distribution term in models using intrinsic equilibrium constants are most probably merely to track the solubility behavior of the solid phase. The EM of an Al oxide was studied with respect to pH. The isotherm showed clear maximum mobility at low and high pH values with the zero point of charge (ZPC) ranging from pH 9.5 to 9.8. The ZPC lowers with increasing electrolyte concentration due to the increased competitive behavior of the cations in solution for the surface sites. Assuming a constant ionization energy of the surface sites, a mass balanced model that predicted both anion-cation adsorption data and potentiometric titration data (backtitration technique) also correlated well with the EM data. The EM behavior was modeled based on the varying mobility of each type of surface species present on the oxide at various pH values. Whereas traditional models treat the oxide as being capable of forming a surface charge that induces ion adsorption, this model treats the oxide as being capable of undergoing ion exchange or substitution reactions resulting in surfaces that exhibit mobility in an applied electric field. The proposed model assumes that anion adsorption results in positive mobility, and cation adsorption results in negative mobility.

Additional Index Words: point of zero salt effect (PZSE), zero point of charge (ZPC), surface charge, intrinsic equilibrium constants (K^m), Boltzmann distribution term, solid phase dissolution, electrokinetics.

SURFACE CHARGE RESEARCH by soil and colloidal scientists typically describe surface chemical reactions in terms of pH and surface potential (Ψ_o). Electrokinetic data confirm that surface potential is pH dependent, and electrostatic studies state that the surface potential varies linearly with surface charge (σ_o)

$$\sigma_o = C\Psi_o \quad [1]$$

where C = capacitance density. Equation [1] is useful for colloid research if the colloidal particles are assumed to behave like capacitors, i.e., a constant capacitance model (Schindler and Gamsjäger, 1972).

Electrokinetics may involve either electrophoresis, electroosmosis, streaming potential, or sedimentation potential. The zeta potential measured by electrokinetics is the potential at the surface of the plane of shear, which in turn is influenced by the charge of the entire solid colloid up to the plane of shear. Electrokinetic measurements were recognized early in soil science as an important tool for understanding surface charge phenomena (Dayhuff and Hoagland, 1924; Mattson, 1926). A major hypothesis suggested by Arrhenius (1922), in which electrokinetics played an important confirming role, was that clays may act as an

ampholyte. Electrokinetic research has since generally been reserved for investigating floc stability, predominantly with respect to its application in water treatment.

A limitation of electrokinetics is that no information on the number of surface sites per unit area is obtained. For this information the chemist resorts to potentiometric titration data. Since these titrations must adhere to the principle of electroneutrality, each proton adsorbed by the surface must increase surface charge by one equivalent charge unit. Thus, proton adsorption or desorption as determined by potentiometric analysis is generally considered synonymous with surface charge. There are, however, some inconsistencies that dramatically complicate this otherwise simple description of surface charge. First of all, potentiometric titration curves of soils yield no definite breaks to indicate end points. This problem was observed early in soil research by Bradfield (1923). Another problem is that the surface charge predicted by potentiometric titration curves is extremely large at only a few pH units above and below the zero point of charge (ZPC). Though this inconsistency with the surface charge behavior as determined by electrokinetics was questioned by Lyklema (1968), it has been generally ignored.

Use of electrokinetics for describing surface charge characteristics has not been aggressively pursued in the soil science literature; instead, the charge behavior of a soil or oxide sample is usually characterized through potentiometric titration or cation-anion exchange methods. Unfortunately, each of these methods yields different results (Sposito, 1984) and have resulted in an array of zero point definitions and surface charge interpretations. The terms used are often methodology dependent and are, therefore, vague in their physical interpretations. The cation-anion exchange method has become an acceptable method in soil science following Schofield (1949). Schulthess and Sparks (1986, 1987) show that the cation-anion exchange methods yield identical data to potentiometric titration methods if a backtitration technique is used. They argue that the traditional titration methods do not account for the solubility of the solid phase, which in turn acts as a significant source (or sink) for H_3O^+ ions in the titration procedure. Ignoring the solubility phenomena has resulted in a long list of questionable surface charge data and theories, as well as an array of zero point definitions.

In this paper, we shall review the limitations of adsorption models that are based on traditional potentiometric titration data. Furthermore, the electrokinetic behavior of an Al oxide will be compared with the proton isotherm behavior determined by the backtitration technique (Schulthess and Sparks, 1986). This is necessary to completely correlate the surface charge behavior as determined by the three methods mentioned above: cation-anion exchange, potentiometric titrations, and electrokinetics. The model used to describe the potentiometric titration data and the cation-

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anion exchange data by Schulthess and Sparks (1987) will be shown to be also useful in describing electrokinetic data. The latter model does not use intrinsic equilibrium constants nor Boltzmann distribution terms as opposed to several other methods that have been employed by soil chemists. Justification for not including these terms follows.

MATERIALS AND METHODS

Theoretical Considerations

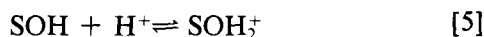
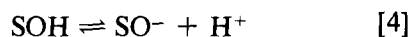
Potentiometric titration curves of soils yield no definite breaks to indicate end points, as is observed in the titration of liquid solutions. This inconsistency is ascribed to the basic assumption that the ionization of each surface site affects the acidity of the neighboring surface sites (Huang, 1981). The amount of work required to ionize the surface is further assumed to be related to the concentration ratio of the potential determining ion (PDI) based on the Boltzmann factor (Hiemenz, 1977)

$$\frac{(H^+)_{\text{surface}}}{(H^+)_{\text{bulk}}} = \exp\left(\frac{-w}{kT}\right) = \exp\left(\frac{-ze\Psi_o}{kT}\right) \quad [2]$$

where w = work required to bring the proton from the bulk solution to the surface with a potential Ψ_o , z = valance of ion, e = unit charge, and kT = energy terms. Another assumption that needs to be made is how to correlate surface charge (σ_o) to surface potential. The constant capacitance model (Eq. [1]) is often used, e.g., Goldberg and Sposito (1984); however, other models have been used, particularly the diffuse double-layer model from the Gouy-Chapman theory

$$\sigma_o = \sqrt{8\epsilon\epsilon_o RTI} \sinh(F\Psi_o/2RT) \quad [3]$$

where ϵ = dielectric constant, ϵ_o = permittivity of free space, F = Faraday's constant, RT = energy terms, and I = ionic strength. Westall and Hohl (1980) were able to fit the surface charge data equally well using several models, including the constant capacitance model and diffuse double-layer model. The electrolytes used to adjust the ionic strength are also assumed to be indifferent; this assumption often also applies to the conjugate acid (Na^+) and base (Cl^-) introduced with the pH adjustments of the medium. Finally, assuming only two surface reactions



the theory on variable ionization energy states that the intrinsic equilibrium constants may be defined as

$$K_b^{int} = \frac{\{SO^-\}(H^+)\exp(-F\Psi_o/RT)}{\{SOH\}} \quad [6]$$

$$K_a^{int} = \frac{\{SOH_2^+\}}{\{SOH\}(H^+)\exp(-F\Psi_o/RT)} \quad [7]$$

where S = surface, and all the values are in activities. The equations are then used to generate curves that predict surface charge vs. pH data obtained from a potentiometric titration analysis of the solid oxide.

Schulthess and Sparks (1986) modified the traditional potentiometric titration procedures by backtitrating the supernatant solutions and correcting for the interfering solubility behavior of the solid phase. The resulting isotherms (H^+ removed vs. pH) were not convex, showed definite maximum values, and had clearly defined breaks to indicate end points. These observations seriously challenge the theory that

the ionization energy of the surface sites vary with degree of titration. Schulthess and Sparks (1987) later developed a surface speciation model based on mass balanced equations and constant ionization energy of the surface sites.

Solubility diagrams ($-\log[aq. \text{ species}]$ vs. pH) of oxides and minerals confirm a logarithmic relationship between the solubility of the solid phase and the pH of the medium (see Stumm and Morgan, 1981). At pH values $>$ pH of minimum solubility, the solubility usually increases 10-fold for each unit increase of pH; at pH values $<$ pH of minimum solubility, the solubility sometimes increases 1000-fold for each unit decrease of pH. The slope of the lines on the solubility diagrams are generally integer values (i.e., 1:1, 1:2, 1:3).

How does solubility affect potentiometric titration curves and surface charge analyses of oxides? First, the ZPC is near the pH of minimum solubility (Parks and de Bruyn, 1962). The exponential terms in Eq. [6] and [7] would be equal to 1.0 at the pH of ZPC ($\sigma_o = 0$, $\Psi_o = 0$). As the pH (or H^+ activity) changes, the remaining terms in Eq. [6] and [7] would also change so as to maintain the K^{int} values constant. Since the solubility of the solid phase has been ignored, the surface charge data is overestimated as follows:

$$\begin{aligned} \sigma_o &= \{SOH_2^+\}_{\text{measured}} - \{SO^-\}_{\text{measured}} \\ &= \{SOH_2^+\}_{\text{true}} - \{SO^-\}_{\text{true}} \pm [\text{dissolved}]. \quad [8] \end{aligned}$$

Parker et al. (1979) observe that the dissolution of Al would consume H^+ ions without affecting the surface charge. The aqueous phase reactions cannot be distinguished from the solid phase reactions, however, unless they are physically separated. Figure 1 illustrates this overestimation of surface charge. The σ_{true} curve was from the data obtained by Schulthess and Sparks (1987), and the dissolution effect was determined from a solubility analysis of the same data. (The degree of hydrolysis of Al in solution is easily obtained by potentiometric titration of the supernatant solution. The magnitude of the buffering capacity at pH 4.7 or 9.0 is directly related to the Al concentration present. For an illustration of this buffering capacity effect see Fig. 3 in Schulthess and Sparks, 1986.) The net surface charge curve is also presented in Fig. 1 along with the surface charge data using the traditional potentiometric titration method (viz., singular reference curve method). The close match of the net (summation generated) surface charge curve with the traditional experimental data clearly proves that the singular reference curve method misrepresents the surface charge phenomena. This is particularly true in the alkaline region and at pH $<$ 4.5 for this Al oxide.

Van Riemsdijk et al. (1987) state, "it is not yet possible to identify the exact nature of all relevant surface complexes with spectroscopic techniques." Consequently, cation-anion exchange, potentiometric titration analyses, and electrokinetics are currently our best sources for elucidating the nature of the surface chemical reactions. The presence of buffered zones in potentiometric titration analyses are clear indicators that chemical reactions are taking place. These buffered zones are easily misinterpreted, however, when the methodology and theoretical analysis of the data ignore the solubility of the solid phase. By correcting for the solubility phenomena, Schulthess and Sparks (1987) were able to observe several distinct changes in the titration patterns and subsequently modeled their data with several surface reactions (Fig. 2); on the other hand, if the solubility behavior remains unaccounted for, then the potentiometric titration data can be interpreted by only two surface reactions, such as Eq. [4] and [5], or even one surface reaction (e.g., van Riemsdijk et al., 1987). Ignoring the solubility of the solid phase causes a large distortion of the isotherm analyses.

The high surface charge values a few pH units above and below the ZPC using traditional potentiometric titration

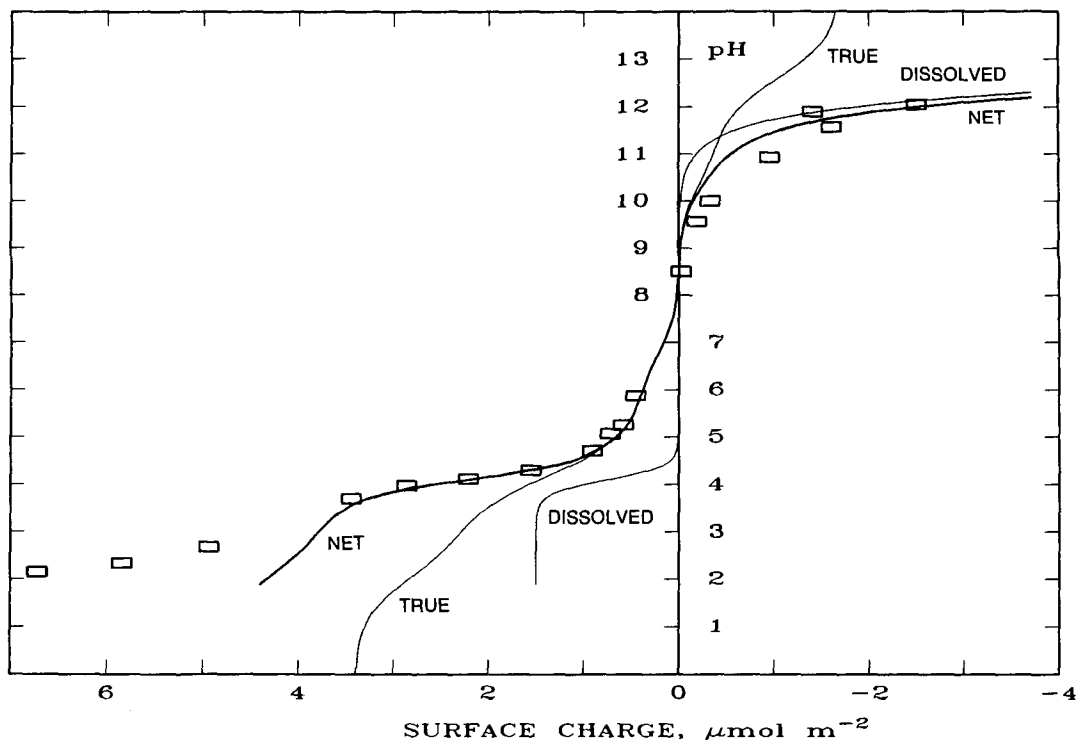


Fig. 1. Illustration of components of surface charge data. TRUE = potentiometric titration analysis (backtitration technique) by Schulthess and Sparks (1987); DISSOLVED = apparent adsorption of protons due to dissolution of the Al oxide; NET = TRUE + DISSOLVED. The (□) symbols are surface charge values obtained by traditional potentiometric titration analysis (singular reference curve method). Note that the curve labeled TRUE also agrees well with cation-anion exchange data obtained by Schulthess and Sparks (1987). Initial ionic strength was zero.

methods are generally not recognized as being unrealistic and inconsistent with electrokinetic data. To generate predictions for the σ_o -pH isotherm at least two parameters need to be determined: K^{int} values and the capacitance value if applying the constant capacitance model. The criteria for determining the magnitude of the assumed parameters is based on the goodness-of-fit of the generated predictions with the experimental data. The capacitance density cannot be determined experimentally and is often treated as an empirical, adjustable model parameter (Goldberg and Sposito, 1984). Since the traditional potentiometric titration data show a convex behavior at high and low pH values, the goodness-of-fit soon deteriorates. Multilayer models are more effective in predicting the titration data at higher σ_o values. The entire procedure yields questionable conclusions, however, because the data are not true surface charge values when singular reference curve titration methods are used. The solubility behavior of the solid phase greatly overshadows the true surface adsorption reactions. The mathematical consequences of including the Boltzmann distribution term in Eq. [6] and [7] are, therefore, mostly tracking the solubility behavior of the solid phase.

Electrophoretic Mobility Study

The Al oxide used for these experiments was the same washed oxide used in earlier potentiometric titration analyses by Schulthess and Sparks (1987); i.e., γ - Al_2O_3 made by the Degussa Corp. of Teterboro, NJ, under the name of Aluminum Oxide C[®]. The oxide was believed to be clean of impurities, but may contain adsorbed CO_2 and a small amount of an unknown metal chloride (M^+Cl^-). The concentration of the stock Al oxide suspension was reported earlier to be 84.06 g L^{-1} and to have a specific surface area, using ethylene glycol monomethyl ether (EGME), of $83.1 \text{ m}^2 \text{ g}^{-1}$. The average primary particle size (dry) was 20 nm (supplied by the manufacturer).

Samples were prepared by adding 0.5 mL of the stock Al oxide suspension to 125-mL polyethylene bottles which were then pH adjusted with known quantities of either 0.24 M HCl or 0.24 M NaOH; the initial electrolyte concentration was adjusted with a concentrated NaCl solution. The total volume was kept constant at 70.0 mL with deionized water, and an N_2 atmosphere was maintained at all times. After equilibrating overnight on a reciprocating shaker, the pH of each suspension was measured and the electrophoretic mobility (EM) was analyzed on a Zeta-Meter (ZM-80) by Zeta-Meter, Inc., NY. The cell used was electrophoresis cell no. 1125 made by Zeta-Meter, Inc. The Plexiglas cell had the Pt electrodes separated by 10 cm. The manufacturer suggests that the conductivity be $<0.1 \text{ S m}^{-1}$ when using Pt electrodes rather than Mo electrodes; otherwise $O_2(g)$ formation at the anode and $H_2(g)$ formation at the cathode will cause erroneous readings. The EM readings were obtained by measuring the time required for each particle to travel $160 \mu\text{m}$ under an applied potential (80–250 V) separated by 10 cm; that is, EM is the velocity of the particle ($\mu\text{m s}^{-1}$) induced by an applied electric field (cm V^{-1}), such that:

$$EM = \frac{160 \mu\text{m}}{t} \times \frac{10 \text{ cm}}{V}, \quad \left[\frac{\mu\text{m cm}}{\text{V s}} \right] \quad [9]$$

The EM was averaged over a maximum of 20 readings in two directions. The pH range studied was from 2.5 to 11.5, and the initial electrolyte concentrations were 0.0, 0.001, and 0.007 M NaCl. Several portions of the experiment were repeated to ensure reproducibility and detail of the resulting curves.

RESULTS AND DISCUSSION

The EM for the Al oxide with respect to pH, shown in Fig. 3, has two maximum values. At $\text{pH} < 7.0$ the EM values are $3.0 \pm 0.5 \mu\text{m cm V}^{-1} \text{ s}^{-1}$ with samples

with low electrolyte concentrations having slightly higher EM values than samples with high electrolyte concentration. At $\text{pH} > 10.5$ the EM values are $-2.3 \mu\text{m cm V}^{-1} \text{s}^{-1}$ with no differences observed under various electrolyte concentrations. The zero point of charge (ZPC) decreased from 9.8 to 9.5 with increase in electrolyte concentration.

The region between $\text{pH} 7.0$ and 10.5 is particularly interesting. The point of zero salt effect (PZSE) for this Al oxide was determined earlier by Schulthess and Sparks (1987) to be at $\text{pH} 7.5$ for high electrolyte concentrations and at $\text{pH} 7.76$ for low electrolyte concentrations. Figure 3 does show a drop in the EM values at the above predicted PZSE values. The drop in the EM values are not sudden, but rather lower gradually from $\text{pH} 7.5$ to 9.5 ; at $\text{pH} 9.5$ to 10.5 the EM values do drop abruptly.

Suggestions for a physical interpretation of the surface reactions were outlined by Schulthess and Sparks (1987) based on a potentiometric titration analysis modified by a backtitration step to adjust for the variable solubility of the solid phase. The model consists of pH and salt-dependent reactions, which are illustrated in Fig. 2 as the vertical reactions, and competitive salt-dependent (pH -independent) reactions, which are illustrated in Fig. 2 as the horizontal reactions. The key difference from other models is that there are no ions that are considered indifferent or inert, and the ion concentrations play an important role in the speciation of the surface. The model was mass balanced, and the equilibrium constants assumed that the surface ionization energy was constant. None of the values used was empirically adjusted; all the equilibrium values were directly derived from the data. Note that the physical description of the Al oxide surface as outlined in Fig. 2 is not confirmed; however, there is substantial evidence that the surface has adsorbed Cl^- at low pH and HCO_3^- or Na^+ at high pH conditions. These surface interpretations do emphasize that ion adsorption on the surface does take place and that the oxide does not exist in a charged state in absence of a counterion. It is not possible to centrifuge the oxide suspension and use the packed oxide paste as either an anode or cathode.

This EM study shows that each type of surface species responds with varying degrees of mobility under

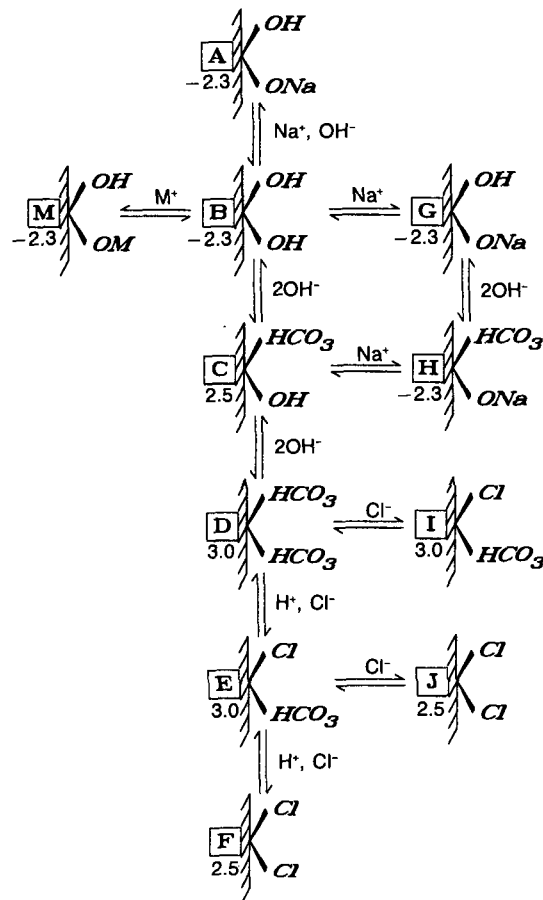


Fig. 2. Aluminum oxide speciation model suggested by Schulthess and Sparks (1987). The EM values associated with each species is shown below their corresponding symbols; units are in $\mu\text{m cm V}^{-1} \text{s}^{-1}$.

an applied electric field. Predictions of the Al oxide's EM may be made based on mass balanced equations presented by Schulthess and Sparks (1987). The EM values corresponding to each of the surface species shown in Fig. 2 were determined by matching the measured EM values with the surface species that was predicted dominant under the assigned conditions. The results show $\text{EM} = 2.5$ (species C, F and J), 3.0 (species D, E and I), and $-2.3 \mu\text{m cm V}^{-1} \text{s}^{-1}$ (species A,

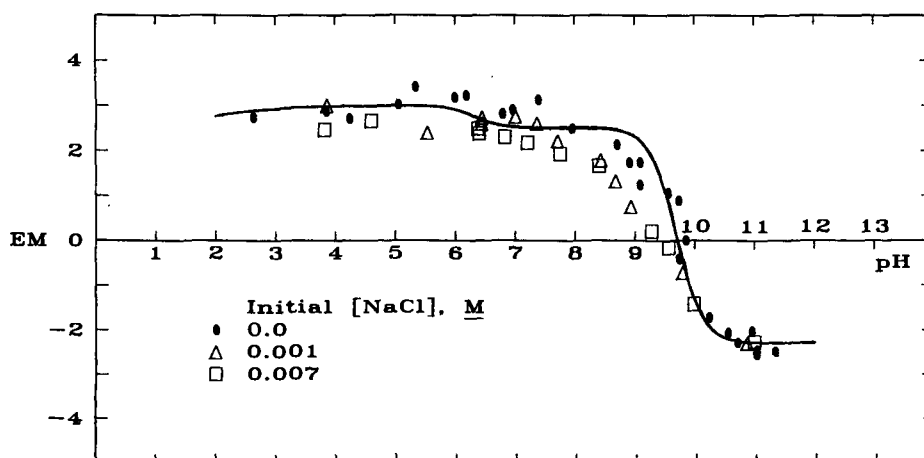


Fig. 3. Electrophoretic mobility ($\mu\text{m cm V}^{-1} \text{s}^{-1}$) vs. pH for Al oxide. Solid line is EM predicted based on speciation model shown in Fig. 2.

B, G, H, and M). That is, all the species that have cation adsorption (H^+ , Na^+ , M^+) yield a constant negative EM value; species having HCO_3^- or Cl^- adsorption yield a positive EM value. These EM values generate the line drawn in Fig. 3 for the condition of zero initial NaCl additions. The EM predictions for the samples with high electrolyte concentrations were slightly lower at $pH < 9.0$; however, these predicted values still overestimated the experimental values. The suggested model predicts no sensitivity of EM values to salt concentrations at the extremely high and low pH values, but does predict some salt sensitivity for most pH conditions, particularly near the PZSE and ZPC. The prediction for the ZPC is excellent. From these observations and from the model outlined in Fig. 2, it follows that the pH of ZPC lowers with increase in electrolyte concentration due to the increase in cation adsorption. Cation adsorption (or exchange for H^+ ions) also results in lower EM values in the pH region between the predicted PZSE and ZPC. This is in contradiction with the current view that cation adsorption increases EM values and anion adsorption decreases EM values (Parks, 1965; Singh and Uehara, 1986). Our hypothesis, however, is consistent with the cation-anion adsorption data and potentiometric titration analyses discussed by Schulthess and Sparks (1987).

Our experiments indicate that the Boltzmann distribution of ions (Eq. [2]) may be misapplied in describing the oxide surface behavior. If a surface charge exists (as is illustrated by Eq. [4] and [5]), then a surface potential must also exist. However, if the surface is closely associated with counterions, or has no net surface charge (as is illustrated in Fig. 2), then Eq. [2] does not apply. We suggest that the charge behavior observed by electrokinetics is a result of an electric field induced shearing of counterions from the surface. More specifically, there is no net charge existing on the solid surface in absence of an applied electric field in water. Since the Al oxide does not exhibit a charged behavior when dry (Degussa Tech. Bull. 56), it follows that the shearing strength is a function of the dielectric constant of the medium and the bonding strength of the counterions onto the surface. Whereas traditional models treat the oxide as being capable of forming a true surface charge that induces ion adsorption, this

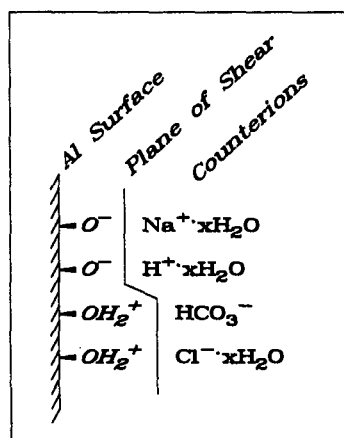


Fig. 4. Suggested location of plane of shear under an applied electric field.

model treats the oxide as being capable of undergoing ion exchange or substitution reactions resulting in a surface that exhibits mobility in an applied electric field; the oxide surface remains neutral at all other times. The plane (or zone) of shear may be somewhere in a diffuse double-layer region (Hiemenz, 1977); however, the induced shearing is pictured here to be between the surface and the closely associated counterions (Fig. 4). This description is not affected if the counterions are hydrated, or if H_2O bridging exists between the counterions and the surface. Thus, the surface is always neutral, but will become temporarily charged if the counterions are sheared off by an applied electric field.

The authors realize that this hypothesis also needs to be tested in terms of explaining yet other phenomena observed in the solid-aqueous phase physical chemistry of oxides; including coagulation and other forms of electrokinetics. The research emphasis must be to pursue models that are consistent with data from a variety of independent experiments.

CONCLUSIONS

The Al oxide studied exhibited positive mobility at low pH and negative mobility at high pH, with the ZPC at pH 9.5 to 9.8. The magnitude of the mobility was constant at the high pH values, but varied slightly with salt concentrations at the low pH values. The speciation model suggested by Schulthess and Sparks (1987) can be used to model the EM behavior where each type of surface species ($-Cl$, $-HCO_3$, $-OM$) responds with varying degrees of mobility to an applied electric field. The proposed model assumes that anion adsorption results in positive mobility, and cation adsorption results in negative mobility. The ZPC also lowers with increase in aqueous electrolyte concentration due to the increased cation adsorption.

There is no theoretical reason for cation-anion exchange methods, potentiometric titration methods, and electrokinetics to disagree with respect to describing the surface charge behavior. Schulthess and Sparks (1987) demonstrated that the cation-anion exchange methods yield identical results to potentiometric methods if the solubility of the solid phase is accounted for. Our EM studies also confirm the observations made by the former two methods.

The mathematical effect of the Boltzmann distribution term used in many surface charge models is most probably merely tracking the solubility behavior of the solid phase. There is no definitive proof for the theory of variable ionization energy. There is also no reason to ignore the solubility phenomena and thus allow the large "surface charge" values to remain unquestioned. Unless solubility phenomena are considered, the application of models that use the Boltzmann distribution term and singular reference potentiometric titration data, including the constant capacitance and diffuse double-layer (DDL) models, are questionable.

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