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SURFACE CHARGE PROPERTIES OF KAOLINITE

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Abstract—The surface charge components of 2 Georgia kaolinites of differing degrees of crystallinity (KGa-1 and KGa-2) were determined using procedures based on charge balance concepts. Permanent structural charge density (σ_0) was determined by measuring the surface excess of Cs, which is highly selective to permanent charge sites. The values of σ_0 determined were -6.3 ± 0.1 and -13.6 ± 0.5 mmol kg^{-1} for kaolinites KGa-1 and KGa-2, respectively. The net proton surface charge density (σ_H) was determined as a function of pH by potentiometric titration in 0.01 mol dm^{-3} LiCl. Correction from apparent to absolute values of σ_H was made by accounting for Al release during dissolution, background ion adsorption and charge balance. Lithium and Cl adsorption accounted for the remainder of the surface charge components. Changes in surface charge properties with time were measured after mixing times of 1, 3 and 15 h, the latter representing "equilibrium". Time-dependent behavior is believed to be caused by mineral dissolution followed by readsorption or precipitation of Al on the mineral surface. Both the point of zero net charge (p.z.n.c.) and the point of zero net proton charge (p.z.n.p.c.) changed with mixing time, generally increasing. The "equilibrium" p.z.n.c. values were approximately 3.6 for KGa-1 and 3.5 for KGa-2, whereas the corresponding p.z.n.p.c. values were about 5.0 and 5.4. The p.z.n.c. results were in good agreement with previous studies, but the values of p.z.n.p.c. were higher than most other values reported for specimen kaolinite.

Key Words—Dissolution, Kaolinite, Point of Zero Charge, Potentiometric Titration, Proton Surface Charge, Structural Charge, Surface Charge, Surface Chemistry.

INTRODUCTION

Knowledge of the surface charge characteristics of kaolinite is essential to deciphering the mechanisms of its reactions with xenobiotic compounds (Haderlein and Schwarzenbach 1993) and mapping the pathways of its weathering reactions in sediments and soils (Stumm 1992; Chorover and Sposito 1995b). Prominent among these characteristics are the density of surface charge created by isomorphic substitutions in a mineral structure (denoted σ_0) and that created by proton adsorption and desorption reactions with a contiguous aqueous solution (denoted σ_H). The sign of σ_0 is always negative for kaolinite, arising either directly from Al(III) substitution for Si(IV) in the tetrahedral sheet of the mineral (Bolland et al. 1976), or indirectly from isomorphic substitutions in 2:1 layer type clay mineral inclusions (Lim et al. 1980; Jepson 1984; Kim et al. 1996). The sign of σ_H varies with aqueous solution pH, taking on a zero value at the p.z.n.p.c. (Sposito 1992) and becoming negative at higher pH values.

Significant variability exists among published experimental studies of the surface charge behavior of specimen kaolinites. Its points of zero charge (Sposito 1992) offer a prototypical example, as shown in Table 1. The data in Table 1 are not intended to be comprehensive, but only to illustrate the wide range of pH values in the published literature. Isoelectric points (i.e.p.; pH value at which the electrophoretic mobility is zero) range from 3.0 to 5.0, while p.z.n.p.c. values vary from 3.0 to above 7. Some of the disagreement can be attributed to differences in sample preparation and to the use of different models to interpret data, but the breadth of the distribution of pH values in Table 1 is much larger than what is typical for specimen oxide minerals. Examples are i.e.p. = 9.2 ± 0.6 and p.z.n.p.c. = 8.5 ± 0.2 for γ-Al_2O_3, based on data compiled by Goldberg et al. (1996).

Recently Chorover and Sposito (1993, 1995a), building on work by Charlet and Sposito (1987) and Anderson and Sposito (1991, 1992), have developed and applied an experimental methodology for measuring surface charge components and testing the resulting data for consistency with the law of surface charge balance:

$$\sigma_0 + \sigma_H + \Delta q = 0 \qquad [1]$$

where Δq is the net adsorbed ion surface charge density, the difference of adsorbed cation and anion charge, exclusive of that contributed by adsorbed protons and hydroxide ions (Sposito 1992). In this paper, we present the first application of this new methodology to specimen kaolinites of varying crystallinity. The primary objectives of our research were to determine the surface charge characteristics of specimen kaolinite unambiguously and to ascertain the nominal effects of degree of crystallinity.

MATERIALS AND METHODS

Stock Suspensions

Samples (0.2 kg) of 2 specimen kaolinites, KGa-1 and KGa-2, described as "well crystallized" and

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Table 1. Points of zero charge† reported for kaolinite.

	Value	Reference
Isoelectric point (i.e.p.)	3.3, 4.6	Parks (1967)
	5.0	Ferris and Jepson (1975)
	4.25	Carroll-Webb and Walther (1988)
	3	Braggs et al. (1994)
Point of zero net proton charge (p.z.n.p.c.)	<4	Schindler et al. (1987)
	4.5	Motta and Miranda (1989)
	4.5	Xie and Walther (1992)
	5.0	Zhou and Gunter (1992)
	7.5	Wieland and Stumm (1992)
	3.0	Braggs et al. (1994)
	4.66	Sverjensky (1994)
Point of zero net charge (p.z.n.c.)	4.8	Ferris and Jepson (1975)
	<4	Bolland et al. (1976)
	4	Zhou and Gunter (1992)

† i.e.p. = pH value at which electrophoretic mobility = 0. p.z.n.p.c. = pH value at which $\sigma_H = 0$. p.z.n.c. = pH value at which $\Delta q = 0$.

"poorly crystallized" by van Olphen and Fripiat (1979), were obtained from the Source Clays Repository of the Clay Minerals Society. The samples were suspended repeatedly in 1 mol dm^{-3} NaCl/HCl or LiCl/HCl solution at pH 3. After centrifugation of the suspension at 10,000 RCF, the supernatant solution was discarded and replaced with fresh solution. After the supernatant solution pH value had dropped to 3, the samples were suspended in non-acidified LiCl solution and centrifuged again. As the supernatant solution pH value approached 5, the ionic strength was progressively lowered to that used in the titration experiments (0.01 mol dm^{-3}). The Li-saturated kaolinite stock suspensions were stored at pH 5.0–5.5 in sealed 0.25-L centrifuge bottles.

Permanent Structural Charge Density (σ_0)

The method of Chorover and Sposito (1993) was followed to determine σ_0 for each kaolinite sample. Briefly, a portion of kaolinite stock suspension was saturated with Cs by repeated washing in CsCl, with a final supernatant solution ionic strength of 0.05 moles per kilogram of solution (molinity, $\hat{m}$). Triplicate samples were prepared containing 10 g dry kaolinite per kg solution in 0.05 $\hat{m}$ CsCl at pH 5.5–6.0. Following centrifugation, the supernatant solution was discarded and the remaining entrained CsCl solution was removed by washing with ethanol. The samples were then dried at 65 °C for 48 h to enhance formation of inner-sphere Cs surface complexes. Next, the samples were washed in 0.01 $\hat{m}$ LiCl solution to remove outer-sphere surface complexes of Cs. The clay suspensions were centrifuged, and the supernatant LiCl solution was removed for analysis, leaving only the kaolinite sample and entrained LiCl solution. Finally, Cs was twice-extracted with 1 $\hat{m}$ ammonium acetate (NH_4OAc). The LiCl and NH_4OAc solutions were analyzed for Cs by atomic emission spectroscopy (Perkin Elmer Model 2380). Permanent structural charge density, σ_0, was calculated as minus the difference between moles Cs in the NH_4OAc extract and moles Cs in the entrained LiCl solution, per kg of dry kaolinite.

Proton Titration and Ion Adsorption Measurements

Samples of the stock suspension containing 350 mg of dry kaolinite were placed in 35-mL centrifuge tubes. To each tube, 0.01 $\hat{m}$ LiCl containing a predetermined amount of 0.01 $\hat{m}$ HCl or LiOH was added so that the total mass of solution was 35 g. A given LiCl/HCl (or LiCl/LiOH) electrolyte solution mixed with kaolinite represents a single point in a discontinuous proton titration. Each mixture was replicated once, with a kaolinite-free blank prepared for each replicate. An Orion model 8102BN combination pH electrode was calibrated by Gran titration (Gran 1952; Chorover and Sposito 1993), so that electrode output could be converted directly to hydrogen ion concentration ($[H^+]$). Proton concentration instead of activity was determined in order to avoid the use of activity-coefficient models (Chorover and Sposito 1995a).

The samples were mixed by slow rotation (about 7 revolutions per min) for periods of 1, 3 or 14–16 h. Following centrifugation, the supernatant solution was carefully transferred to 60-mL high density polyethylene (HDPE) bottles. Electrode output was read on an aliquot of each solution (sample and blank), then converted to $[H^+]$.

The samples were equilibrated with 1 $\hat{m}$ NH_4NO_3 on a reciprocal shaker for at least 30 min to extract adsorbed ions. Following centrifugation, the supernatant solution for each sample was transferred to a tared 60-mL HDPE bottle. This procedure was repeated, with the second supernatant solution added to the first. The NH_4NO_3 and LiCl solutions were analyzed for Li, Al and Si by inductively coupled argon plasma spectroscopy (ICP, Perkin Elmer Model P-40). Selected samples were also analyzed by ICP for Fe, but the resultant surface excess of Fe was negligible compared to those for the other ions, so these data are not reported. The solutions were analyzed for Cl using a Buchler model 442–5000 digital chloridometer.

DATA ANALYSIS

The apparent proton surface charge density, $\sigma_{H,\mathrm{titr}}$, was calculated as (Chorover and Sposito 1993):

$$\sigma_{H,\mathrm{titr}} = M_{\mathrm{soln}}\left\{([H^+]_b - [H^+]_s) - \left(\frac{K_w}{[H^+]_b} - \frac{K_w}{[H^+]_s}\right)\right\} \quad [2]$$

where M_{soln} is the mass of electrolyte solution (per unit dry mass) equilibrated with kaolinite, $[H^+]$ is the so-

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lution proton concentration, K_w is the dissociation product of water (10^{-14}), and the subscripts s and b refer to sample and blank solutions, respectively. For highly acidic samples in which there was significant Al release caused by kaolinite dissolution (generally at pH 3–4), $\sigma_{H,titr}$ was corrected for Al in solution by the equation (Schindler et al. 1987; Wieland and Stumm 1992):

$$\sigma_{H,titr,Al} = \sigma_{H,titr} - M_{soln}\{3[Al^{3+}] + 2[AlOH^{2+}] + [Al(OH)_2^{+}]\} \quad [3]$$

where the concentrations of the 3 Al species were calculated using the total Al concentration in solution, the pH value and published Al hydrolysis constants (Nordstrom and May 1996). This correction accounts for protons that would be consumed in Al release and generated by Al hydrolysis at pH $\leq$ 6.

The apparent proton surface charge density in Equation 2 or 3 is corrected relative to the blank solution only, and thus does not include a correction for the unknown value of σ_H at the beginning of titration (Lyklema 1987; Sposito 1992), which cannot be measured using proton balance on the aqueous solution phase only. One way to make this correction is to note the definition (Charlet and Sposito 1987):

$$\sigma_H \equiv \sigma_{H,titr,Al} - \sigma_{H,titr,Al}\ (\text{p.z.n.p.c.}) \quad [4]$$

where the second term on the right side is the value of the apparent proton surface charge density (with Al hydrolysis correction as in Equation 3) at the p.z.n.p.c., a constant independent of pH. The combination of Equations 1 and 4 yields the charge balance expression (Anderson and Sposito 1992):

$$\sigma_{H,titr,Al}\ (\text{p.z.n.p.c.}) = \sigma_{H,titr,Al} + \sigma_0 + \Delta q \quad [5]$$

at any pH value. By averaging $\sigma_{H,titr,Al}$ (p.z.n.p.c.) values determined at all points of a titration curve, we may calculate σ_H with the expression:

$$\sigma_H = \sigma_{H,titr,Al} - \langle\sigma_{H,titr,Al}\ (\text{p.z.n.p.c.})\rangle_{ave} \quad [6]$$

The surface excess of a given ion i, n_i (mol kg^{-1}), was calculated by the equation (Chorover and Sposito 1993):

$$n_i = N_{i,NH_4NO_3} - M_{entr}\hat{m}_i \quad [7]$$

where N_i is moles of species i, per unit mass of dry kaolinite, extracted in the NH_4NO_3 step; M_{entr} is the mass of entrained LiCl solution per unit kaolinite mass prior to the NH_4NO_3 step; and $\hat{m}_i$ is the molinity of species i in the LiCl solution. The adsorbed ion charge density, q_i (mol$_c$ kg^{-1}), is the product, $n_i \cdot |z_i|$, where z_i is the valence of species i. Lithium and Cl surface excesses were expressed as q values and subtracted to estimate Δq in Equation 1.

The p.z.n.p.c. was calculated in 2 ways (Anderson and Sposito 1992). One was linear regression of σ_H (Equation 6) against $-\log[H^+]$ to find its value when $\sigma_H = 0$ (x-intercept). The other was by plotting the sum ($\Delta q + \sigma_0$) against $-\log[H^+]$ and determining, by linear regression, its value when the sum equals zero (x-intercept). By charge balance (Equation 1), this $-\log[H^+]$ value should equal p.z.n.p.c., thus providing a test of mutual consistency between titration and ion adsorption data, because ($\Delta q + \sigma_0$) is also used in the calculation of σ_H (p.z.n.p.c.) (Equations 5 and 6). The p.z.n.p.c. was calculated by fitting Δq to a linear function of $-\log[H^+]$ with regression analysis, then solving the resultant function for the condition $\Delta q = 0$ (x-intercept).

RESULTS AND DISCUSSION

Permanent Structural Charge

The values of σ_0 obtained for kaolinites KGa-1 and KGa-2 were -6.3 ± 0.1 and -13.6 ± 0.5 mmol$_c$ kg^{-1}. Bolland et al. (1976) reported a σ_0 value of -15 ± 5 mmol$_c$ kg^{-1} for kaolinite API-9, a sedimentary reference clay mineral obtained from American Petroleum Institute Project No. 9, and -17 ± 5 mmol$_c$ kg^{-1} for St. Austell kaolinite, a hydrothermal clay mineral to which Ferris and Jepson (1975) assigned a σ_0 value of zero. Wieland and Stumm (1992) estimated that σ_0 for St. Austell kaolinite lies between -20 and -50 mmol$_c$ kg^{-1}. This divergence of results further exemplifies the variability in published surface charge characteristics for kaolinite, as discussed in connection with Table 1.

Lim et al. (1980) determined the "Cs retention capacity", defined as the difference between adsorbed Cs^+ displaced by NH_4^+ and that displaced by Ca^{2+}, for 7 Georgia kaolinites similar to kaolinites KGa-1 and KGa-2. This quantity was interpreted by Lim et al. (1980) as a measure of $|\sigma_0|$. It was found to have a significant correlation ($R^* = 0.93$) with specific surface area and with the difference between the Cs^+ and K^+ surface excesses, which fact was concluded to reflect the influence of weathered micaceous inclusions. Correlations between estimates of the content of these inclusions and Cs retention capacity led Lim et al. (1980) to suggest that σ_0 for kaolinite that is free of inclusion would lie in the range 0 to -10 mmol$_c$ kg^{-1}. This range is consistent with the σ_0 values determined in the present study. The specific surface areas of KGa-1 and KGa-2 kaolinite are 8.8 and 21.6 m^2 g^{-1}, (S. Goldberg, personal communication, 1995), in consonance with the positive correlation between $|\sigma_0|$ and specific surface area observed by Lim et al. (1980). Kim et al. (1996) concluded, on the basis of ^{133}Cs nuclear magnetic resonance spectra, X-ray photoelectron spectra and transmission electron micrographs, that Cs^+ strongly adsorbed by KGa-1 kaolinite is present in a very small quantity of smectite-like interlayers interstratified with the 1:1 clay mineral layers. This spectral evidence also supports the interpretation of

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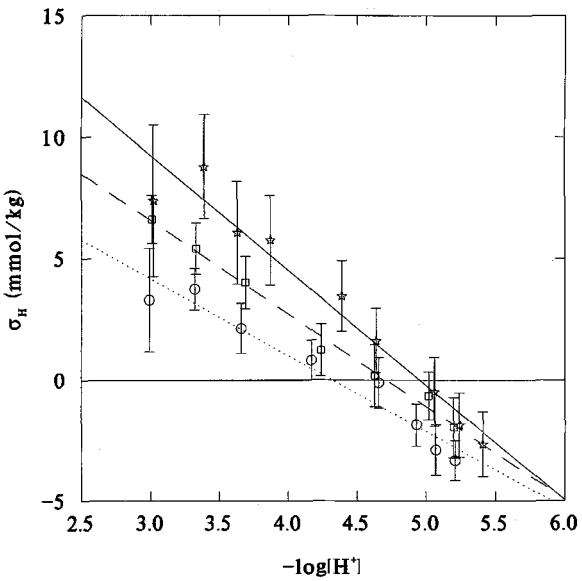


Figure 1. Net proton surface charge density (σ_H) plotted against $-\log[H^+]$ for kaolinite KGa-1. A least-squares linear regression line is drawn through each data set. Equilibration times: circle and dotted line = 1 h, square and dashed line = 3 h, star and solid line = 14–16 h. The intersection of the regression line with the horizontal line $\sigma_H = 0$ represents the p.z.n.p.c.

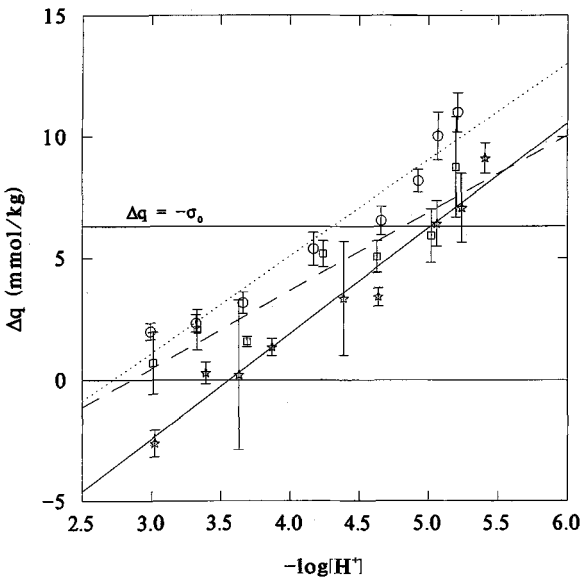


Figure 2. Net adsorbed ion charge (Δq) plotted against $-\log[H^+]$ for kaolinite KGa-1. Equilibration times: circle and dotted line = 1 h, square and dashed line = 3 h, star and solid line = 14–16 h. The intersection of the regression line with the horizontal line $\Delta q = 0$ represents the p.z.n.p.c.; intersection with the horizontal line $\Delta q = -\sigma_0$ represents the p.z.n.p.c.

our Cs adsorption data as a quantitative measure of σ_0 associated with siloxane surfaces.

Surface Charge Balance

Graphs of σ_H (Equation 6) and Δq (based on Equation 7) plotted against $-\log[H^+]$ are presented in Figures 1 and 2 for kaolinite KGa-1 and in Figures 3 and 4 for kaolinite KGa-2. It is evident (Figures 1 and 3) that σ_H is less positive for KGa-1 than KGa-2 at any aqueous proton concentration in the range investigated. There is also a noticeable increase in σ_H with time of equilibration, as observed also by Wieland and Stumm (1992), who found no significant change in σ_H after 10 h equilibration. On the basis of this latter result, the data for 14–16 h equilibration in the present study can be interpreted as "equilibrium" values. There is some tendency for Δq to decrease with equilibration time, and for Δq to be less positive for KGa-1 than KGa-2 at any proton concentration (Figures 2 and 4). These differences in σ_H and Δq between the 2 kaolinites correlate with the differences in their specific surface area.

Surface charge balance (Equation 1) implies that a graph of Δq against σ_H should be a straight line with slope equal to -1.0 and y-intercept equal to $|\sigma_0|$ (Chorover and Sposito 1995a). The results of a linear regression analysis of the (Δq, σ_H) data obtained for both kaolinites and the 3 equilibration times are listed in Table 2. All linear correlations were statistically sig-

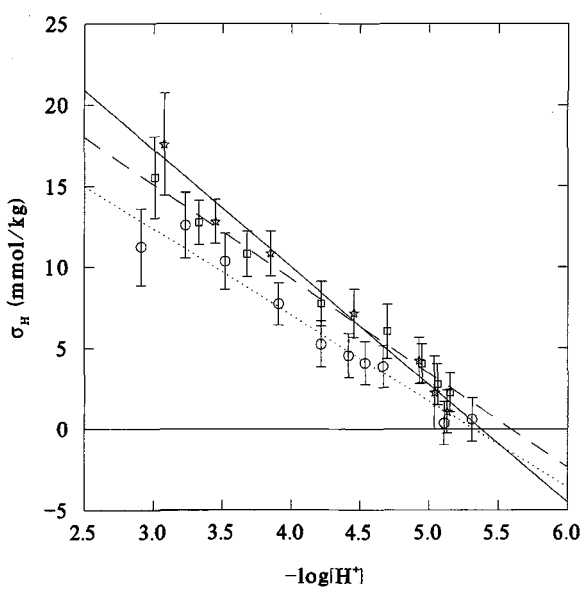


Figure 3. Net proton surface charge density (σ_H) plotted against $-\log[H^+]$ for kaolinite KGa-2. Equilibration times: circle and dotted line = 1 h, square and dashed line = 3 h, star and solid line = 14–16 h. The intersection of the regression line with the horizontal line $\sigma_H = 0$ represents the p.z.n.p.c.

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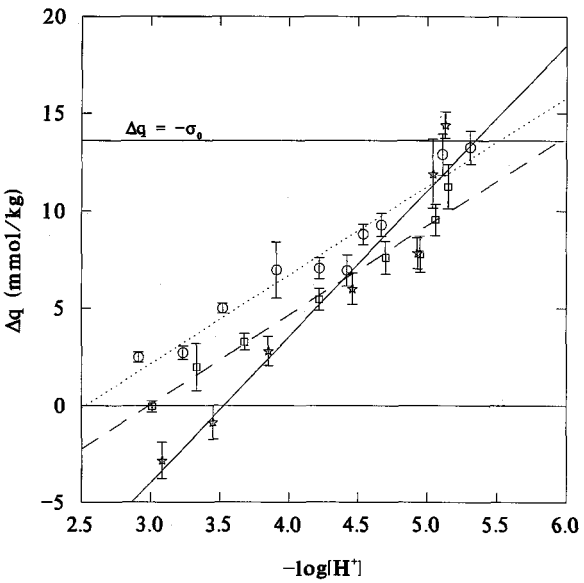


Figure 4. Net adsorbed ion charge (Δq) plotted against $-\log[H^+]$ for kaolinite KGa-2. Equilibration times: circle and dotted line = 1 h, square and dashed line = 3 h, star and solid line = 14–16 h. The intersection of the regression line with the horizontal line $\Delta q = 0$ represents the p.z.n.c.; intersection with the horizontal line $\Delta q = -\sigma_0$ represents the p.z.n.p.c.

nificant ($p = 0.05$). The regression slopes and y-intercepts agreed with their theoretical values within a $p = 0.05$ confidence interval (Steel and Torrie 1960). Thus, consistency with surface charge balance, which has not been demonstrated experimentally in any previous study of the surface charge characteristics of specimen kaolinite, was achieved within the precision of our experiments.

Points of Zero Charge

Values of the p.z.n.c. and p.z.n.p.c. determined for kaolinites KGa-1 and KGa-2 after equilibration times of 1, 3 and 14–16 h are listed in Table 3. Within the precision of our experiments, p.z.n.p.c. values calculated from linear regression of σ_H on $-\log[H^+]$ agree with those calculated from linear regression of (Δq and σ_0) on $-\log[H^+]$, again demonstrating the internal consistency of the titration and ion adsorption data. For both kaolinites and any equilibration time, p.z.n.c. < p.z.n.p.c. as required by the law of surface charge balance whenever $\sigma_0 < 0$ (Sposito 1992).

The "equilibrium" p.z.n.p.c. for kaolinite KGa-1 is 4.99 ± 0.03 and that of KGa-2 is 5.36 ± 0.02, based on averaging the estimate pairs in Table 2. The p.z.n.p.c. for KGa-1 appears to increase with equilibration time (Figure 1), from about 4.3 at 1 h to about 5.0 at 14–16 h. This may be the result of alteration of the kaolinite surface under acidic conditions through time, in agreement with conclusions reached by Wieland and Stumm (1992). The p.z.n.p.c. for KGa-2 appears to change differently with increasing equilibration time: upward between 1 and 3 h, then downward after 14–16 h (Figure 3).

Table 2. Slope and intercept parameters† as determined by linear regression of Δq on σ_H (test of charge balance).

Kaolinite	Equilibration time (h)	Slope	Intercept (mmol$_c$ kg^{-1})
KGa-1	1	−1.25 ± 0.15	6.36 ± 0.40
	3	−0.85 ± 0.28	5.97 ± 1.03
	14–16	−0.86 ± 0.26	5.87 ± 1.28
Theoretical value:	∞	−1	6.3 ± 0.1
KGa-2	1	−0.83 ± 0.19	12.6 ± 1.4
	3	−0.79 ± 0.13	12.0 ± 1.1
	14–16	−1.03 ± 0.25	13.9 ± 2.4
Theoretical value:	∞	−1	13.6 ± 0.5

† Parameter value ± confidence interval ($p = 0.05$).

The p.z.n.c. also appears to increase with mixing time for both clay minerals, with "equilibrium" values of 3.56 for KGa-1 and 3.52 for KGa-2 (Figures 2 and 4, and Table 3). The values of q_{Li} ranged from 1.8 to 11 mmol$_c$ kg^{-1} and 5.0 to 18 mmol$_c$ kg^{-1} for KGa-1 and KGa-2 (data not shown), increasing with $-\log[H^+]$. The corresponding ranges for q_{Cl} were −0.2 to +5.2 and 2.7 to 8.1 mmol$_c$ kg^{-1} (data not shown), decreasing with increasing $-\log[H^+]$. In general, q_{Li} and q_{Cl} both decreased with increasing equilibration time for a given $-\log[H^+]$, although this trend was more marked for q_{Li}.

Braggs et al. (1994) found p.z.n.p.c. ≈ 3 for a Georgia kaolinite, far below the values reported in this study. A possible explanation for this result is that their equilibration time, although not reported, was likely on the order of minutes since the authors performed a continuous titration. Table 3 suggests that there is a decrease in p.z.n.p.c. with decreasing equilibration time. Schindler et al. (1987) observed p.z.n.p.c. ≈ 4.1 for kaolinite KGa-1 suspended in $NaClO_4$ at ionic strengths of 0.1 and 1.0 mol dm^{-3}, but their σ_H values for 0.01 mol dm^{-3} were consistently positive down to pH 4 (the experimental limit).

Table 3. Points of zero net proton charge (p.z.n.p.c.) and points of zero net charge (p.z.n.c.) for kaolinites KGa-1 and KGa-2.

Kaolinite	Equilibration time (h)	p.z.n.p.c. ($\sigma_0 + \Delta q = 0$)	p.z.n.p.c. ($\sigma_H = 0$)	p.z.n.c. ($\Delta q = 0$)
KGa-1	1	4.31	4.32	2.72
	3	4.81	4.73	2.84
	14–16	5.01	4.96	3.56
KGa-2	1	5.52	5.33	2.53
	3	5.95	5.60	2.98
	14–16	5.34	5.38	3.52

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The model applied by Schindler et al. (1987) predicted p.z.n.p.c. ≈ 4.8 at the lowest ionic strength, but the disagreement between the model predictions and experimental σ_H data was significant. As with Braggs et al. (1994), a short equilibration time in the experiments of Schindler et al. (1987) is a possible explanation of a lower p.z.n.p.c. Zhou and Gunter (1992) did not report an equilibration time but their titration data indicate p.z.n.p.c. ≤ 5 for kaolinite KGa-1, similar to the results in the present study. Sverjensky (1994) predicted p.z.n.p.c. = 4.66 for well crystallized kaolinite, based on a theoretical model involving crystal chemistry, solvation effects and electrostatic interactions.

Wieland and Stumm (1992) performed proton titration experiments on time scales similar to those in the present study. However, these authors assigned an "edge surface" p.z.n.p.c. equal to 7.5 on the basis of prior model dependent concepts of kaolinite acid-base chemistry. This ansatz was, in effect, the same as referencing $\sigma_{H,\text{titr}}$ to its measured value at pH 7.5 (see Equation 4). Thus, Wieland and Stumm (1992) determined a value for $\sigma_{H,\text{titr}}$ (p.z.n.p.c.) by selecting the value of p.z.n.p.c. on purely theoretical grounds. All of the other authors whose experimental p.z.n.p.c. values for kaolinite are given in Table 1 also have selected an a priori value for $\sigma_{H,\text{titr}}$ (p.z.n.p.c.), since they simply equated σ_H with the right side of Equation 2. If $\sigma_{H,\text{titr}}$ (p.z.n.p.c.) is indeed equal to zero, as this practice assumes, experimental measurements of the right side of Equation 5 will show this unambiguously, by charge balance.

Dissolution Effects

The release of Si and Al into the aqueous solution phase was an increasing function of equilibration time in our experiments, but did not change significantly with pH. The concentration of Si released by kaolinite KGa-2 (11–21 μm̂) was consistently higher than that released by kaolinite KGa-1 (5–14 μm̂), whereas Al concentrations for both kaolinites tended to be at or below 3 μm̂, close to the ICP detection limit. The values of n_{Al} and n_{Si} measured were highly variable. It is likely that NH_4^+ used in the extraction procedure removed structural Al and Si near the clay mineral surface, in addition to the Al and Si actually adsorbed to the surface; therefore, true Si and Al surface excesses could not be accurately estimated by our procedures.

The dominance of dissolved Si over Al during short-term kaolinite dissolution is contrary to the observations of Carroll-Webb and Walther (1988), who found the opposite relationship at pH < 6 for dissolution times less than 200 h. Our results do agree, however, with those of Wieland and Stumm (1992), who commented that the difference with Carroll-Webb and Walther (1988) may lie in the fact that the latter did not treat their KGa-1 sample with strong acid during preparation (see, for example, Buchanan and Oppenheim 1968). Carroll-Webb and Walther (1988) eventually did observe a shift into Si dominance after steady-state conditions were reached, in agreement with Wieland and Stumm (1992). The release of Si over Al may be related to Al adsorption by and/or Al hydroxide precipitation onto the kaolinite surface. Wieland and Stumm (1992) described their Al release data quantitatively with a model involving Al adsorption at pH ≤ 4.5 and amorphous Al hydroxide precipitation above pH 4.5. Charlet et al. (1993) have presented experimental data to demonstrate the ubiquity of Al adsorption on clay minerals and oxides at low pH and ionic strength. Dissolution followed by structural ion adsorption (and/or precipitation) onto the kaolinite surface would clearly alter the surface charge properties of the mineral and at least partially cause the observed migration of p.z.n.c. and p.z.n.p.c. with equilibration time (Table 3).

CONCLUSIONS

The calculated values of permanent structural charge density, σ_0, were -6.3 ± 0.1 and -13.6 ± 0.5 mmol kg^{-1} for kaolinites KGa-1 and KGa-2. Typical literature values are larger in absolute value, but may exceed those of pure kaolinite (Lim et al. 1980; Kim et al. 1996). The present data are believed to be the more accurate, because of the high selectivity of the index cation (Cs) for permanent charge sites and the relative quality of the kaolinite samples.

The values of p.z.n.c. and p.z.n.p.c. generally appeared to increase with equilibration time for both kaolinites (p.z.n.p.c. for KGa-2 was the exception). This variation is likely a result of dissolution and readsorption reactions at the kaolinite surface, thus creating a less-ordered peripheral layer having altered adsorption properties. Surface charge and adsorption studies in the future should include consideration of surface equilibration time. It is assumed in this study that the properties measured for the 14–16 h mixing time represented the "equilibrium" condition (see also Wieland and Stumm 1992).

The equilibrium p.z.n.c. was approximately 3.6 for KGa-1 and 3.5 for KGa-2. These results are in general agreement with values determined in previous studies. The equilibrium p.z.n.p.c. values were approximately 5.0 (KGa-1) and 5.4 (KGa-2). Direct comparison of these values with previous results, however, is complicated by differences in experimental procedure and in methods of data analysis. This issue aside, the p.z.n.p.c. values found in the present study are generally higher than those found in previously reported experiments.

Silicon concentrations in the LiCl electrolyte solution increased with mixing time and were consistently greater than corresponding values for Al. This difference may be from Al readsorption and/or precipitation

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reactions on the kaolinite surface, a process that would alter the surface charge properties of the mineral and contribute to the changes observed in p.z.n.c. and p.z.n.p.c. with equilibration time.

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