

Adsorption Sites of Kaolin

N. A. ARMSTRONG* and C. D. CLARKE*

Abstract □ The electrophoretic mobility and adsorptive properties of kaolin and kaolin pretreated with anionic and cationic materials were examined over a range of pH values. Pretreatment with anionic compounds had little effect on mobility, while adsorption of cationic species markedly reduced mobility. These results are explained by reference to the structure of kaolin, and the interdependence of adsorption properties and electrophoretic mobility are discussed.

Keyphrases □ Kaolin—electrophoretic mobility and adsorptive properties, effect of pretreatment with anionic and cationic materials, various pH values □ Adsorptive properties—kaolin, effect of pretreatment with anionic and cationic materials, various pH values □ Electrophoretic mobility—kaolin, effect of pretreatment with anionic and cationic materials, various pH values

Kaolin and other clays have long been used for medicinal purposes, their therapeutic action being attributed to their adsorptive capacity. Recently, the uptake of benzoic acid and gentian violet by kaolin has been extensively studied (1–3), and the mechanism of adsorption of anionic and cationic materials has been discussed in relation to the structure of the clay and the likely adsorption sites on the surface of the kaolin particle.

The primary adsorptive mechanism is believed to be electrostatic charges on the kaolin surface. Furthermore, the adsorptive sites of certain substances have been established fairly definitely. Therefore, if kaolin is subjected to preliminary treatment with substances whose site of adsorption is known, and this kaolin is subsequently used to study the adsorptive properties and electrophoretic mobility of the clay, information may be obtained on the location and properties of the electrostatic charges on the kaolin surface.

EXPERIMENTAL

Light kaolin, BP quality, was dried at 100° (3 hr), blended thoroughly, and stored in tightly closed containers. The weight mean diameter of the kaolin was 3.3 μm (sedimentation balance¹), and the surface area was 11.2 m²/g (nitrogen adsorption, using 0.163 nm² as the cross-sectional area of a nitrogen molecule²). Sodium hexadecyl sulfate³ and other reagents were used without further purification.

Microelectrophoretic Techniques—A water-jacketed microelectrophoresis cell mounted on a binocular microscope was used (4). In all experiments, a 0.004% (w/v) suspension of kaolin in 0.004 M potassium chloride containing varying quantities of 0.02 N HCl or NaOH was used to give the required pH within the 3.0–10.0 range. The addition of such small quantities of acid or alkali had a negligible effect on the current flowing through the cell. After preparation, the suspensions were shaken in a water bath for 30 min; individual flasks were then removed, and the pH of the system was measured. The remainder of the suspension was used for flushing through and subsequently filling the electrophoresis cell.

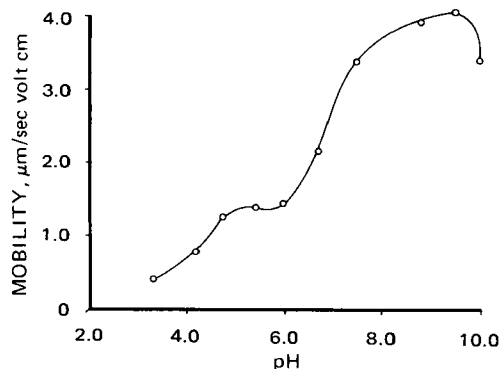


Figure 1—Variation with pH of the electrophoretic mobility of kaolin in 0.004 M potassium chloride.

The time for 10 particles to traverse the calibrated distance in both directions was measured at the upper stationary layer, and the electrophoretic mobility of the kaolin at each pH value was calculated from the mean transit time. The mobility of samples of kaolin that had been equilibrated with solutions of sodium hexadecyl sulfate, gentian violet, cetrinide⁴, benzoic acid, alizarin red S, sodium pyrogallol, or sodium pyrophosphate was determined over a similar pH range. All measurements were carried out at 24 ± 0.1°.

Zero Point of Charge—The clay suspensions used in the electrophoresis studies were not sufficiently concentrated to permit ready visual determination of the edge zero point of charge by flocculation–deflocculation transitions. However, the edge zero point of charge of these suspensions could be satisfactorily determined by placing the suspensions in standard cells and examining them photoelectrically after standing for 24 hr.

Electron Microscopy—An electron microscope⁵ was used, and samples were examined by pipetting one drop of a 1% dispersion of kaolin in water onto the carbon film of the specimen holder. To investigate the ratio between the edge and face areas of the kaolin platelets, a kaolin specimen was shadowed with gold–palladium at a 30° angle.

Adsorption Studies—Kaolin (100 g) was added to a 1% cetrinide solution (400 ml), and the suspension was shaken for 16 hr. The sediment was removed by centrifugation, washed with water, and centrifuged again. The moist sediment cake was dried (vacuum oven, 50° for 8 hr), passed through a 0.25-mm sieve, and blended to ensure homogeneity. Further kaolin samples were treated identically with sodium lauryl sulfate solution (1%) and with water to constitute a control sample.

The effect of this treatment on the surface area of the kaolin was negligible. The uptake of gentian violet onto these treated samples of kaolin was determined as follows. Kaolin (2 g) was added to flasks containing gentian violet (50 mg), ethylenediaminetetraacetic acid (100 mg), and Teorell and Stenhagen buffer (2.5 ml), together with sufficient 0.1 N HCl or NaOH to give the required pH; purified water was added to a total volume of 100 ml. The flasks were agitated at 24° for precise periods of time from 7 to 70 min, the solid was removed by centrifugation, and the gentian violet in the supernate was determined spectrophotometrically at 590 nm. The magnesium content of the supernate was measured by atomic absorption spectroscopy⁶.

RESULTS AND DISCUSSION

Electron microscopy showed that the kaolin exists as character-

¹ Model PC 650, Gallenkamp Ltd., London, United Kingdom.

² Model 212D sorptometer, Perkin-Elmer Ltd., Beaconsfield, United Kingdom.

³ Proctor and Gamble Ltd., Newcastle on Tyne, United Kingdom.

⁴ Cetrinide BP, Glovers Ltd., Leeds, United Kingdom.

⁵ JEM 7, Japan Electronic Optics Laboratory Co. Ltd., Tokyo, Japan.

⁶ Model 290B, Perkin-Elmer Ltd., Beaconsfield, United Kingdom.

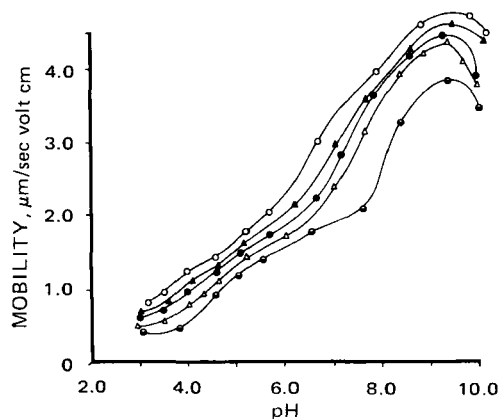


Figure 2—Variation with pH of the electrophoretic mobility of kaolin treated with anionic material. Key: ●, kaolin plus sodium hexadecyl sulfate; △, kaolin plus sodium pyrophosphate; ○, kaolin plus sodium pyrogallol; ▲, kaolin plus alizarin red S; and ◐, kaolin plus benzoic acid.

istic hexagonal platelets, as described by Woodward and Lyons (5). The average thickness-diameter ratio was 1:20, giving an edge-cleavage surface area of 1:9. This figure is in good agreement with reported findings (6, 7), although a ratio of 44% edge area and 56% cleavage surface area was reported (8) for kaolin from the same source as used in this study. Therefore, the kaolin is considered to be characterized by a particle cleavage layer surface area that is considerably greater than that of the edge surface.

Effect of pH on Electrophoretic Mobility of Kaolin—The hydrogen-ion concentration markedly affected the mobility of kaolin (Fig. 1). The increase in mobility with pH to a maximum value at about pH 9.5 was only modified by the near plateau in the pH 5.0–6.0 region. The decrease in mobility at pH values above 9.5 confirms an earlier report (9) and is attributed to erosion of the kaolin structure. Dissolution of lattice aluminum occurs at pH values above 9.5 (1).

Below pH 4.3, a few clay particles reversed their direction of travel, as previously noted (10). Schofield (11) postulated the existence of clays that exhibit an isoelectric point and are positively charged below a particular pH. Since, irrespective of pH, the negative charge on the face of the kaolin platelet is greater than the positive edge charge, the kaolin used is unlikely to exhibit an isoelectric point. However, Woodward and Lyons (5) described platelet aggregations that show a greater edge surface area and that could conceivably exhibit an overall zero point of charge.

The photoelectrically determined edge zero point of charge of the kaolin suspensions in 0.004 M potassium chloride occurred at pH 6.0, which is in good agreement with the value obtained from ion-exchange studies (12).

This value for the zero point of charge of kaolin corresponds to the plateau region of Fig. 1. With a negative edge and cleavage face charge, the mobility rose rapidly with an increase in pH to a maximum at about pH 9.5. This result was probably due to the exchange of the sodium (added as sodium hydroxide to adjust pH) for divalent clay counterions, resulting in an increase in negative charge. The magnitude of the edge negative charge may also be increased by increased adsorption of hydroxyl ions on the edge surface (13).

Electrophoretic Mobility of Pretreated Kaolin—Since the

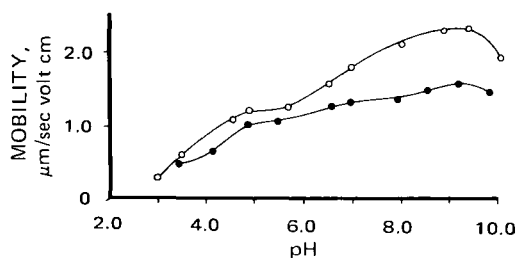


Figure 3—Variation with pH of the electrophoretic mobility of kaolin treated with cationic material. Key: ○, kaolin plus gentian violet; and ●, kaolin plus cetrimide.

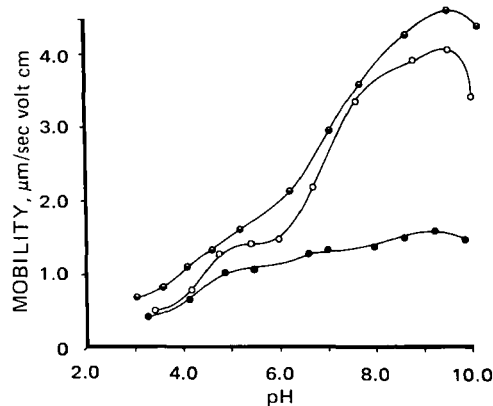


Figure 4—Variation with pH of the electrophoretic mobility of natural kaolin and of kaolin treated with anionic and cationic material. Key: ○, kaolin; ●, kaolin plus alizarin red S; and ●, kaolin plus cetrimide.

negative charge of kaolin is situated on the cleavage surface and the edge surface can bear a positive charge in acid conditions, adsorption of a cationic material on the cleavage layer should permit the contribution of the edge charge to the overall mobility to become apparent. Conversely, following adsorption of an edge-adsorbed species, the role of the cleavage surface charge in electrophoresis should be more readily discernible.

Several workers claimed that anionic materials are adsorbed onto the edges of clay minerals, e.g., sodium hexadecyl sulfate (8), sodium pyrophosphate (14), sodium pyrogallol (15), and alizarin red S (13). When samples of kaolin were treated with these materials, a higher maximum electrophoretic mobility was obtained compared to untreated kaolin (Fig. 2). The shape of the mobility curve of kaolin treated with benzoic acid also suggests that this substance is edge adsorbed (3).

Conversely, the cationic substance cetrimide is claimed to be adsorbed onto the cleavage surface of kaolin (16), and this view is supported by the fact that the mobility curve of kaolin pretreated with cetrimide and also gentian violet showed much reduced mobility compared to that of untreated kaolin or kaolin bearing adsorbed anionic substances (Fig. 3). A leveling of the mobility curve was still evident between pH 5.0 and 6.0, suggesting that this near plateau reflects the character of the particle edge surface, which is relatively free of adsorbed cetrimide.

To facilitate comparison, Fig. 4 shows the variation in mobility with pH of kaolin, kaolin plus anionic material (alizarin red S), and kaolin plus cationic material (cetrimide). The adsorption of cationic material on the cleavage surface caused this large area to have its negative charge partly or wholly neutralized, thus decreasing the negativity of the particle and thereby reducing mobility. On the other hand, adsorption of anionic material on the positively charged edge increased the total negative charge and therefore in-

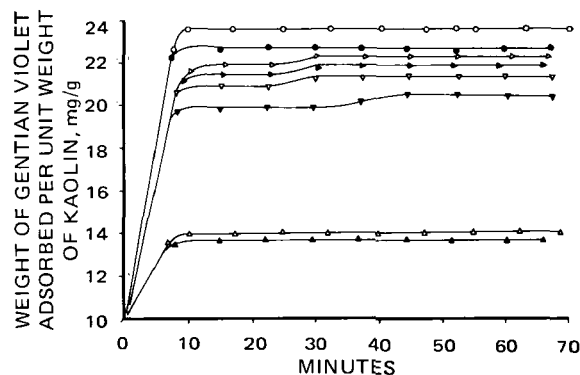


Figure 5—Variation with pH of the uptake of a 0.05% (w/v) solution of gentian violet on natural kaolin and on kaolin treated with anionic and cationic materials. Key: kaolin, pH 7.4 (▷) and 5.7 (◄); washed kaolin, pH 7.4 (▽) and 5.4 (▼); kaolin plus sodium hexadecyl sulfate, pH 7.5 (○) and 5.6 (●); and kaolin plus cetrimide, pH 7.6 (△) and 5.4 (▲).

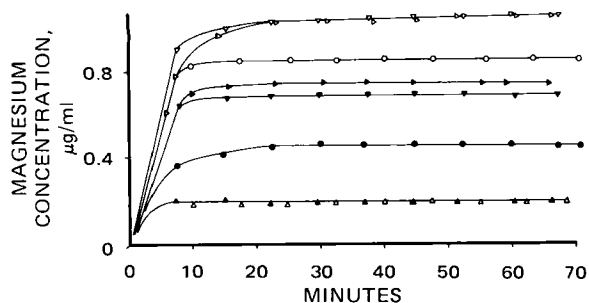


Figure 6—Variation in magnesium exchange with pH of natural kaolin and of kaolin treated with anionic and cationic material. Key: kaolin, pH 7.4 (◊) and 5.7 (◐); washed kaolin, pH 7.4 (▽) and 5.4 (▼); kaolin plus sodium hexadecyl sulfate, pH 7.5 (○) and 5.6 (●); and kaolin plus cetrimide, pH 7.6 (△) and 5.4 (▲).

creased mobility. The pH at which maximum mobility was reached was identical for all three forms of kaolin.

Adsorptive Properties of Pretreated Kaolin—Previously, it was suggested that the exchange of monovalent ions in the suspension medium for clay counterions, e.g., magnesium, plays an important role in cation adsorption (1).

Figure 5 shows the rate of uptake of gentian violet onto kaolin and kaolin pretreated with anionic material (sodium lauryl sulfate) and cationic material (cetrimide). Uptake was studied at two pH values, 5.7 and 7.4, both being in the range where a 0.05% gentian violet solution does not fade significantly during the period of experimental observation, thus permitting spectrophotometric determination (1). Compared to untreated kaolin, kaolin pretreated with cetrimide showed a marked decrease in its adsorptive capacity toward gentian violet, although a small increase in uptake was obtained with increases in pH. In monitoring the increase of magnesium ions in the supernate (as being indicative of variations in the ion-exchange process), no difference was seen in the amount of cation exchange at these two pH levels (Fig. 6).

In contrast, kaolin treated with sodium lauryl sulfate showed differences both in dye uptake (Fig. 5) and magnesium exchanged (Fig. 6) at the two pH values. The differences were of comparable magnitude to those exhibited by the standard and control clays; i.e., the saturation of the edge adsorption sites of kaolin has no effect on total dye uptake or on the levels of magnesium involved in cation exchange.

Both the adsorptive and electrophoretic data presented here confirm that the characteristic charge on kaolin and hence the site of cation exchange are situated on the cleavage layer surface of the clay and are not, as has been suggested, an edge effect.

The picture of kaolin that emerges is of a clay bearing a negative charge on the cleavage faces due to lattice defects, the edge charge

being reflective of the exposed atoms. While the cleavage plane negative charge is unaffected by pH, the sign and magnitude of the charges on the edge faces are strongly dependent on pH. The base-exchange capacity of kaolin in acidic or neutral solution is due to isomorphous replacement within the lattice in a similar manner to that proposed for montmorillonite and other clays. In alkaline solutions, however, the edge faces of the kaolin become negatively charged and can participate in exchange reactions. Thus, the fact that kaolin has never been shown to exhibit a positive potential by decreasing the pH is due to the negative charge of the greater area of the cleavage surface outweighing the positive charge on the smaller edge face area.

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* Present address: Southlands Hospital, Shoreham-by-Sea, United Kingdom.

* To whom inquiries should be directed.