

ELECTROACOUSTIC STUDY OF ADSORPTION OF CETYLPYRIDINIUM CHLORIDE ON KAOLINITE

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Abstract—Adsorption of cetylpyridinium chloride (CPC) onto kaolinite can be followed using the electroacoustic effect. The dynamic mobility, measured at a frequency of 1 MHz, varies from about -2 to $+1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ in a number of steps, reflecting the adsorption of two separate layers, with the bilayer being more obvious, especially at pH 5–8. The behaviour at different pHs reflects the different charge characteristics of the basal cleavage planes and the crystal edges. When the amount of added CPC is equal to the cation exchange capacity of the clay, the kinetic charge changes from negative to positive and there is a pronounced break in the conductivity curve. It is also possible to estimate the edge to face area from such measurements and so obtain a measure of the aspect ratio of the clay crystallites. The (minimum) value for this clay is about 5:1.

Key Words—Electroacoustics, Adsorption, Cetylpyridinium ion, Kaolin, Electrokinetics, Dynamic mobility.

INTRODUCTION

Electroacoustic methods have been used to investigate the adsorption of metal ions onto phosphate and oxide surfaces (O'Brien, 1991). The adsorption of *n*-alkyl pyridinium salts, particularly cetylpyridinium chloride (CPC) and bromide (CPB), onto the surfaces of clay minerals such as kaolinite, montmorillonite, and vermiculite has been studied by a variety of techniques. Greenland and Quirk (1962, 1963) found CPB to be strongly adsorbed on montmorillonite, and from comparisons with water and nitrogen (BET) adsorption measurements, concluded that CPB adsorption was a valuable method for the determination of the surface areas of clay minerals. They further concluded that the CPB method tended to underestimate the surface areas of materials with low surface charge densities. Their measurements, including X-ray diffraction data obtained from CPB-clay mineral complexes, indicated that at maximum adsorption the CPB molecules form monolayers covering the internal surfaces of expanding clay minerals, such as montmorillonite and vermiculite. Each molecule was found to occupy an area at the surface of 0.54 nm^2 , with the pyridine ring apparently lying flat on the surface. On the external surfaces of non-expanding minerals such as kaolinite, a bilayer formed at maximum coverage, with each adsorbed molecule or ion having a mean coverage of 0.27 nm^2 . These results were confirmed by Slade *et al.* (1978), who concluded that the CPB molecules formed close-packed arrays oriented at 57° to the internal silicate surfaces.

The formation of bilayers on the surfaces of kaolinites at high surfactant concentrations occurs because the hydrophobic interaction between the hydrocarbon tails of the first layer and the solvent is thereby reduced.

The bilayer contains counterions which offset to some extent the electrostatic interactions between the head groups. This is similar to the structure postulated by Hayter and Hunter (1972) for the adsorbed quaternary ion film at the mercury-solution interface. The formation of a bilayer is indicated by the fact that, as increasing amounts of CPB are adsorbed by the kaolinite, it becomes initially hydrophobic and then again hydrophilic. Evidence for the incorporation of counterions (Br^- or Cl^-) into the bilayer comes from the calorimetric study of Wierer and Dobias (1988). Kunyima *et al.* (1990) provide some evidence that, at very low surfactant concentrations, local monolayers (hemimicelles) and local bilayers (admicelles) may form at clay mineral surfaces.

The foregoing discussion applies mainly to clay minerals in neutral or near neutral suspensions. Since kaolinite has edges on which the sign of the surface charge may be altered by varying the pH of the suspension, its adsorption behaviour towards cationic surfactants is expected to change significantly with pH. Some such variation was found by Welzen *et al.* (1980) in their study of the adsorption of cetyltrimethylammonium bromide (CTAB) onto kaolinite.

In the current study, we investigate the adsorption of a cationic surfactant, cetylpyridinium chloride, onto a kaolinite surface.

EXPERIMENTAL

The kaolinite used in this study was supplied by Kaolin Australia Pty Ltd (Eckafine BDF). The material had a particle density of 2.7 g cm^{-3} . Electron micrographs of the sample showed sheet-like crystals between 50 nm and $1 \mu\text{m}$ in diameter. Cetylpyridinium chloride monohydrate was obtained from Aldrich and

used without further purification. Doubly distilled water, with a conductivity less than $1 \mu\text{S cm}^{-1}$, was used for all experiments.

Kaolinite preparation

The homoionic kaolinite, with a maximum particle diameter less than $2 \mu\text{m}$, was prepared as described by Posner and Quirk (1964). The clay was washed five times with 1.0 M NaCl solutions at pH 3 and then repeatedly with double-distilled water until it began to disperse near pH 7. It was then settled under gravity to obtain a sample with a maximum particle diameter of approximately $2 \mu\text{m}$. The resulting suspension, which had a volume fraction 0.755%, was stored between pH 7 and 8 with a background electrolyte concentration of 10^{-3} M .

The kaolinite thus prepared had a surface area, measured at pH 7 by the CPC adsorption method of Greenland and Quirk (1962), of $26 \pm 1 \text{ m}^2 \text{ g}^{-1}$. Single point BET, using nitrogen as adsorbate, determined the area to be $18.1 \pm 0.1 \text{ m}^2 \text{ g}^{-1}$.

Prior to electroacoustic measurements, the pH of a 250 cm^3 aliquot of the stock suspension was adjusted to pH 10; the suspension was dispersed by stirring (Ultra Turrax T25) for 10 minutes and then by ultrasound (Branson B-32) for 30 minutes. The pH of the suspension was then adjusted to the value required for each experiment.

Electroacoustic measurements

Electroacoustic measurements on the kaolinite suspensions were made using an ESA-8000 apparatus (Matec Applied Sciences, Hopkinton, Massachusetts, USA). Details of the construction and operation of this apparatus have been given by Babchin *et al.* (1989) and by O'Brien *et al.* (1991). Measurements were made in the single point mode using the SSP-1 titration cell assembly which is equipped with pH electrodes, a thermocouple, and a dip-type conductivity probe. The dip-type ESA probe was calibrated using a 2.97% volume fraction silica sol (Ludox TM, Du Pont). A magnetic stirrer was used in addition to the high-speed paddle stirrer supplied with the instrument.

The ESA signal is given in terms of the dynamic mobility μ_d by (O'Brien, 1988):

$$\text{ESA amplitude} = C\phi(\Delta\rho/\rho)\cdot\mu_d,$$

where ϕ is the volume fraction, ρ is the density of the liquid, and $\Delta\rho$ is the difference in density between solid and liquid. C is an instrument constant and the ESA amplitude is in mPa per unit field strength (V m^{-1}). In their calibration procedure, Matec suggest that a 10% silica sample should be assigned a dynamic mobility calculated from the Smoluchowski equation ($=\epsilon\zeta/\eta$) with a zeta potential of -28 mV . (This is their way of taking account of the dependence of the viscosity, and hence the mobility, on temperature; note that it

does not imply that the zeta potential of the silica is, indeed, -28 mV . The true ζ would be considerably more negative than that.) The relation between the ESA signal and the volume fraction is not linear above about 4% and so, for our lower concentration standard sample, the appropriate value of zeta is -31 mV . Our instrument gave a signal amplitude of $6.38 \text{ mPa}\cdot\text{m}\cdot\text{V}^{-1}$ for the Ludox, and assuming a density of 2.2 g cm^{-3} for the solid, the value of C is $7.49 \times 10^9 \text{ mPa s m}^{-1}$. This needs a slight temperature correction from 7.49 to 7.38 for our experimental conditions. Then for the kaolinite:

$$\begin{aligned}\mu_d &= \text{ESA} \times 10^8 / (7.38 \times 10^9 \times 1.7 \times 0.00755) \\ &= 1.056 \times \text{ESA}\end{aligned}$$

for μ_d in ($\mu\text{m cm/V s}$), assuming a density of 2.7 g cm^{-3} for kaolinite.

Once the initial dynamic mobility of the kaolinite suspension had been determined, the colloid was titrated against a 0.05 M solution of cetylpyridinium chloride (CPC). After each addition of CPC the suspension was allowed to equilibrate until the ESA signal, as viewed on the oscilloscope, was steady. The duration varied according to the stage of the titration, but equilibration could take 30 minutes. A single run spanned about 6 hours.

Titration were carried out on suspensions with initial pHs of 5.7, 8.5, and 10.1. In each case the pH of the CPC solution was adjusted to the same value, in order to minimise pH variation of the suspension throughout the experiment. The experiments at pH 10.1 were conducted using an N_2 'blanket' to minimise CO_2 ingress. In practice it was not possible to maintain constant pH throughout the CPC addition because of (1) hydrogen ion release from the kaolinite by exchange with the CP^+ ions; (2) CO_2 ingress (at high pH) and, possibly, (3) partial hydrolysis of the CPC solution during the course of the titration.

The pH varied in each experiment over about one pH unit. A correction was made to the raw conductivity data for this change but, although significant, it made no discernible difference to the intersection points for different regions of the conductivity curves.

RESULTS

Figures 1, 2, and 3 show the variation in the dynamic mobility and the conductivity of the kaolinite suspensions with the quantity of CPC added at initial suspension pHs of 5.7, 8.5, and 10.1, respectively. In each instance the temperature of the suspension was maintained at $25.7 \pm 0.2^\circ\text{C}$ throughout the titration.

The pH of the suspension dropped substantially with CPC addition over certain concentration ranges, presumably due to H^+ release from the kaolinite surface. Where the initial pH was 5.7, the pH dropped from 5.7 to 4.5 between 1 and 8 mmol/100 g of CPC ad-

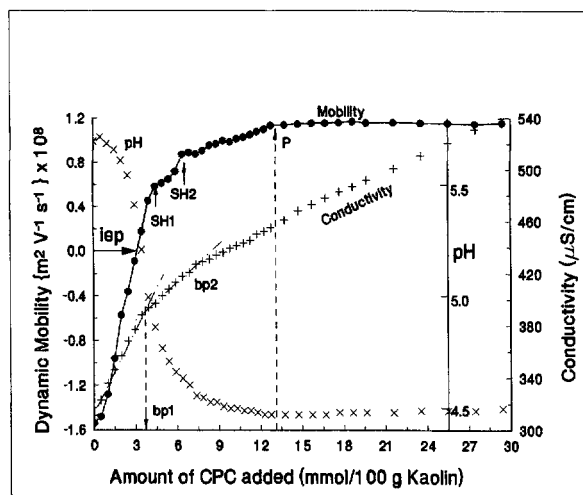


Figure 1. Dynamic mobility (●), conductivity (+), and pH (x) of a kaolinite suspension as a function of added cetylpyridinium chloride (CPC) in acid solution (about pH 5). The critical points on the mobility curve are indicated with arrows at 4.5 (SH1), 6.55 (SH2), and 13.1 (P) mmol/100 g kaolin. The break in the conductivity curve (bp1) occurs at 3.7 mmol/100 g, near the iep.

dition. Although this is a significant pH change, it corresponds to a release of only about $9 \mu\text{mol}$ of H^+ into the solution, or about 2% of the added CP^+ ion. At the intermediate pH the drop corresponded to a negligible ($<0.002\%$) release of H^+ . For the pH 10.1 sample there was a more gradual drop from 10.2 to 9.0 between 2 and 15 mmol/100 g addition. Some of this may be due to CO_2 ingress and/or partial hydrolysis of the CPC during the course of the experiments. Prominent features in the mobility curves are indicated in the Figures.

Figures 1–3 show that the mobilities of the kaolinite particles drop as increasing amounts of CP^+ ions are adsorbed, and the surface charge is neutralised. A well-defined isoelectric point occurs, where the dynamic mobility is reduced to zero, after the addition of a certain amount of CPC. The amount required increases slightly with increase in the initial pH of the suspension and is indicated by the arrows marked iep. The surface charge on the clay is related to the initial pH, as is clear from the observed increase in the initial mobilities with pH, from $-1.54 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ at pH 5.7 to -2.10 at pH 10.1. At the lowest pH, the iep occurs a little before the breakpoint in the conductivity curve (marked bp1) but in neutral to basic conditions (Figures 2 and 3) the two are very nearly identical.

The most striking feature of the dynamic mobility curves is that at all three pHs the final mobility values are the same, and very close to $1.1 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (the point marked P, for plateau, in the figures). This we take to be characteristic of the clay coated with CPC. At lower pHs there are a number of shoulders (SH1, 2, and 3) which suggest the completion of some

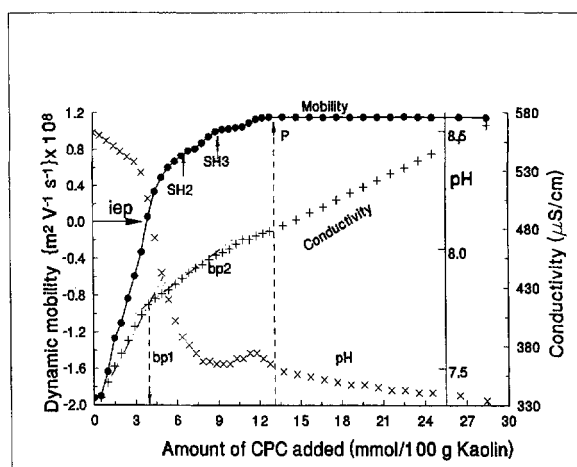


Figure 2. Dynamic mobility, conductivity, and pH as a function of added CPC, for an initial pH of 8.5. Critical points occur at 6.55 (SH2), 9 (SH3), and 13.1 (P) on the mobility curve and the conductivity break (bp1) is at 3.98 mmol/100 g, which is identical to the independently measured cation exchange capacity and also corresponds closely with the zero in the mobility (the iep).

intermediate stage in the adsorption process. Even at the highest pH where the only intermediate shoulder is very poorly defined, it still occurs at about half the plateau value.

DISCUSSION

It seems likely that the point marked bp1 corresponds to the cation exchange capacity (CEC) of the clay, which has been measured as $3.96 \pm 0.02 \text{ meq}/100 \text{ g}$ by the silver thiourea adsorption method of

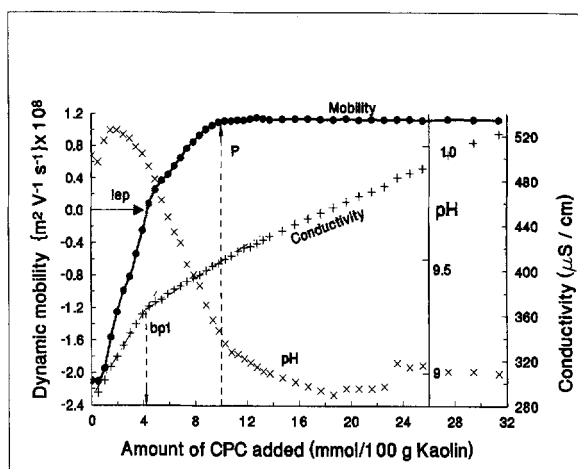


Figure 3. Dynamic mobility, conductivity and pH as a function of added CPC with an initial pH of 10. The conductivity break is at 4.2 mmol/100 g and corresponds exactly to the iep, as indicated. The plateau, P, appears to occur at 10 mmol/100 g in this case.

Chhabra *et al.* (1975). The amount of CPC required to reach this point corresponds to the number of milliequivalents of CP^+ ions required to displace the exchangeable Na^+ and H^+ ions on the kaolinite surface at the experimental pH. Once the point bp1 (=iep) is reached, the clay mineral charge is being completely balanced by CP^+ ions and so no further Na^+ or H^+ ions can be displaced into solution; the slope of the conductivity curve drops accordingly. The only contribution to the conductivity then is from the effective addition of Cl^- counterions to the bulk solution; the CP^+ ions must be mostly adsorbed on the kaolinite surface.

This change of slope at bp1 does not correspond to the attainment of the critical micelle concentration (*cmc*) of CPC in the bulk solution, which is approximately 9×10^{-4} M. If all of the added CP^+ remained in solution it would require only about 4.6 mmol CPC/100 g kaolin and this might be confused with the point bp1 in each of the conductance curves in Figures 1–3. However, experiments with different volume fractions of clay showed that the break-point in the conductance curves occurred at a fixed ratio of added CPC to clay. In any case, the fact that the ESA signal drops to zero indicates that the bulk of the added CP^+ ion is being adsorbed on the clay to neutralise its charge.

The shoulders on the mobility curves at intermediate pHs (SH1–3) can best be interpreted after considering the final plateau, P, which we assume to correspond to the establishment of a complete bilayer of CP^+ over the entire kaolin surface. The development of the bilayer is most obvious in Figures 1 and 2 where the final plateau is established at 13.1 mmol/100 g kaolin in each case. This corresponds to a total surface area of 21.3 m²/g, assuming an area of 27 nm² per ion. The result becomes more significant with the appearance of a shoulder on the curve at just half this value (SH2). This corresponds to the laying down of the first layer and is in reasonable agreement with the estimate of 18.1 m²/g for the BET surface area. That value is much closer to the BET surface area than to the estimate of 26 m²/g obtained from measurements of adsorption of CP^+ ion from solution.

Another shoulder (SH1) appears on the low pH curve (Figure 1) at an addition of 4.5 mmol/100 g kaolin and its significance is enhanced by the appearance of a shoulder at exactly twice that value (SH3) in Figure 2. These values presumably relate to monolayers and bilayers, respectively. We suggest that the point at which the basal planes are covered with the CP^+ ions corresponds to the lower value. If that suggestion is accepted it allows us to calculate the axial ratio of the clay mineral in the following way. Assuming that the crystals are regular hexagons with a distance between opposite vertices, a , and thickness, t , the face area will be $3\sqrt{3}a^2/4$ and the ratio of face to edge area is $0.433 a/t$. The face area is then 14.6 m²/g and the axial ratio

is 5:1 which would suggest a rather thicker particle than usual.

The results at pH 10 differ slightly from those at lower pH. The final plateau (P) appears at about 10 mmol/100 g and there is a small shoulder at about half this value, suggesting an area of only about 16.3 m²/g. There is here no obvious difference in behaviour between edges and faces since the positive edge charges disappear in basic solution.

The notion that bilayer coverage is achieved after a CPC addition of approximately 13 mmol/100 g at neutral pH is supported by empirical observations of the suspension behaviour. With increasing CPC addition the colloid, initially hydrophilic, becomes progressively more hydrophobic as monolayer coverage is approached. As a second layer is added the colloid becomes less hydrophobic. Samples taken from the titration cell after the addition of 11.0 mmol/100 g of CPC at low to neutral pH, showed a significant degree of froth flotation after shaking. A sample at 12.6 mmol/100 g showed only minor traces of hydrophobic material, and at 13.7 mmol/100 g the sample appeared entirely hydrophilic.

The estimates of surface area given above are expected to be higher than the true value since they do not allow for the amount of CPC which remains in solution when the bilayer coverage has been achieved. The error is expected to be smaller for the estimated face area since the driving force required to saturate the faces is significantly less than that required for the edges. This would tend to overestimate the amount of adsorption occurring on the edges and so underestimate the axial ratio. Perhaps this explains why the value obtained here implies that the particles are rather thicker than expected.

There are a number of changes in the slope of the conductance curves, apart from bp1, and the most prominent is marked as bp2 on the figures. We have placed little emphasis on them because the necessary temperature control is difficult to maintain during a long experiment in the present apparatus. Nonetheless, the point bp2 does appear to be closely related to the shoulder SH2 in Figure 1 and SH3 in Figure 2. In principle, thermostatic (and possibly also pH-) stabilisation should enable a more meaningful combination of electroacoustic and conductivity data to be collected.

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