

CHARGE REVERSAL OF KAOLINITE BY HYDROLYZABLE METAL IONS: AN ELECTROACOUSTIC STUDY

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Abstract—Electroacoustic measurements at 1 MHz, using the Electro-Sonic Amplitude (ESA), on a kaolinite suspension provide a ready method for following the adsorption of hydrolyzable metal ions onto the clay surface. Co^{2+} , Cd^{2+} and Cu^{2+} ions show similar behavior: The initially negative surface becomes less negative, approaches zero, and may become positive at pH values around neutral, depending on the initial metal concentration. At higher pH, electrokinetic potential goes through a maximum. If the surface has become positive, it becomes less so; and at still higher pH values it may become negative again, depending on the metal ion concentration. The behavior can be interpreted using the model proposed by James and Healy.

Key Words—Adsorption, Cadmium, Charge reversal, Cobalt, Copper, Electroacoustics, Electrokinetics, Kaolin, Metal ions (hydrolyzable).

INTRODUCTION

O'Brien *et al.* (1990), Scales and Jones (1992), and James *et al.* (1991) have recently shown the value of the electroacoustic method for the determination of electrokinetic properties. This paper extends the procedure to an application for which it is specially suited: studies of the hydrolysis and adsorption of metal ions onto a colloid surface. The adsorption of ions such as Co(II), La(III), and Th(IV) onto colloidal silica and titania was studied by James and Healy (1972). They showed that the adsorption and hydrolysis were not directly related but observed a qualitative relationship between the pH of high affinity adsorption and the pH of hydrolysis. Charge reversals due to the adsorption of ionic species and subsequent surface precipitation were characterized in terms of the electrophoretic mobility, which was monitored using a particle electrophoresis (Zetameter) apparatus. In this paper, it will be shown that electroacoustics can be used to follow the charge reversal on silica and that a similar adsorption process occurs with kaolinite suspensions.

James and Healy's (1972) work established the occurrence of three changes in sign of the electrokinetic potential with increasing pH which they referred to as "charge reversals" (CRs) even though, strictly speaking, the second one should more properly be called a point of zeta reversal (PZR) in the nomenclature of Fuerstenau (Hunter, 1981). The first (CR1) represents the point-of-zero charge (PZC) of the substrate, and the second is attributed to the specific adsorption of the partially hydrolyzed metal ion to produce a charge reversal (CR2). At higher pH, it appeared that the adsorbed hydroxy ion $\text{M}(\text{OH})^+$ was converted into the metal hydroxide, which partially or completely covered the surface. At still higher pH, the ζ -potential turned from positive to negative at a pH (CR3) that

approached the normal PZC of the metal hydroxide as the thickness of the hydroxide layer increased. Since the present measurements are confined to electrokinetics, the mobility zeros are best described as isoelectric points (IEPs), but these can often be identified with the PZC values determined for the system with only indifferent ions present. Since the kaolinite suspension does not have a well defined PZC or IEP, it is expected to exhibit only charge reversals CR2 and, possibly, CR3.

EXPERIMENTAL METHODS

Materials

The Eckafine BDF Kaolinite powder used in this study was supplied by Kaolin Australia Pty. Limited, with a measured particle density of 2.7 g cm^{-3} . Transmission electron micrographs of the sample show essentially hexagonal sheetlike crystals between 50 nm and $1 \mu\text{m}$ in diameter.

The silica sample was a crushed quartz (size $< 1 \mu\text{m}$) with a wide range of size and shape and a surface area estimated to be about 10 m^2 per gram.

Preparation of suspensions

For adsorption measurements. The kaolinite sample was prepared in the manner described for montmorillonite by Posner and Quirk (1964): It was washed at pH 3 with 1 M NaNO_3 to remove any adsorbed aluminum and to generate a homoionic clay. The washed kaolinite was stored in dilute (ca. 0.001 M) NaNO_3 solution at near neutral pH and a particle volume fraction of 1%. From the stock suspension of approximately 3 liters, 85 ml aliquots were taken and diluted with 10^{-3} M NaNO_3 solution (155 ml). The resulting suspension was thoroughly mixed and dispersed in an ultrasonic bath (Bransonic 32) for 15 minutes. One

drop of 1.0 M HNO₃ was added prior to the addition of a solution containing the hydrolyzable metal ion (10 ml). The suspension (0.34% kaolinite particles by volume) was sonicated for a further 15 minutes before cooling to 25°C.

For electrophoresis/electroacoustic comparison. Sufficient kaolinite powder to produce a 0.5% volume fraction suspension was dispersed in 10⁻³ M salt solution (250 ml) at pH 10. After intense stirring (Ultra Turrax T25) and sonication for 15 minutes, the suspension pH was readjusted back to 10. Electroacoustic measurements were made on the clean kaolinite at intervals of about 0.5 pH units from pH 10 down to 3.5.

Determination of kaolinite surface area

The method of surface area determination was based on that of Greenland and Quirk (1962, 1963) using cetyl pyridinium chloride (CPC) as the adsorbing agent. The adsorption of CPC was determined by shaking 1% volume fraction kaolinite suspension (20 ml) with CPC solutions (25 ml) of differing concentrations and, after centrifuging, measuring the UV absorption of the supernatant at 259 nm.

The surface area of kaolinite was calculated assuming an area of 0.27 nm² per adsorbed CP⁺ ion, corresponding to a bilayer of CP⁺ on the kaolinite surface. Agreement (to within about 5%) was obtained between estimates of area using two different initial CPC concentrations.

Characterization of adsorption—measurement of the dynamic mobility

Details of the use of the ESA-8000 electroacoustic apparatus (Matec Applied Sciences, Hopkinton, Mass. U.S.A.) are given by O'Brien *et al.* (1990) and James *et al.* (1991). The ESA probe was calibrated against a standard silica suspension (Ludox TM at 2.6% by volume). The electrokinetic and conductance properties of the kaolinite suspension containing the hydrolyzable metal ion were measured in the SSP-1 titration cell assembly, using the single point mode at 25°C. The suspension pH was varied by the drop-wise addition of 0.1 M sodium hydroxide solution.

Comparison of alternating and static field electrokinetics for kaolinite with no added hydrolyzable ion

After electroacoustic measurement at each pH, a small sample (10 mL) of the suspension was centrifuged and the supernatant used as a diluent for some particles. This very dilute particle suspension was used to determine the electrophoretic mobility in a Micro-electrophoresis apparatus (Rank Bros., Bottisham, Cambridge, U.K. Mark II). The zeta potentials obtained by this method were compared with those obtained by electroacoustics using the same procedure as

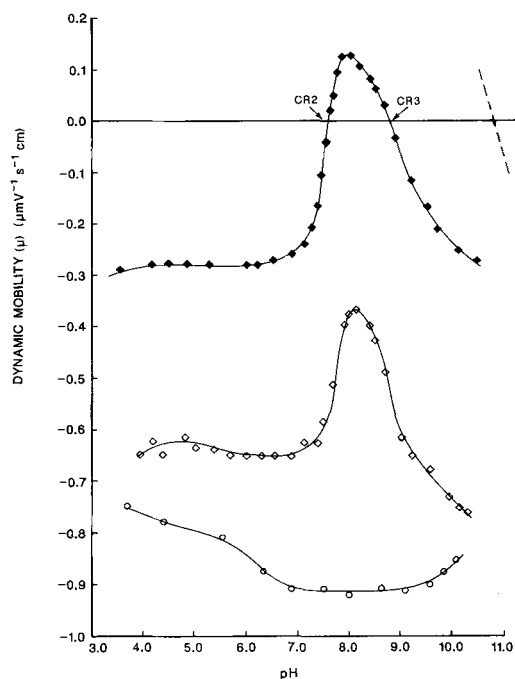


Figure 1. Dynamic mobility of silica (crushed quartz) as a function of pH: at 0.4% by volume in 10⁻³ M NaNO₃ solution (○); at 0.3% by volume in Co(NO₃)₂ solution: 2.4 × 10⁻³ M (◇) and 10⁻² M (◆). The PZC of Co(OH)₂ is indicated by the dashed line at the right of the pH axis.

James *et al.* (1991) but with the pH being varied from 10 down rather than from acid to basic values.

At each pH, a small sample was also taken for size determination by photon correlation spectroscopy (PCS) using the same procedure as James *et al.* (1991): A few drops of the suspension were rapidly diluted in 10⁻³ M salt solution to preserve the aggregate structure and the effective mass average particle size measured at each pH. This value was used in the estimation of the ζ-potential from electroacoustic measurements.

RESULTS

The mean surface area of the kaolinite particles in suspension was calculated as 26 ± 1 m² g⁻¹ using the CPC adsorption method. BET measurements gave a figure of 18 m²/g and an electroacoustic study of CP⁺ adsorption by Rowlands and Hunter (1992) gave 21 m²/g, which seems to be a more reliable figure.

Figure 1 shows the behavior of the quartz suspension alone and in the presence of two concentrations of added Co²⁺ ion. The result is similar to that observed by James and Healy (1972), even though the high sensitivity of the electroacoustic method is able to distinguish much smaller differences in mobilities at different metal ion concentrations. (A mobility of 1 μm V⁻¹ s⁻¹ cm corresponds to a ζ-potential of about 15 mV for these particles.)

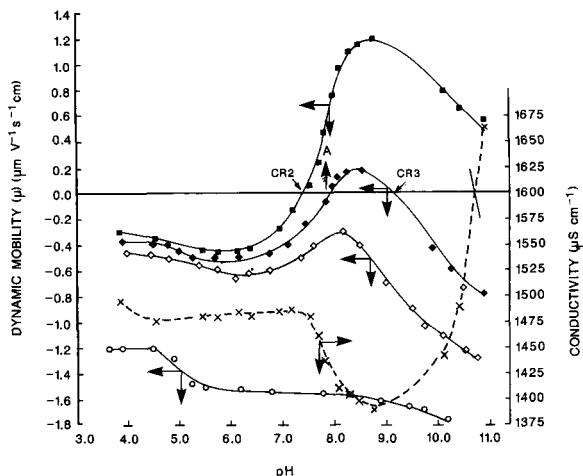


Figure 2. Dynamic mobility of kaolinite (0.34% by volume) as a function of pH in the absence and presence of Co(II) ion. In absence of Co(II) ion (O). In $\text{Co}(\text{NO}_3)_2$: 10^{-3} M (\diamond); 2×10^{-3} M (\blacklozenge); and 4×10^{-3} M (\blacksquare). The solution conductivity (at 2000 Hz) in the presence of 4×10^{-3} M Co^{2+} is shown thus: --- x --- x ---. All solutions have a background of 10^{-3} M NaNO_3 solution. The isolated vertical arrow (A) marks the pH at which precipitation of the hydroxide would be expected to occur in the bulk solution. Paired arrows indicate the axes to which the curves refer.

The Co^{2+} concentration at which the systems first show a point of reversal of zeta potential at around pH 7 occurs in our system (Figure 1) at a concentration of about 0.005 M Co^{2+} , about 100 times higher than that required by James and Healy (1972). Note also that the uppermost charge reversal (CR3) occurs at a much lower pH than the PZC of $\text{Co}(\text{OH})_2$, which occurs at about pH 10.7.

Figures 2, 3, and 4 show the dynamic mobility response to adsorption on kaolinite as a function of pH and initial ion concentration for Co(II), Cd(II), and Cu(II) respectively. These curves also display the conductance of the suspension with an initial ion concentration of 4.0×10^{-3} M. In all three cases, there is clear evidence of the adsorption of the metal ion at a characteristic pH where the mobility swings from negative to positive and the solution conductivity shows a pronounced drop. This occurs at a lower pH for Cu^{2+} than for the other two. Co^{2+} adsorbs close to pH 7, and Cd^{2+} is very similar. The point at which the hydroxide would be expected to precipitate in bulk solution at a metal ion concentration of 4×10^{-3} M is indicated on the figures, and in each case it is at a slightly higher pH than that at which the adsorption becomes evident. (The depletion of metal ion due to adsorption, even at these particle concentrations, hardly affects the bulk precipitation pH at all; it shifts about 0.05 pH units.) The kaolinite results are similar to those for the quartz system.

On silica, James and Healy (1972) found no evidence

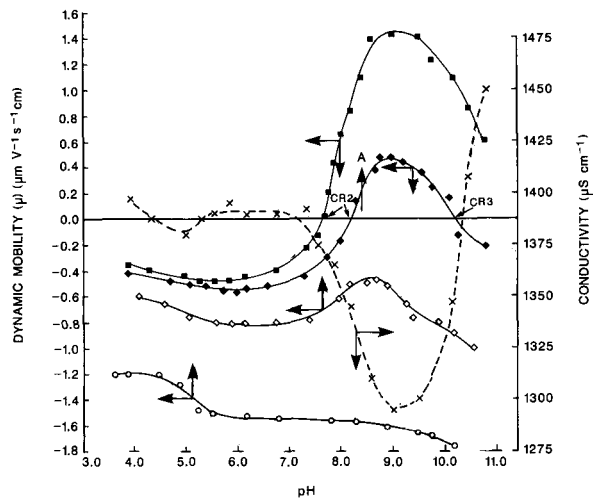


Figure 3. Dynamic mobility of kaolinite (0.34% by volume) as a function of pH in the absence and presence of Cd(II) ion. In absence of Cd(II) ion (O). In $\text{Cd}(\text{NO}_3)_2$: 10^{-3} M (\diamond); 2×10^{-3} M (\blacklozenge); and 4×10^{-3} M (\blacksquare). The solution conductivity (at 2000 Hz) in the presence of 4×10^{-3} M Cd^{2+} is shown thus: --- x --- x ---. All solutions have a background of 10^{-3} M NaNO_3 solution. The isolated vertical arrow (A) marks the pH at which precipitation of the hydroxide would be expected to occur in the bulk solution.

of specific adsorption of the metal ion since the PZC of the underlying oxide appeared to be unaffected by the presence of the metal ion and the mobility, at least for small additions of the ion, was little different from that of the oxide. Our results on quartz do not extend to a low enough pH to see what the PZC is, either for the bare system or for that in the presence of the metal ion. Earlier measurements on crushed quartz by Healy *et al.* (1968) show a region from pH 3 to 7 where the DC mobility is essentially constant at about -2×10^{-8} $\text{m}^2 \text{V}^{-1} \text{s}^{-1}$ and that agrees qualitatively with the present result.

For kaolinite, the mobility never goes quite to zero in acid solution, but (1) it is a great deal smaller (in absolute value) after addition of the metal ion at low pH, and (2) the effect does not depend strongly on metal ion concentration as it does with quartz (Figure 1). For Co^{2+} in particular at low pH, the spread of dynamic mobility values after addition of the metal is very small.

The conductance curve reflects the adsorption behavior of the metal ion and the uptake of hydroxyl ion as the peak in the mobility develops. At higher pH as the maximum is passed, there is a corresponding minimum in the conductance, which subsequently rises as excess hydroxyl is added to the system. The conductance curve for the Cu^{2+} system exhibits a shallow minimum at the anticipated pH followed by a much deeper minimum at higher pH.

Figure 5 shows a comparison between zeta potentials of kaolinite in the absence of the hydrolyzable metal

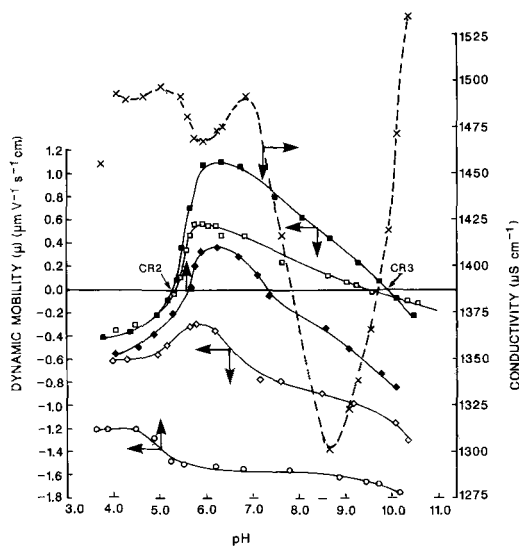


Figure 4. Dynamic mobility of kaolinite (0.34% by volume) as a function of pH in the absence and presence of Cu(II) ion and in absence of Cu(II) ion (○). In $\text{Cu}(\text{NO}_3)_2$: 10^{-3} M (◇); 2×10^{-3} M (◆); and 4×10^{-3} M (■). The solution conductivity (at 2000 Hz) in the presence of 4×10^{-3} M Cu^{2+} is shown thus: --- × --- × ---. All solutions have a background of 10^{-3} M NaNO_3 solution. The isolated vertical arrow (A) marks the pH at which precipitation of the hydroxide would be expected to occur in the bulk solution. Paired arrows indicate the axes to which the curves refer. Points marked (□) are a repeat run of the sample at 4×10^{-3} M $[\text{Cu}^{2+}]$ after a delay of several weeks.

ion, calculated from measurements of the DC (electrophoretic) mobility and the dynamic (electroacoustic) mobility. Reasonably good agreement is displayed over the entire pH range, though in the region below pH 6.2 the rate of particle coagulation was too rapid to enable a correction to the electroacoustic data. The dynamic mobilities, such as those used in Figures 1–4, can be determined directly from the ESA signal. But to convert them to ζ -potentials requires an estimate of the inertia correction (O'Brien *et al.*, 1990), and this in turn requires a measurement of the effective mass average particle size, which we obtained by PCS using the method of James *et al.* (1991). We did not undertake that extra step in the metal adsorption studies, but the results in Figure 5 show that it could be done if one wished to make more quantitative modeling studies of the interfacial charge and potential during the adsorption process.

DISCUSSION

The very large difference observed (Figure 1) in the concentration of Co^{2+} ion required to produce a reversal of zeta potential in our quartz system compared to that shown by James and Healy (1972) is entirely explicable in terms of the surface area available for adsorption in the two systems. James and Healy used

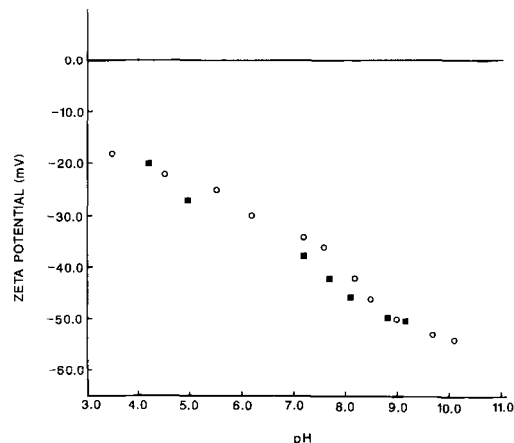


Figure 5. Comparison of the zeta potential value of kaolinite calculated from the dynamic (high frequency) mobility (○) with that estimated from the electrophoretic (DC) mobility (■). Apparent mass average radius's estimated by light scattering data on a rapidly diluted sample of the system at each pH.

a particle concentration of 0.1 g/liter, with an area per liter of around 2.5 m^2 . In our system, the particle concentration was about 8 g/liter, with an area per liter two orders of magnitude larger than theirs.

The large difference between CR3 (pH 8.8) and the PZC of $\text{Co}(\text{OH})_2$ at pH 10.7 suggests that there is only partial coverage by the adsorbed hydroxide, even though the total amount of Co^{2+} present is sufficient to provide more than a monolayer.

Each of the systems in Figures 2–4 shows two charge reversals. According to James and Healy, the first one (CR2) occurs at the pH of strong specific adsorption of the partially hydrolyzed metal ion ($\text{M}(\text{OH})^+$). As more base is added, a more or less complete layer of the metal hydroxide is established on the surface of the underlying kaolinite. It is the buildup of this layer that causes the progressive increase in positive charge on the clay surface. Confirmation of this description has been provided for the case of Co^{2+} adsorbed on kaolinite by an X-ray Photoelectron Spectroscopy study by Dillard and Koppelman (1982). Note also that again here we observe the same area dependence as in the case of quartz. The concentration of metal ion required to produce a reversal in sign of the zeta potential is 100 times that observed by James and Healy (1972), and this is equal to the ratio of the measured areas in the two cases.

At a sufficiently high pH, the adsorption of hydroxyl ion begins to become more important and the charge reaches a plateau and then begins to fall. The PZC that occurs at the highest pH (CR3) should correspond to that of the metal hydroxide, but James and Healy showed that that did not occur on silica until there was enough metal ion present to provide a few complete layers of the hydroxide. In our more concentrated ka-

olinite systems that would not be expected to occur because the total amount of metal ion present, if spread over the available kaolinite surface, would occupy about 0.3 nm² per metal ion, i.e., approximately one monolayer. Nevertheless, the system appears to be headed for a CR3 value at least as high as the PZC of Co(OH)₂. This is in contrast to the behavior of our quartz, where CR3 occurs well below the PZC of the hydroxide even though the area of surface is so much lower in that case. It seems that on kaolinite a thinner surface layer is able to reproduce the behavior of the hydroxide than is the case with quartz.

The large drop that occurs in the mobility of the kaolinite on first addition of each of the metal ions (Figure 2) is presumably due to the ion exchange process that is expected to occur. The situation differs from that encountered in the James and Healy (1972) work on silica, since in the present case we are adding the metal ion at concentrations some 100 times higher than those used in their study. Certainly one would expect those divalent ions to exchange with the sodium ions present on the surface, but it is not so obvious what the effect would be on the dynamic mobility or ζ -potential. The electrokinetic charge measured on kaolinite is always much less than what one would expect from the cation exchange capacity (CEC). In this case the CEC is 4.0 millimoles of monovalent ion per 100 g of clay, which corresponds to a surface charge density (σ) of about 18 $\mu\text{C}/\text{cm}^2$ compared to the electrokinetic value estimated from (Hunter, 1987):

$$\sigma = 11.74 \sqrt{c} \sinh(\zeta/51.4)$$

of only about 0.3 $\mu\text{C}/\text{cm}^2$. (Here c is in mole/L and ζ is in mV.) Over 95% of the negative charge is balanced by Na⁺ cations, which are so strongly bound that they contribute nothing to the electrokinetic charge. Substitution of some or all of them by the divalent Co²⁺ evidently still has an effect on the electrokinetics, but it would be unwise to estimate the extent of the substitution from such a limited range of measurements.

The conductance curves of Figures 2 and 3 clearly reflect the changing ion concentration as the adsorption of hydrolysis products and surface precipitation of the metal hydroxide takes place. A significant drop in the conductance occurs as the system undergoes the first charge reversal (CR2), reflecting the large amount of ion adsorption occurring; and in each case, this occurs just before the pH at which bulk precipitation is expected (indicated by the isolated vertical arrow). At the pH corresponding to the peak of the dynamic mobility curve, an increase in conductance occurs as the added hydroxide ion remains in solution. This trend becomes even more marked as the solution becomes depleted of metal ion.

Figure 4 shows a similar trend in the conductance of the suspension for the Cu(II) system, though the major minimum in the conductance is, in this case,

displaced to significantly higher pH compared to the maximum in the mobility. Only a shallow minimum occurs at the point where the adsorption is strongest. A repeat run, several weeks later, on this system at $4 \times 10^{-3}\text{M}$ [Cu²⁺] shows the sensitivity of the height of the maximum to the details of the sample preparation procedure, though the points at which charge reversal occur are reasonably reproducible.

The presence of a deep minimum in the conductance curve at higher pH in the case of Cu²⁺ compared to Cd²⁺ and Co²⁺ indicates some difference in the mechanism in the two cases. Cd²⁺ and Co²⁺ are almost identical in their behavior, even in respect to the small dip in conductivity at very low pH. The difference between them and the Cu²⁺ is probably related to the much lower solubility of the latter. The first shallow minimum in Figure 4 occurs where the adsorption process begins, but this is perhaps overshadowed by a subsequent precipitation of copper hydroxide in the bulk solution, giving rise to the much deeper minimum in conductance.

In agreement with other recent studies, the comparison of data in Figure 5 suggests that electrokinetic properties such as zeta potential can be determined from electroacoustic measurements. In systems where adsorption and surface precipitation occur, however, careful monitoring of the effective mass-average particle size would be essential. The correlation between DC electrophoretic and dynamic mobilities shown in Figure 5 also implies that the dislike shape of the kaolinite particles was not critical, as calculations were made using O'Brien's (1988, 1990) theory for spherical particles.

It should be noted that the dynamic mobility of the bare kaolinite shown in Figure 2 does not correspond exactly with that shown in Figure 5 since the two samples were treated rather differently. The preparation method described in the Experimental Methods section applies to the material in Figure 2, but the material in Figure 5 is derived from another study in which the clay was used without prior salt washing and with potassium ion as the counterion. This treatment has evidently made the ζ -potential of the latter sample rather more sensitive to pH, possibly as a result of aluminum adsorbed on the clay mineral exchange sites.

CONCLUSIONS

The electroacoustic method is ideally suited to the study of the changes which occur in surface charge status of a colloidal suspension in the presence of a hydrolyzable metal ion. The method is rapid and very simple to apply and the behavior can be studied over a wide range of particle concentrations (from about 0.5–10% by volume or 1–30% by mass for a typical inorganic soil). Since the adsorption behavior is determined by the amount of available surface area, the ability to measure the electrokinetic charge at arbitrary

concentrations makes it possible to study systems that are not accessible by other methods.

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