

DIVISION S-2—SOIL CHEMISTRY

Backtitration Technique for Proton Isotherm Modeling of Oxide Surfaces¹

C. P. SCHULTHESS AND D. L. SPARKS²

ABSTRACT

Batch potentiometric titration analyses were made on a γ - Al_2O_3 colloidal suspension and interpreted in terms of the electroneutrality principle. Three titration methods involving a singular reference curve were compared. The first reference used was theoretical, the latter two were representative supernatant curves: an electrolyte solution, and an aliquot of the zero point of titration (ZPT) supernatant. All three methods resulted in similar charge isotherms and a zero point of charge (ZPC) = 8.60. A fourth titration method was developed involving each supernatant of the batch titration sample to act as a unique reference. This latter method is a backtitration technique which accounts for all sources that also consume H^+ ions, leaving the difference to be the adsorbed proton concentration only. The NaClO_4 electrolyte solution used is postulated to be adsorbed with competitive cation and anion exchange mechanisms with a point of zero salt effect (PZSE) = 7.50.

Additional Index Words: electroneutrality, proton isotherm, ZPC, PZSE.

Schulthess, C.P., and D.L. Sparks. 1986. Backtitration technique for proton isotherm modeling of oxide surfaces. *Soil Sci. Soc. Am. J.* 50:1406-1411.

¹ Published with the approval of the Director of the Delaware Agric. Exp. Stn. as Miscellaneous Paper no. 1121 Contribution no. 199 of the Dep. of Plant Science, Univ. of Delaware, Newark, DE 19717-1303. Received 8 Nov. 1985.

² University Graduate Research Assistant and Associate Professor of Soil Chemistry, respectively.

BEFORE CHARACTERIZING AND MODELING the surface charge behavior of a soil or colloidal system, one must decide which method to use, what terminology to adopt, and how the model will be used to interpret the data. Some of the methods available involve electrokinetics, cation-anion exchange, and potentiometric titration curves.

Unlike electrokinetics, which involves the entire colloid, the cation-anion exchange and potentiometric titration methods measure surface sorption behavior. These data are then interpreted in terms of surface charge, or permanent charge, according to the sorption model used. Veitch (1904) made an early attempt to compare the accuracy and practicality of two methods to determine soil acidity: the NaCl method (cation exchange) and the lime-water method (titrimetric), recommending the latter. Interest in titrating soils soon led to interpretive complications. Potentiometric titration curves of soils yield no definite breaks to indicate end points, as is usually expected of weak acids. Bradfield (1923, 1924) claimed that the error was due to methodology. He obtained "definite breaks" by adding the soil (weak acid) to the alkali solution (strong base) as is usual for chemical analyses. Mattson (1931) called the pH of exchange neutrality (EN) to be the pH where anion adsorption equals cation adsorption.

He made very extensive studies on the relationship between pH and ion exchange, and treated the soil surfaces as behaving amphoterically. Grahame (1947) gave an excellent review on electrical double layer theory and helped set the stage for future modeling of surface charge. Schofield (1949) challenged the "old" titration methods and suggested using a cation-anion exchange method with acid NH_4Cl . His work, and that of others who followed, greatly influenced the field of soil science. It became acceptable to use ion exchange methods to determine surface charge (CEC vs. AEC), and potentiometric titrations were generally reserved for zero point of charge (ZPC) analyses only.

Various interpretations of potentiometric titration curves are still being presented. Westall and Hohl (1980) compared five electrostatic models of the oxide-solution interface and found them all to fit the potentiometric data rather well. Lyklema (1968) observed that the surface charge vs. pH curves for all oxides are convex. Since this leads to high surface charge density, he postulated a potential and charge distribution inside the solid assuming an exponential decay of porosity, with large radii ions having low penetration depth. Parks and de Bruyn (1962) argued that the ZPC was at the pH of minimum solubility of the solid species.

Another challenge for soil and colloid chemists is the myriad of "zero point" vocabulary. Parker et al. (1979) insisted that terms like zero point of charge (ZPC), or isoelectric point (IEP) are too vague. They suggested terms like point of zero salt effect (PZSE) and point of zero net charge (PZNC). Sposito (1981) also suggested the term point of zero net proton charge (PZNPC). Bowden et al. (1977) used the terms isoelectric point of the solid (IEPS) and pristine point of zero charge (PPZC), and Hendershot (1978) worked with zero point of titration (ZPT). Furthermore, the abbreviations ZPC and PZC are used interchangeably.

Parks (1965) reviewed reported ZPC values for oxides using electrokinetics. There seems to be general agreement on the values reported with only a few exceptions. Additionally, Parks (1967) proposed using a weighted average of the component ZPC values of the soil matrix as an initial estimate of the soil's ZPC value. Parfitt (1980) observed that "isoelectric weathering" may also take place in that the ZPC approaches the soil pH with time.

In this paper we are primarily concerned with determining why potentiometric titration curves yield surface charge vs. pH data. The assumptions and limitations of three "singular reference curve" methods commonly found in the literature will be discussed in detail. Finally, a "backtitration technique" will be presented to better describe the solid-solution interface, and it will be used to model the proton isotherm on an Al-oxide surface. In evaluating methodologies it is advisable to work with simple systems so as to avoid possible secondary effects that might obscure "obvious" results. A $\gamma\text{-Al}_2\text{O}_3$ colloid was chosen for this study because of the great importance of Al-oxides in soils, especially tropical soils. The theoretical discussion that follows is applicable to all potentiometric titrations.

MATERIALS AND METHODS

Theoretical Considerations

The principle of electroneutrality must hold true for every point on all titration curves, i.e., the sum of all negative charges is equal to the sum of all positive charges

$$\sum \text{negative charges} = \sum \text{positive charges} \quad [1]$$

For example, the titration of an amphoteric oxide surface with HClO_4 or NaOH in the presence of NaClO_4 electrolyte solution, would result in

$$\begin{aligned} (\text{OH}^-) + (\text{ClO}_4^-) + \left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} \\ = (\text{H}^+) + (\text{Na}^+) + \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\} \end{aligned} \quad [2]$$

or,

$$\begin{aligned} \sigma_o &= \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\} - \left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} \\ &= (C_A - C_B) - (\text{H}^+ - \text{OH}^-) \end{aligned} \quad [3]$$

where

σ_o = surface charge,
 $\left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\}$ = the concentration of negative charges on the surface of the colloid,

$\left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\}$ = the concentration of positive charges on the surface of the colloid,

$$(\text{H}^+) = 10^{-\text{pH}},$$

$$(\text{OH}^-) = 10^{\text{pH} - \text{pK}_w},$$

$$(\text{ClO}_4^-) = (\text{NaClO}_4)_{\text{added}} + (\text{HClO}_4)_{\text{added}},$$

$$(\text{Na}^+) = (\text{NaClO}_4)_{\text{added}} + (\text{NaOH})_{\text{added}}, \text{ and}$$

$$\begin{aligned} (\text{ClO}_4^-) - (\text{Na}^+) &= (\text{HClO}_4)_{\text{added}} - (\text{NaOH})_{\text{added}} \\ &= C_A - C_B. \end{aligned}$$

When the surface charge is neutral, the negative and positive charges are equal, $\left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} = \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\}$, and the surface is said to have zero charge. At the pH of ZPC, Eq. [3] simplifies to:

$$(C_A - C_B) - (\text{H}^+ - \text{OH}^-) = 0 \quad [4]$$

The question one may ask is, how does one know at what pH value does Eq. [4] hold true? Gouy (1910) and Chapman (1913) derived an equation correlating the potential of a surface, to the surface charge. Using Nernst's (1889) equation, the surface potential can be correlated to the concentration of potential determining ions (PDI) in solution. The PDI for the experiments in this study are H^+ and OH^- . The Na^+ and ClO_4^- ions are assumed to be indifferent at the surface and not to act as PDI (Yopps and Fuerstenau, 1964). Thus, the adsorption of H^+ or OH^- onto the surface is assumed to control the charge of the surface studied. Combining the Gouy-Chapman equation with Eq. [3] gives

$$\begin{aligned} \sigma_o &= \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\} - \left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} \\ &= (C_A - C_B) - (\text{H}^+ - \text{OH}^-) \\ &= \pm \left(\frac{2kT\epsilon n_o}{\pi} \right)^{1/2} \sinh\{1.15(\text{pH}_{\text{ZPC}} - \text{pH})\}. \end{aligned} \quad [5]$$

If $\text{pH} = \text{pH}_{\text{ZPC}}$, then $\sigma_o = 0$ and $\left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} = \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\}$ for any ionic strength. If $\text{pH} > \text{pH}_{\text{ZPC}}$, then $\sigma_o < 0$ and $\left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} > \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\}$. Conversely, if $\text{pH} < \text{pH}_{\text{ZPC}}$, then $\sigma_o > 0$ and $\left\{ \begin{array}{l} \text{negative} \\ \text{surface} \end{array} \right\} < \left\{ \begin{array}{l} \text{positive} \\ \text{surface} \end{array} \right\}$. Furthermore, at a fixed pH value $> \text{pH}_{\text{ZPC}}$,

an increase in electrolyte concentration, n_o , will increase both $|\sigma_o|$ (making σ_o more negative) and C_B (more base is needed to attain the pH value desired). At a fixed pH value $< \text{pH}_{\text{ZPC}}$, an increase in n_o will increase both $|\sigma_o|$ (making σ_o more positive) and C_A (more acid is needed to attain the pH value desired). Thus, if several charge curves (σ_o vs. pH) at various ionic strengths are superimposed, the pH value where the curves intersect is the ZPC.

The following methods below outline various ways in which Eq. [5] may be applied. The results and limitations of each method will be discussed later. The colloid studied was a $\gamma\text{-Al}_2\text{O}_3$ made by the Degussa Corp., of Teterboro, NJ, under the trade mark name of Aluminum Oxide-C. A stock suspension of 105 g L^{-1} was prepared with deionized water and allowed to equilibrate for several days before use. The concentration of the oxide suspension was checked by gravimetric analysis. The oxide had a BET surface area of $100 \pm 15 \text{ m}^2 \text{ g}^{-1}$, and the average primary particle size (dry) was 20 nm (supplied by the manufacturer).

Experimental Procedures

A batch titration of the colloid was made using 125-mL polyethylene bottles containing 10 mL of the $\gamma\text{-Al}_2\text{O}_3$ suspension (105 g L^{-1}), and a predetermined amount of NaClO_4 for various initial ionic strength settings (e.g., 2 mL of 0.25 M NaClO_4 will yield $I = 0.01 \text{ M}$ in a 50-mL sample). To a row of approximately 20 samples, varying amounts of 0.25 M HClO_4 or 0.25 M NaOH solutions were added to vary the pH in each sample. For example: half a batch may contain 500, 400, 300, 250, 200, 150, 100, 75, 50, 25, and 10 μL of 0.25 M NaOH , and the other half may contain similar amounts of 0.25 M HClO_4 . There was also at least one sample with no acid or base additions. The volume of acid or base additions were carefully monitored by the use of 2.000-mL micrometer syringes, distributed by Cole-Parmer Inst. Co., which deliver the desired solution in 0.002-mL increments. Each sample was then diluted to a final volume of 50 mL with deionized water.

Finally, after all the additions were made, the samples were tightly capped and shaken overnight on a reciprocating shaker at room temperature. After equilibrating, the suspension pH of each sample was measured and the pH data of the entire batch were plotted against mmol of acid (or base) added. The process was repeated for three ionic strengths (0.001, 0.01, and 0.1 M). Each run was repeated in parts to ensure reproducibility and detail of the resulting curves. The data and their resulting curves were used in methods I, II, and III which are outlined below. Each sample was saved and later treated according to method IV given below.

Method I

The $\gamma\text{-Al}_2\text{O}_3$ titration data were applied to Eq. [3] to estimate the surface charge. Plotting surface charge vs. pH should yield three lines intersecting at the pH of ZPC.

Method II

An electrolyte solution, prepared by adding 10 mL of deionized water rather than 10 mL of the colloidal suspension, was also titrated by a simple acid-base titration method where the pH was recorded for each increment of 0.25 M acid or 0.25 M base that was added. This procedure was repeated for various ionic strengths and plotted as pH vs. mmol of acid (or base) added to the electrolyte solution. From each graph, the difference in mmol of acid (or base) added at a given pH value between the titration of the colloidal sample and the titration of the corresponding electrolyte solution was measured and plotted separately as surface

charge vs. pH for each ionic strength. The pH value where these lines intersect each other is referred to as the ZPC.

Method III

Several samples were made with no acid or base additions. After these "zero addition" samples were equilibrated overnight and pH measured along with the other samples, they were centrifuged and filtered through $0.2 \mu\text{m}$ filter paper. The supernatant of these "zero addition" samples, which will be referred to as ZPT supernatant solutions, were used as the blank reference. This blank consists of the electrolyte solution in which all the samples were suspended in, plus all the species which are soluble under the particular pH condition of no acid or base addition. A 50-mL aliquot of this blank reference solution was titrated and the pH was recorded for each increment of 0.25 M acid or 0.25 M base that was added. The data were plotted as mmol of acid (or base) added vs. pH. For each ionic strength run the difference in mmol of acid (or base) added for the colloid titration and the blank reference titration at any given pH value was measured and plotted as surface charge vs. pH. The pH value where these lines intersect each other is referred to as the ZPC.

Method IV

After equilibrating overnight and measuring the pH of the suspensions, all the samples were individually centrifuged and filtered. Each of the supernatants was weighed, pH measured, and backtitrated with pH 7 as the end point. The backtitrations were done with an autotitrating system (Radiometer, Copenhagen, Denmark) using a constant titration rate of 0.5 or 0.05 mL min^{-1} , and 0.03 M HClO_4 as the titrant for the alkaline supernatants or 0.03 M NaOH as the titrant for the acid supernatants. The volume of titrant added to the supernatants, V_{BT} , was the volume necessary to achieve a supernatant pH of 7.00. Since the volume of the supernatant was never equal to the initial 50 mL due to losses in the separation and filtration process, the V_{BT} values were adjusted linearly with respect to the weight recovered. The difference between mmol of acid (or base) added and the solution alkalinity (or acidity) remaining yields the $\mu\text{mol m}^{-2}$ of H^+ adsorbed or desorbed ($\Gamma_{\text{H}^+.\text{OH}^-}$):

$$\Gamma_{\text{H}^+.\text{OH}^-} = \left[(V_A C_A - V_B C_B) + (V_{\text{BT},A} C_{\text{BT},A} - V_{\text{BT},B} C_{\text{BT},B}) \frac{50\rho}{W} \right] \times 10^3 / \text{Ag} \quad [6]$$

where subscript A = acid; B = base;

W = weight of supernatant backtitrated, g (max. weight = 50 g);

ρ = density of supernatant (assume $\rho = 1.00 \text{ g mL}^{-1}$);

V = volume of acid or base added to the colloid suspension, mL;

C = concentration of titrant = 0.25 M;

V_{BT} = volume of acid or base added in backtitration, mL;

C_{BT} = concentration of backtitrant = 0.03 M;

$10^3 \mu\text{mol} = 1.0 \text{ mmol}$; and

$\text{Ag} = (\text{specific surface area}) \times (\text{weight of colloid titrated}) = (10^2 \text{ m}^2 \text{ g}^{-1}) \times (1.05 \text{ g})$.

Proton adsorption and hydroxyl desorption are experimentally indistinguishable. The $\Gamma_{\text{H}^+.\text{OH}^-}$ values were plotted against the supernatant pH for each batch run and repeated for several ionic strengths. The surface charge and the amount of acid sorbed are not synonymous terms.

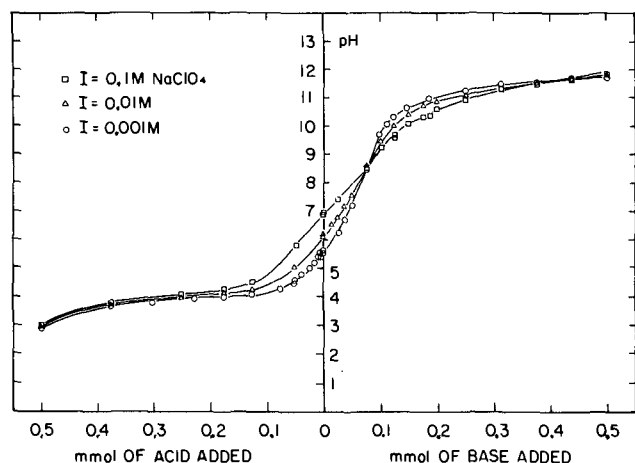


Fig. 1. Batch titration of $\gamma\text{-Al}_2\text{O}_3$ at various ionic strengths with HClO_4 and NaOH . $[\gamma\text{-Al}_2\text{O}_3] = 1.05 \text{ g } 50 \text{ mL}^{-1}$, total volume = 50 mL , pH of suspension after equilibrating overnight.

RESULTS AND DISCUSSION

Singular Reference Curves (Methods I, II, and III)

Figure 1 shows the pH of the suspension vs. the mmol of acid or base added to the colloid. Solving Eq. [3] with the oxide titration data shown in Fig. 1, yields the surface charge vs. pH behavior shown in Fig. 2. This procedure assumes that the only reactions involved in the system are with the hydronium or hydroxyl ions either sorbing or desorbing from the oxide surface, and that no reactions exist in the aqueous bulk solution. The ZPC is at the intersection of the three ionic strength conditions as anticipated by Eq. [5]. The surface charge scale is shifted to set a value of zero charge at the intersection in Fig. 2.

Rather than solving Eq. [3] for each data point, the solution to the equation of electroneutrality may be done graphically. That is, if a reference solution without the colloid sample is titrated, then the surface charge would be

$$\begin{aligned} \sigma_o &= (C_A - C_B)_{\text{sample}} - (H^+ - OH^-)_{\text{sample}} \\ -0 &= (C_A - C_B)_{\text{ref}} - (H^+ - OH^-)_{\text{ref}} \\ \sigma_o &= (C_A - C_B)_{\text{sample}} - (C_A - C_B)_{\text{ref}} \\ &\quad + (H^+ - OH^-)_{\text{ref}} - (H^+ - OH^-)_{\text{sample}} \end{aligned} \quad [7]$$

and if $(H^+ - OH^-)_{\text{ref}} = (H^+ - OH^-)_{\text{sample}}$, such as by subtracting the reference curve from the sample curve at a given pH value, then

$$\begin{aligned} \sigma_o &= (C_A - C_B)_{\text{sample}} - (C_A - C_B)_{\text{ref}} \\ &= \Delta(C_A - C_B). \end{aligned} \quad [8]$$

Method II uses an electrolyte solution of NaClO_4 , in concentrations equivalent to those used for the sample titrations, as the reference curve. The open symbols in Fig. 3 show the resulting titration curves of the reference electrolyte solutions. For comparison with method I, the solid line in Fig. 3 (labeled T) shows the resulting pH values if $(C_A - C_B)_{\text{ref}} = (H^+ - OH^-)_{\text{ref}}$. The solid line and the electrolyte solution titration curves are almost identical emphasizing the indifference of the electrolyte solutions towards the acid or base additions. At a given pH value, the difference

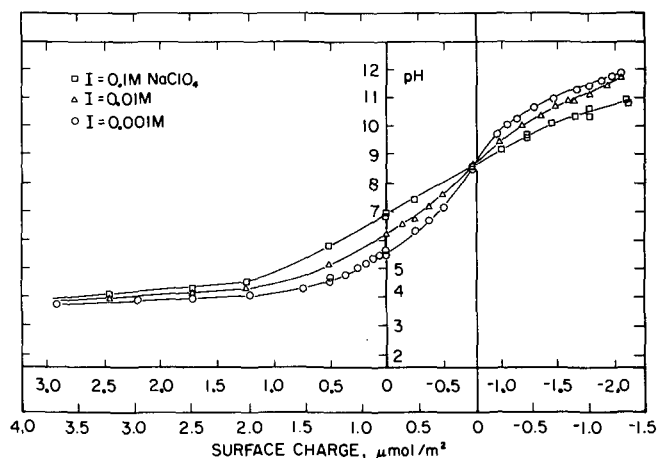


Fig. 2. Surface charge vs. pH of $\gamma\text{-Al}_2\text{O}_3$ at various ionic strengths. Produced from batch titration data (Fig. 1) and Eq. [3].

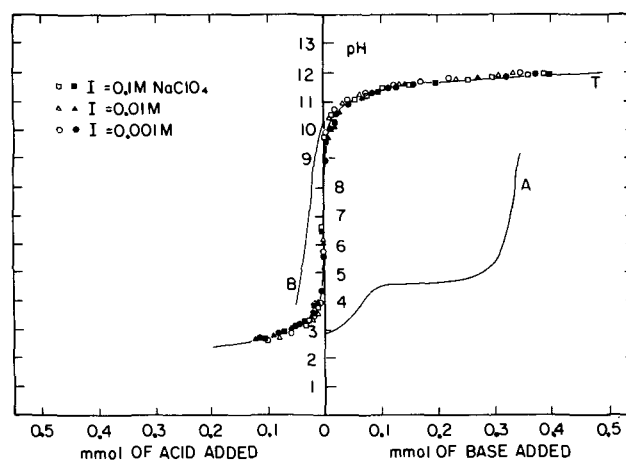


Fig. 3. Titration of reference solutions at various ionic strengths. Solid line 'T' is the theoretical curve. Open symbols are for titration of reference electrolyte solutions. Solid symbols are for titration of ZPT supernatant solutions. Solid line 'A' is titration of acidic supernatant (pH = 2.89). Solid line 'B' is titration of basic supernatant (pH = 10.34).

between the reference curve (from Fig. 3) and the corresponding sample curve (from Fig. 1) yields surface charge vs. pH curves (not shown). As expressed earlier by Eq. [5], the pH value where the curves intersect each other is the ZPC.

Equation [2] itemizes the negative and positive charges expected to be present in the system studied. However, Eq. [2] is not complete due to the $\gamma\text{-Al}_2\text{O}_3$ colloid partially dissolving and introducing Al species into the solution phase. The actual form and concentration of the dissolved Al is pH dependent. To complete Eq. [2], knowledge of the solubility of the colloid and speciation of the dissolved species is required. This information is not always easy to obtain and small errors are often not acceptable.

If a proper reference is chosen which contains an adequate sample of the species in solution, then subtracting the sample curve from the reference curve at a given pH value would also yield Eq. [8]. In method III the reference chosen was the ZPT supernatant, or the colloidal suspension with zero acid or base additions. The solid symbols in Fig. 3 show the titration of the supernatant solutions at various ionic strengths.

Subtracting the sample curves (from Fig. 1) from the corresponding supernatant curves (from Fig. 3) also produce surface charge vs. pH relationships (not shown).

Surface charge analyses using methods I, II, and III resulted in very similar convex curves; the ZPC is at pH 8.60. According to Eq. [8], the pH of ZPC should coincide with the surface charge value equal to zero. Instead, the curves intersect at $-0.775 \mu\text{mol m}^{-2}$ for methods I and II, and at $-0.725 \mu\text{mol m}^{-2}$ for method III. Huang (1981) comments that if the intersection is located in the alkaline region of the titration then there is specific cationic adsorption taking place. If the intersection is located in the acidic region, then there is specific anionic adsorption taking place. Finally, if the pH of ZPC is at $\sigma_o = 0$, then there is no specific adsorption of electrolytes present. The possibility of specific cationic adsorption exists for all three methods used in this study.

However, these methods are not free of problems. Each titration curve has an undetermined amount of error. Subtracting a sample titration curve from its corresponding reference curve compounds the errors present. Thus, since all the results are nearly the same, method I is preferred over method II or III. At the pH of ZPC, the interference due to variations in electrolyte concentrations in the solution is assumed to be minimal. The interference due to solubility of the sample will also be at a minimum at the pH of ZPC (Parks and de Bruyn, 1962). Therefore, it is not recommended that a reference solution be subtracted from the sample titration curve if the ZPC value is the only parameter desired.

Backtitration Technique (Method IV)

The graphical solutions to Eq. [1] used in methods II and III are still inadequate. The surface charge behavior analyses showed that the colloidal surface charge increases to extremely high negative or positive values (Fig. 2). This is not realistic since the surface cannot accommodate such large charges. Lyklema (1968) points out a contradiction between surface charge observations and electrokinetic behavior of Si

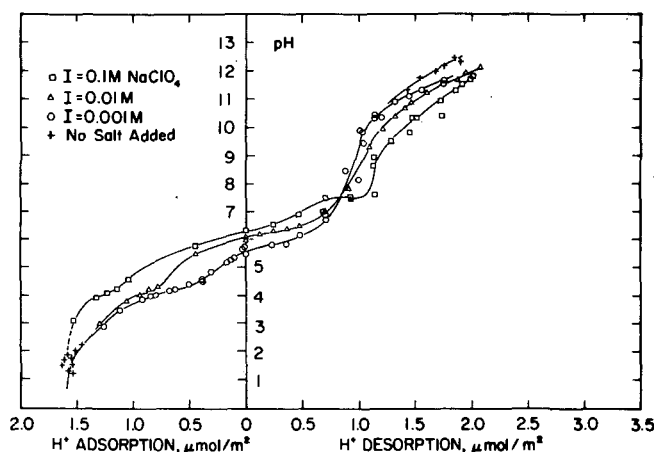


Fig. 4. Apparent adsorption or desorption of H^+ ion on $\gamma\text{-Al}_2\text{O}_3$ at various ionic strengths vs. pH of supernatant. Produced from batch titration data (Fig. 1) and backtitration to pH 7 for each data point.

and Fe oxides. The solution to this problem lies in properly defining the system.

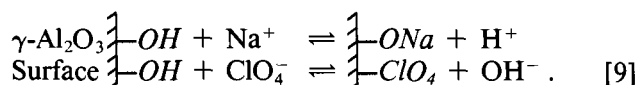
The solubility of the $\gamma\text{-Al}_2\text{O}_3$ was not properly accounted for in method III. It is pH dependent, and various concentrations of Al in solution exert different effects on the shape of the colloidal titration curve shown in Fig. 1. The titration of an acidic supernatant (labeled A) is different from the titration of a basic supernatant (labeled B), both of which are shown in Fig. 3 for $I = 0.001 \text{ M}$. Both A and B are also different from the titration of the ZPT supernatant shown by the solid symbols in Fig. 3. Parker et al. (1979) observe that the dissolution of Al would consume H^+ ions without affecting the surface charge.

Method IV treats each sample individually. The reference of each sample is the supernatant of the particular sample studied. All possible species existing in the aqueous phase will form part of the reference. Each supernatant is backtitrated to a common end point, and the mmol consumed is the alkalinity or acidity of the aqueous phase. Subtracting the sample's acid (or base) concentration from the concentration of base (or acid) used in the backtitration will yield the amount of acid (or base) consumed by the surface. Stumm and Morgan (1981) give a rigorous analysis of alkalimetric and acidimetric titration curves. The "phenolphthalein end point" is at pH values near 8.3, but lowers with increasing amounts of soluble Al in solution (down to 7.9) or with increasing CO_2 loss to the atmosphere during titration (down to 7-7.3). The end point used for each run was fixed at pH 7.00 for simplicity since few analytical errors were observed using this value. Equation [6] was applied to balance the amount of acid (or base) added with the amount of base (or acid) consumed by the supernatants. Hohl and Stumm (1976) also employed a similar procedure to determine the maximum exchange capacity of a $\gamma\text{-Al}_2\text{O}_3$. They did not, however, run the procedure at various pH values. They also subtracted the calculated dissolved Al concentration which is not necessary since the backtitration takes this value into account.

Figure 4 shows the H^+ adsorption values obtained. The various ionic strength runs intersect at a pH value of 7.50 with a H^+ desorption value of $0.85 \mu\text{mol m}^{-2}$. This point will be considered the PZSE for this particular system studied. This is close to the intersection value observed with the singular reference curve methods discussed earlier.

At higher ionic strength the curves in Fig. 4 are flattened, but they still follow closely the low ionic strength curve. These shifts are probably not due to compression of the double layer, but rather due to the competitive behavior of the Na^+ ions with H^+ ions, and ClO_4^- ions with OH^- ions. At high Na^+ concentrations, if a Na^+ ion is specifically adsorbed competitively over a H^+ ion, then the figure would show an increase in apparent H^+ desorption. At high ClO_4^- concentrations, if a ClO_4^- ion replaces a OH^- ion on the colloidal surface by an anion exchange phenomenon, then the figure would show an increase in apparent H^+ adsorption. Each OH^- ion removed from the surface by anion exchange would neutralize a H^+ ion in solution and this would not be readily distinguished from H^+ ion removal by adsorption. Thus, at

the PZSE the amounts of H^+ and OH^- displaced from the surface sites are equal in magnitude and no apparent change in pH is detected with changes in the salt concentration. The electrolytic reactions may be shown schematically as follows



This is in agreement with Perrott et al. (1976) who found for several soils that the amount of OH^- released by NaF was dependent on pH and salt concentration, and that this correlated well with the amount of Al present in the soils. Ferris and Jepson (1975) found that adsorption of Cl^- and Na^+ on gibbsite varied dramatically with pH.

The magnitude and position of the observed breaks are currently being studied. The proton isotherms observed in Fig. 4 may be described in terms of speciation of the oxide surface with respect to pH. However, a proton sorption model would be needed to properly interpret the data. The problem arises in that the ZPC is not the same as the PZSE, the surface charge is not equivalent to the proton isotherms, and the high ionic strength data shown in Fig. 4 may be only an apparent proton isotherm due to cation and anion competition. The presence of titration breaks, plateaus, and maximum adsorption capacities (as observed at the low pH values, and assumed also present for the high pH values) are characteristics which emphasize the presence of unique adsorption sites, and their interaction with the solution phase.

It should also be noted that the underlying assumption of the backtitration technique and the singular reference curve methods is that the missing charge in the solution phase must be present on the surface studied so as to maintain electroneutrality in the system. The singular reference curve methods assume that the surface charge and proton sorption are equivalent. This assumption may prove to be controversial in view of the preliminary results observed in Fig. 4.

CONCLUSIONS

A ZPC of 8.60 was determined for the $\gamma\text{-Al}_2\text{O}_3$ that we studied. This value is defined as the pH value where surface positive and negative charges are equal, and was determined experimentally by titration analyses.

The purpose of subtracting a reference titration curve from the sample titration curve is to graphically solve Eq. [1] so as to maintain electroneutrality. If a proper reference is chosen, then the resulting curve should be an isotherm of surface charge vs. pH. The theoretical solution to Eq. [1] produces very high positive and negative values (Fig. 2). When the reference chosen is the electrolyte solution in which the solid phase is suspended, the resulting isotherm is also convex at high and low pH values. This was also observed when the reference chosen was the supernatant of the sample of zero acid or base additions. None of these three singular reference curve approaches show definite titration breaks, nor are they realistic at extreme pH values.

To properly adjust for the changes in solubility of the $\gamma\text{-Al}_2\text{O}_3$ as the pH changes, a backtitration technique specific to each sample was found to more accurately reveal the adsorption behavior of H^+ on the colloidal surface (Fig. 4). The Na^+ ions are assumed to compete with H^+ ions for the adsorption sites while the ClO_4^- ions are assumed to undergo anion exchange with the surface-OH groups. A PZSE value of 7.50 was determined for the colloid. Though a sorption model is not yet developed which will allow one to make further conclusions, the presence of titration breaks and maximum adsorption capacities emphasize the presence of unique adsorption sites.

REFERENCES

- Bowden, J.W., A.M. Posner, and J.P. Quirk. 1977. Ionic adsorption on variable charge mineral surfaces. Theoretical-charge development and titration curves. *Aust. J. Soil Res.* 15:121-136.
- Bradfield, R. 1923. The nature of the acidity of the colloidal clay of acid soils. *J. Am. Chem. Soc.* 45:2669-2678.
- Bradfield, R. 1924. The effect of the concentration of colloidal clay upon its hydrogen ion concentration. *J. Phys. Chem.* 28:170-175.
- Chapman, D.L. 1913. A contribution to the theory of electrocapillarity. *Philosophical Mag. and J. of Sci. (series 6)* 25:475-481.
- Ferris, A.P., and W.B. Jepson. 1975. The exchange capacities of kaolinite and the preparation of homoionic clays. *J. Colloid and Interf. Sci.* 51:245-259.
- Grahame, D.C. 1947. The electrical double layer and the theory of electrocapillarity. *Chem. Rev.* 41:441-501.
- Gouy, G. 1910. Sur la constitution de la charge électrique à la surface d'un électrolyte. *J. Phys. Radium (série 4)* 9:457-468.
- Hendershot, W.H. 1978. Measurement technique effects of the value of zero point of charge and its displacement from zero point of titration. *Can. J. Soil Sci.* 58:439-442.
- Hohl, H., and W. Stumm. 1976. Interaction of Pb^{2+} with hydrous $\gamma\text{-Al}_2\text{O}_3$. *J. Coll. Interf. Sci.* 55:281-288.
- Huang, C.P. 1981. The surface acidity of hydrous solids. p. 183-217. *In* Marc A. Anderson and Alan J. Rubin (ed.) *Adsorption of inorganics at solid-liquid interfaces*. Ann Arbor Science, Ann Arbor, MI.
- Lyklema, J. 1968. The structure of the electrical double layer on porous surfaces. *J. Electroanal. Chem. Interfacial Electrochem.* 18:341-348.
- Mattson, S. 1931. The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32:343-365.
- Nernst, W. 1889. Die elektromotorische Wirksamkeit der Ionen. *Zeitschrift für Physikalische Chemie (Leipzig)* 4:129-181.
- Parfitt, R.L. 1980. Chemical properties of variable charge soils. p. 167-194. *In* B.K.G. Theng (ed.) *Soils with variable charge*. N.Z. Soc. of Soil Sci., Lower Hutt, New Zealand.
- Parker, J.C., L.W. Zelazny, S. Sampath, and W.G. Harris. 1979. A critical evaluation of the extension of zero point of charge (ZPC) theory to soil systems. *Soil Sci. Soc. Am. J.* 43:668-674.
- Parks, G.A. 1965. The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.* 65:177-198.
- Parks, G.A. 1967. Aqueous surface chemistry of oxides and complex oxide minerals. Isoelectric point and zero point of charge. *Adv. Chem. Ser.* 67:121-160.
- Parks, G.A., and P.L. de Bruyn. 1962. The zero point of charge of oxides. *J. Phys. Chem.* 66:967-973.
- Perrott, K.W., B.F.L. Smith, and R.H.E. Inkson. 1976. The reaction of fluoride with soils and soil minerals. *J. Soil Sci.* 27:58-67.
- Schofield, R.K. 1949. Effect of pH on electric charges carried by clay particles. *J. Soil Sci.* 1:1-8.
- Sposito, G. 1981. The operational definition of the zero point of charge in soils. *Soil Sci. Soc. Am. J.* 45:292-297.
- Stumm, W., and J.J. Morgan. 1981. *Aquatic chemistry*, 2nd. ed. John Wiley & Sons, Inc., New York.
- Veitch, F.P. 1904. Comparison of methods for the estimation of soil acidity. *J. Am. Chem. Soc.* 26:637-662.
- Westall, J., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Adv. Coll. Interf. Sci.* 12:265-294.
- Yopps, J.A., and D.W. Fuerstenau. 1964. The zero point of charge of alpha-aluminum. *J. Colloid Sci.* 19:61-71.