

Equilibration of Kaolinite in Aqueous Inorganic and Surfactant Solutions¹

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Equilibration of a natural kaolinite sample and its purified sodium form in water and aqueous solutions of NaCl and sodium dodecyl benzenesulfonate (SDDBS) and sodium dodecyl sulfonate (SDDS) involves a fast ion-exchange and/or electrostatic adsorption step and a slow step possibly due to dissolution of aluminum species upon prolonged contact of kaolinite with water. Equilibration processes were found to depend on ionic strength, pH, and treatment of the sample. Past studies using kaolinite appear not to have considered the possibility of an intermediate metastable condition which could be responsible for a number of contradicting results found in the literature. Examination of results obtained for the sulfonate under various ionic strengths and hydrogen ion concentrations suggests a complex adsorption mechanism involving ion-exchange, electrostatic, metal activated modes of adsorption and precipitation depending on the solution pH.

INTRODUCTION

The time of contact of clay minerals with water or aqueous solutions may range from a few minutes, as in the case of flotation, to several months, as in the case of tertiary oil recovery. Considerable differences in the response of the mineral owing to changes in surface and rheological properties can occur during such times (1–10). Equilibration of mineral particles with aqueous solutions is a complex process even for simple oxide and salt-type minerals (11–16). The slow approach of equilibrium that is often observed has been attributed to the relatively low surface mobility of some of the dissolved species, particularly hydrolyzable surface cations or anions (7), and the presence of ordered water layer on the mineral that could affect the rate of diffusion of large complex hydroxy species to and from the bulk solution (17–21). Recent studies (22, 23) on clay/

surfactant system have in fact shown a close relationship between the adsorption of anionic surfactants and the structural properties of the water layers in the interfacial region. In this work, the clay/alkylsulfonates system was studied under relevant pH and ionic strength conditions and the results were analyzed to obtain information of the nature of interaction of clay with aqueous inorganic and surfactant solutions.

MATERIALS AND METHODS

Kaolinite. A "well-crystallized" sample of Georgia kaolinite purchased from the clay repository at the University of Missouri was used for the present tests. The surface area determined by nitrogen adsorption was 9.8 m²/g. From this sample, designated as "kaolinite," the homoionic "Na-kaolinite" was prepared in the following manner: (a) The dry clay was treated with water for 10 min in a high-speed mixer at a solid to liquid ratio of 1:2. The product was diluted with distilled water to 2 to 3% solids, allowed to settle, and the supernatant was discarded. This process of washing was repeated 7 to 10

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times until there was no change in the conductivity of the supernatant. (b) The washed kaolinite was agitated with 2 M NaCl solution at high solid to liquid ratio for 15 min; the suspension was diluted and reagitated for 2 hr before sedimentation and decantation; this procedure was repeated 7 to 10 times until a pH of 7 was reached and the conductivity of the supernatant remained constant. (c) The NaCl-treated product was agitated at high solids concentration with 1 M NaCl and at pH 3 to remove $\text{Al}(\text{OH})_3$ surface contamination. The product was diluted and washed until a constant conductivity and a supernatant pH of 7 were obtained. (d) This washed product was treated with 0.1 M NaCl and washed several times until constant conductivity was reached. During the last washing steps the fine clay particles were separated from the coarse impurities by decantation. The Na-kaolinite product thus obtained was filtered and dried at 50°C for 3 to 5 days and stored dry.

Surfactants and chemicals. Sodium dodecyl sulfonate (SDDS) from Aldrich Chemical Company specified to be 99+% pure was used as received. Surface tension versus concentration curve obtained for the dodecyl sulfonate showed it to be surface chemically pure.

A sample of sodium dodecyl benzenesulfonate (SDDBS) from Lachat Chem. (specified to be 95% but analysed to be 85%) was purified as follows. The material was dried under reduced pressure over phosphorus pentoxide at 50 to 60°C, followed by extraction with dry distilled diethylether in a soxhlet apparatus. The first fraction (20–30% by weight) was discarded and from the later fraction (30–40%) the ether was evaporated and the residue was recrystallized three times from acetone. A 98.1% SDDBS product and showing no minimum in surface tension vs concentration curve was obtained. Infrared spectra of the purified material indicated predominance of *p*-DDBS isomer with trace amounts of the ortho-isomer. The inorganic salts used to adjust the ionic strength

and pH were of A.R. grade. Triple-distilled water was used for all tests.

Adsorption. Adsorption tests were conducted in Pyrex vials by precontacting 5 to 20 g of clay with water or salt solution for 2 hr and then adding the surfactant solution. The sealed vials were then agitated on a wrist-action shaker in an incubator maintained at the desired temperature. At the end of the test, a sample of the supernatant solution was centrifuged at 1500g for 20 min, and the liquid above the mineral layer was thoroughly mixed and analyzed for residual concentration of the sulfonate. From the difference between initial and final values, adsorption of the surfactant was calculated. The concentration of the surfactant was determined by the two phase titration technique using a mixed indicator of dimidium bromide and disulfine blue (26).

RESULTS

Aging of Natural Kaolinite

Results obtained for the change in pH of water and NaCl solutions on adding dry kaolinite are given in Fig. 1 as a function of the time of contact of the solid with solutions. Generally, addition of kaolinite to the aqueous solutions produced a sharp drop in the pH during the first few minutes, followed by a slow-increase of pH. It appears from these data that equilibration of dry kaolinite particles with the aqueous phase involves at least two steps, i.e., a fast step that was found to depend on NaCl concentration and a slow step that may be governed by various dissolution processes.

Equilibration of Prewetted Kaolinite in Surfactant Solutions

The results obtained for the adsorption of sodium dodecyl sulfonate on prewetted kaolinite samples at 30°C and an ionic strength of 10^{-2} M NaCl are given in Fig. 2. The adsorption kinetics curves obtained are characterized by the presence of two plateaus, one at an adsorption density of about 1.4

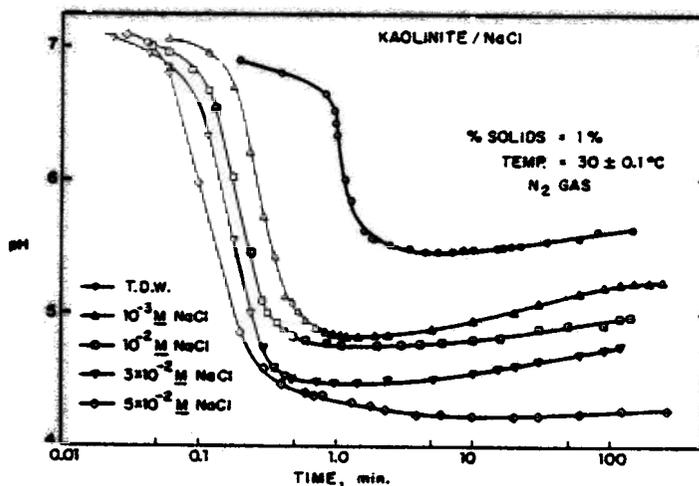


FIG. 1. Effect of addition of dry kaolinite on the pH of deaerated triple-distilled water at various NaCl concentrations as a function of the time of contact of the solid with solutions.

$\mu\text{moles}/\text{m}^2$ and the other at $1.8 \mu\text{moles}/\text{m}^2$. Adsorption increases rapidly during the first 40 min, remains at an apparently constant value for the next 5 hr, and then increases again to reach another limiting value in about 100 hr.

The kinetics curves for the sodium dodecyl benzenesulfonate adsorption on Na-kaolinite at different solid/liquid ratios are given in Fig. 3. These isotherms also show the two step behavior observed for the case

of SDDS/kaolinite system. However, the initial rate of adsorption in this case is much higher and only 5 to 10 min are needed to reach the first apparent equilibrium condition.

Effect of Pretreatment of Kaolinite on Sulfonate Adsorption

Results obtained for the adsorption of dodecyl benzenesulfonate under constant

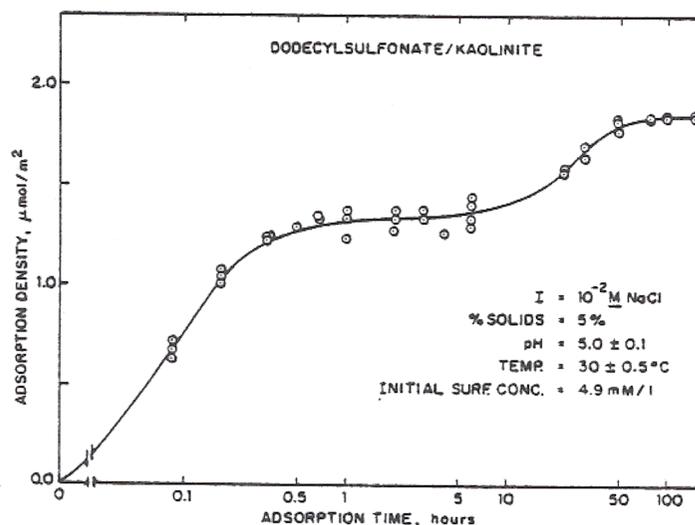


Fig. 2. Adsorption kinetics of dodecyl sulfonate on pretwetted kaolinite.

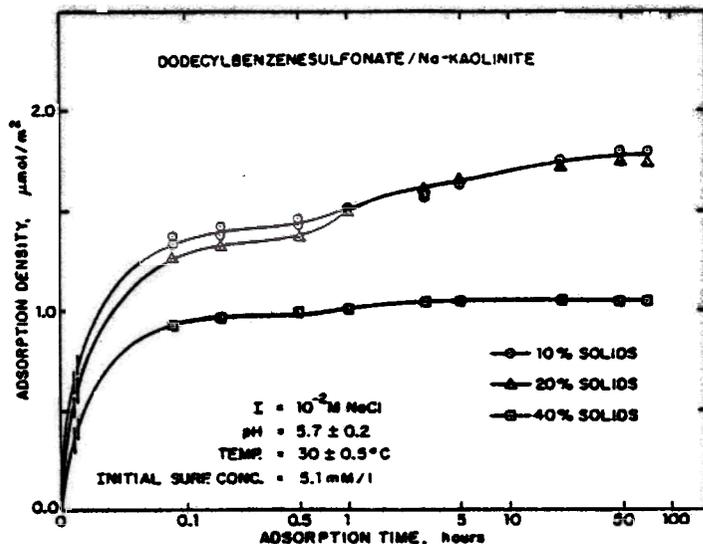


FIG. 3. Adsorption kinetics of dodecyl benzenesulfonate on pretwetted Na-kaolinite at different solid/liquid ratios.

ionic strength conditions and at three different pH values on pretwetted Na-kaolinite and pretwetted as received kaolinite samples are given in Figs. 4–6. The adsorption isotherms are characterized by the presence of maximum under all conditions. It might be noted that in the case of as received sam-

ples, the adsorption tended toward zero or even negative values in concentrated surfactant solutions.

The adsorption capacity of purified Na-kaolinite samples was higher than that of the original as received sample at all pH values.

Effect of pH

The results in Fig. 7 show clearly that adsorption of dodecyl benzenesulfonate on Na-kaolinite sample is highly sensitive to hydrogen ion concentration. To obtain in-

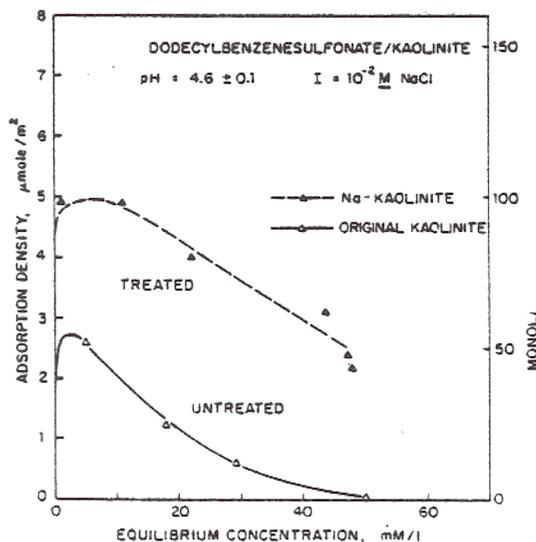


FIG. 4. Adsorption isotherms of SDDBS on the untreated original kaolinite and the Na-kaolinite samples at pH 4.9 ± 0.1 and $30 \pm 0.5^\circ\text{C}$.

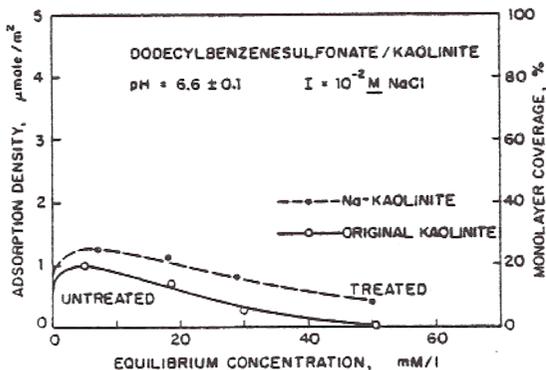


FIG. 5. Adsorption isotherms of SDDBS on the untreated original kaolinite and the Na-kaolinite samples at pH 6.6 ± 0.1 and $30 \pm 0.5^\circ\text{C}$.

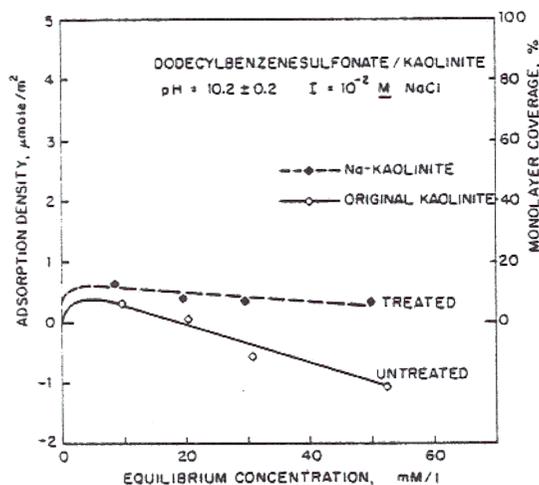


FIG. 6. Adsorption isotherms of SDDBS on the untreated original kaolinite and the Na-kaolinite samples at pH 10.2 ± 0.2.

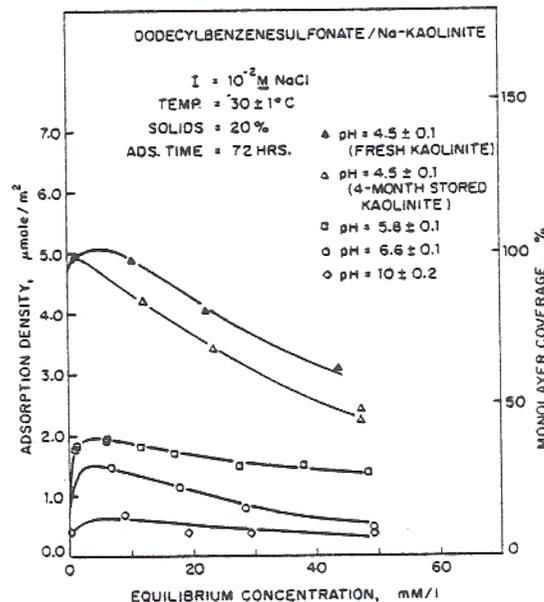


FIG. 7. Adsorption isotherms of SDDBS on Na-kaolinite at various pHs and storage time.

formation on adsorption as a function of final pH under constant equilibrium concentration of the surfactant, the data given in Figs. 4–6 were treated to generate the plots given in Fig. 8. It can be seen that sulfonate adsorption increases markedly with increase in hydrogen ion concentration, particularly in the acidic pH range, but the general shape of the adsorption isotherm is unaltered. In the acidic pH range the maximum amount of SDDBS adsorbed was found to

correspond to a compact monolayer with a molecular area of 33.7 Å²/SDDBS molecule. This value is in agreement with the reported values for close packed monolayers of dodecyl benzenesulfonate on CaCO₃ and Ca₃(PO₄)₂ (25, 26). The adsorption densities in the neutral and alkaline pH range, however, were found to correspond to only 25

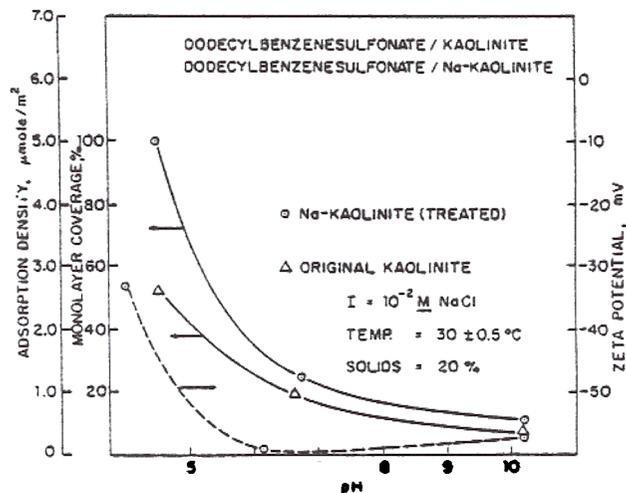


FIG. 8. Effect of pH on SDDBS adsorption on the untreated original kaolinite and Na-kaolinite samples.

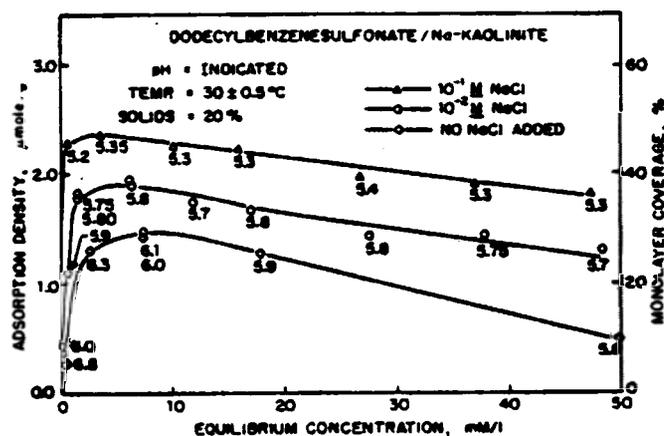


FIG. 9. Effect of ionic strength on the adsorption of SDDBS on Na-kaolinite at natural pH of the pulp.

and 12% of close packed monolayer, respectively.

Adsorption isotherms obtained under various ionic strength conditions for kaolinite/SDDBS system at the natural pH of the pulp are shown in Fig. 9, which suggest that the adsorption of sulfonate on kaolinite is enhanced by the addition of salt. In these tests pH was found to decrease from an initial value of about 6.8 to 5.9 and 5.3 in 10^{-2} and 10^{-1} M NaCl, respectively, and from 6.8 to about 5.8 with 5×10^{-2} M SDDBS alone. To derive the effect of ionic strength alone two series of adsorption experiments were conducted at constant pH values and a summary of these results is given in Fig. 10 as a function of pH at constant equilibrium surfactant concentration levels. It is evident from this figure that adsorption of sulfonate on kaolinite is enhanced but only slightly with increase in ionic strength.

DISCUSSION

Several physicochemical processes can be expected to take place when clays are contacted with electrolyte solutions and to contribute toward determining the overall behavior of the resulting suspensions. Major among such processes are recognized to be hydrolysis of surface species, ion-exchange, electrostatic adsorptions and dissolution of the clay constituents, and adsorption or

precipitation of resultant complexes. The possible role of the above processes in determining the equilibration of kaolinite with aqueous solutions is examined here with the help of data obtained under various conditions of pH, ionic strength, and sulfonate concentrations.

Hydrolysis

The process of equilibration of dry kaolinite with the aqueous phase involves at least

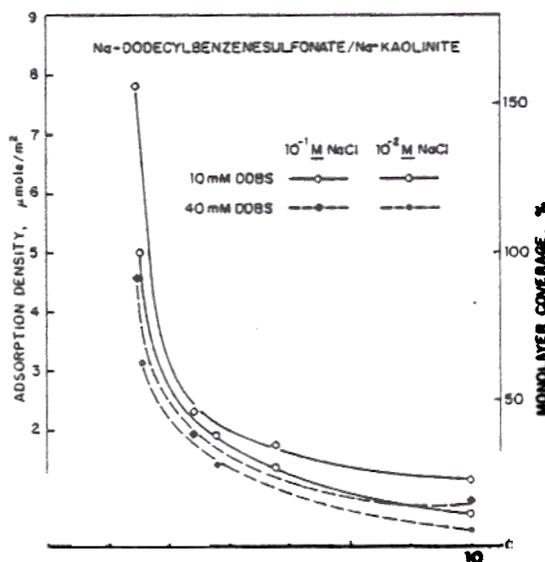
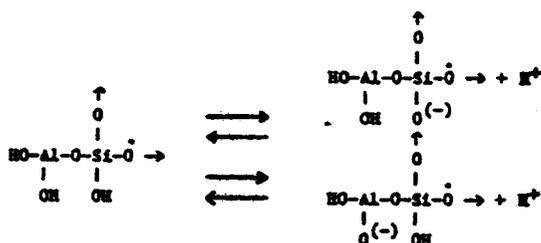


FIG. 10. Effect on ionic strength on the adsorption of SDDBS at constant equilibrium concentration as a function of pH at 30 ± 0.5°C.

two steps (Fig. 1). The fast step can partly be accounted for by hydrolysis reactions involving surface species on kaolinite. Past studies (24, 27–29) have suggested the source of acidity on kaolinite to be the terminal bonds and structural coordination across the edge faces either due to the silanol groups or due to aluminol groups at the strained gibbsite layer. In aqueous solutions, the broken bonds at the edge surface of dry kaolinite will be hydrated and converted to a hydroxylated surface. Bronsted acid generation, which is likely under these conditions can result from one of the following deprotonation processes (fast) (6):



Ion-Exchange

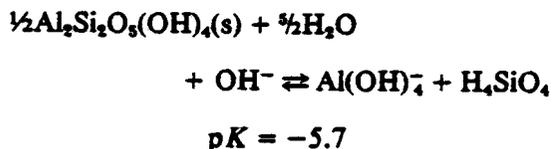
This process is characteristic of clay minerals since exchangeable cations are present as counterions in the clay (5, 30). This possibility is supported by the fact that increased acidity resulted upon adding NaCl to the system (see Fig. 1):



The hydrogen ions released under such conditions should be related to the ion-exchange capacity of the clay. The decrease in pH observed here at $5 \times 10^{-2} M$ NaCl corresponds to about $63 \mu\text{Eq/g}$ of clay. Such an ion-exchange process is expected to be fast and therefore can partly explain the fast pH drop observed.

Additional possibilities for ion-exchange exist in the presence of sulfonate in the system. Information on these can be obtained by examining the pH changes in the kaolin-

ite/SDDBS system under various pH conditions (Fig. 7 and 8). In this case while the final pH of this system in the acidic range was always higher than the initial value (initial pH of 3.1 shifted to a final pH of 4.6), the opposite was true in the neutral and alkaline pH range (initial pH values of 7 and 11 shifted to 6.5 and 9.6, respectively). These observations can be explained in terms of the amphoteric character of the terminal aluminum ions on the kaolinite surface and its anionic and cationic exchange properties. In the acidic pH range, the sulfonate ions can exchange with the surface OH^- ions leading to an increase in the pH of the solution. Such a mechanism is widely accepted by many investigators for the adsorption of phosphates on clays. The drop in the pH of the clay suspension from 11 to 9.6 in the alkaline region can also be explained in terms of the exchange of the negatively charged sulfonate ions with aluminate anions. The formation of aluminate ions is accompanied by OH^- consumption as shown by the following reaction (31):



The surface coverage of 7 to 8% monolayer calculated from the ion-exchange reaction is close to the 12% observed at pH 9.6.

As discussed earlier, exchange between Na^+ and H^+ ions is an important process that explains the results presented in Fig. 9. The decrease in pH is the direct result of ion-exchange between the surface H^+ ions on kaolinite by Na^+ ions from all the added salts. The resulting change in pH will have its own effect on the adsorption of sulfonate on the mineral. This indirect effect can in fact predominate the direct effect of changes in ionic strength (Fig. 10).

From the above discussion it can be concluded that ion-exchange can be a major mechanism responsible for adsorption.

Electrostatic Adsorption

The presence of charge at the edges as well as faces of the kaolinite particles can indeed be expected to influence the adsorption of both organic and inorganic species. In addition to the fact that the nature of these charges will vary considerably from edge to surface of a particle, complications arise also due to readsorption of dissolved charged mineral species such as that of aluminum.

The abnormal two-step adsorption kinetics curve obtained for kaolinite (Figs. 2 and 3) reflects the complex solution chemistry and the resultant interfacial behavior of this mineral.

The amounts adsorbed at the first plateau correspond only to about 5% of compact monolayer suggesting that the adsorption of the sulfonates in this region is limited to the positively charged edge surfaces of the kaolinite particles, which were reported in certain cases to be about 2 to 5% of the total area (6). H^+ and OH^- ions are considered to be the potential determining ions for the charged edge surfaces and therefore with a decrease in pH the number of positive sites on the mineral and the adsorption of the anionic surfactant will increase.

While such a simple mechanism prevails for adsorption of sulfonates on simple oxide minerals (32, 33), its role is expected to be limited in the case of kaolinite because the surface area occupied by the positively charged edge groups does not exceed 2 to 5% of the total surface (6). From the data given in Fig. 3 it has been shown that the total coverage of sulfonate does exceed that of 5% monolayer.

Dissolution of Surface Species

The slow pH changes following the initial fast pH drop observed (Fig. 1) during equilibration of kaolinite with the aqueous phase suggest occurrence of slow processes such as dissolution and hydrolysis of surface species of aluminum and silicon. It has been pointed out recently that there are two water

molecules associated with each edge proton, one completing with coordination sphere of the edge octahedron and the other closely associated with the silanol group (6). Proton mobility from silanol groups to the aluminum octahedra is considered to produce exchangeable aluminum ions after long periods of time. The decrease in the acidity of kaolinite suspension with time is attributed to the release of such exchangeable aluminum ions into the system. The highly charged Al^{3+} species could readsorb on the mineral surface in different forms after a series of hydrolysis reactions that produce complex ions such as $Al(OH)^{2+}$, $Al_6(OH)_{20}^{4+}$, $Al(OH)_3$, and $Al(OH)_4^-$. Such a process can be expected to be very slow in comparison to the dissociation of the weakly acidic groups on kaolinite surface. The adsorption that results from the slow release of aluminum species during the initial period will be of a smaller magnitude than that due to electrostatic or ion-exchange reactions and an apparent equilibrium could therefore be attained (Figs. 2 and 3). At longer contact times, however, the slow release of increasing amounts of charged aluminum species from the basal kaolinite surfaces into the solution followed by their adsorption on the kaolinite surface will be an important process particularly in the acidic and basic pH ranges where concentration of dissolved aluminum species is considerably higher than in the neutral range (see Fig. 11). This will increase the affinity of the negatively charged sulfonate toward kaolinite surface and hence an increase in adsorption, especially at low pH values. Under such conditions a new equilibrium is obtained in time intervals that would be dictated essentially by the kinetics of release of aluminum species and their subsequent hydrolysis and readsorption.

Past studies (36–40) using kaolinite do not appear to have considered this possibility of an intermediate metastable condition. Implications of such a metastable condition in the interpretation of adsorption data should be noted.

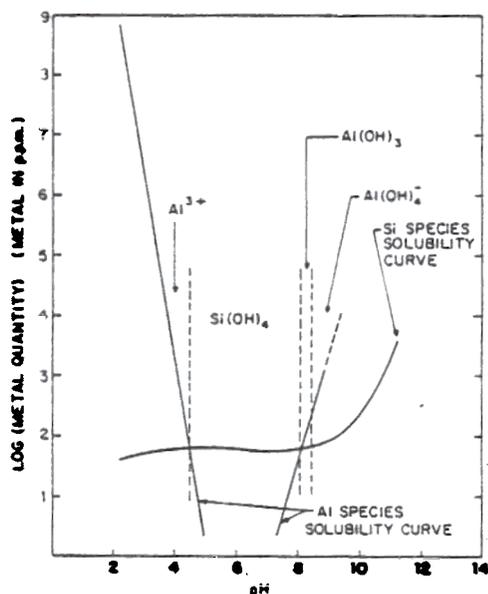


FIG. 11. Solubility-pH diagram of kaolinite [after Buchanan and Oppenheim (7)].

The role of aluminum species and the change in their relative concentrations upon pretreatment of kaolinite in controlling the adsorption of sulfonate can in fact be very significant. For example, the actual coverage obtained for sulfonate adsorption on alumina is found to correspond to a close packed monolayer under acidic pH conditions and such coverage is made possible partly by the generation of secondary positive sites owing to specific adsorption of Al^{3+} ion and its complexes to the basal negative kaolinite crystal. Acid leaching studies of Buchanan and Oppenheim (7) and Conely and Althoff (6) have in fact confirmed the presence of colloidal aluminum hydroxide in varying quantities on aged kaolinite particulates. Also, the dissolved Al^{3+} and its hydroxy complexes can be expected to react with the bulk surfactant species to form aluminum sulfonate complexes that can easily adsorb on the kaolinite surface. Precipitation of aluminum sulfonates in bulk solution is also a major contributing factor. In addition, the presence of other important multivalent cations such as Ca^{2+} released

from clay by an ion-exchange mechanism has been found to cause precipitation of sulfonate at low concentrations; precipitate subsequently redissolved at higher sulfonate concentrations (34). This phenomenon has been shown to contribute toward the adsorption maximum observed for the kaolinite/alkyl sulfonate systems (35).

Pretreatment of Clay

The observed difference in adsorption capacity between the "kaolinite" and "Na-kaolinite" suggests that the kaolinite surface, during the purification process, was subjected to certain physicochemical changes such as removal or introduction of surface complexes or impurities and alterations in the hydration properties of the solids. Prolonged treatment of kaolinite with water for the purpose of removing associated soluble salts can result in the generation of exchangeable aluminum species on the mineral surface as discussed before (5-8). It has been shown recently that even the so-called "Al-free" homoionic sodium kaolinite generates as much as $10^{-4} M Al^{3+}$ in $10^{-4} M NaCl$ solutions. Surface contamination by hydrolyzed silicon species is also possible (7).

It is of interest to note that in the case of as received sample, adsorption of sulfonate tends toward even negative values in concentrated surfactant solution. Such behavior is characteristic for minerals of high water sorption capacity such as montmorillonite and suggests presence of this type of minerals as impurity in the original sample. Apparently the impurities were removed from the Na-kaolinite sample during the washing and decantation steps due to their fine particle size and resultant slow settling. An increase in the effective surface area of the purified Na-kaolinite during the process of treatment may also be partially responsible for its higher adsorption capacity as the measured nitrogen surface area is only a few percent of the theoretical value of this mineral $1073 m^2/g$ (41). Changes in surface prop-

erties can also occur during storage of the purified clay for long periods. Stored samples exhibited lower adsorption capacities than freshly prepared purified kaolinite samples (see Fig. 7). Similar observations have also been made by Martin (30) who emphasized the need for extreme care in the preparation of kaolinite and suggested that experiments on a particular specimen be completed within a few weeks to obtain consistent and meaningful results.

CONCLUSIONS

Both the equilibration of the kaolinite with water and the adsorption of alkylsulfonates on it were found to involve at least two major steps. Also the final adsorption obtained was dependent strongly on the pretreatment that the clay had undergone as well as the extent of subsequent aging.

Changes in pH of water due to its contacting with kaolinite are attributed mainly to the ion-exchange properties of the clay and reactions of dissolved aluminum and silicon species with the bulk water. Sulfonate adsorption, on the other hand, is the result of a combined mechanism involving electrostatic adsorption, ion-exchange, metal activated adsorption and precipitation. Dissolution of aluminum species appears to play a major role in determining the interfacial properties of the system particularly through the latter two modes of adsorption.

ACKNOWLEDGMENTS

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