

MECHANISM OF SULFATE ADSORPTION BY KAOLINITE

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Abstract—Sulfate adsorption on kaolinite was followed at 0.7 $\mu\text{eq/ml}$ to 99 $\mu\text{eq/ml}$ solution concentrations at 30°C and at pH 6.0, and the amount of OH^- ions released and the change in surface charge were determined. Sulfate was adsorbed at positive and neutral sites by displacing OH_2 and OH^- groups, respectively. Adsorption of sulfate occurred predominantly at positive sites at low (0.7 $\mu\text{eq/ml}$ to 0.9 $\mu\text{eq/ml}$) solution concentrations, whereas at higher solution concentrations, the proportion of the sulfate adsorbed at the neutral sites increased, varying from 51% at 4.9 $\mu\text{eq/ml}$ to 68% at 99 $\mu\text{eq/ml}$. The form of sulfate bonding was apparently governed by the level of the positive charge on the clay surface. Higher positive charge at low and intermediate levels of sulfate saturation resulted in the adsorption of sulfate as a divalent anion by forming a 6-member ring with surface Al. With a decrease in positive charge at higher levels of adsorption, the sulfate ion formed both monodentate and bidentate complexes.

Key Words—Adsorption, Bidentate, Hydroxyl, Kaolinite, Monodentate, Sulfate.

INTRODUCTION

It is well recognized that the adsorption of sulfate by soils and soil materials occurs by replacement of M-OH_2^+ or M-OH groups (Parfitt, 1978). In addition, several workers have reported that the adsorption of sulfate by clay minerals occurs by ligand exchange (Chang and Thomas, 1963; Chao *et al.*, 1965; Aylmore *et al.*, 1967). Such investigations reported, however, have not clearly established the exact mechanism of sulfate binding to the clays, and the relationship between the adsorbed sulfate and the change in surface charge is not clear. It is also not certain if the anion is adsorbed as a monodentate species or forms a binuclear bridging complex.

In comparison, the adsorption of sulfate by hydrous metal oxides is well characterized. Hingston *et al.* (1972) proposed that for specific adsorption to occur, an anion must be capable of accepting or donating protons and that maximum adsorption occurs at $\text{pH} = \text{pK}_a$. With the adsorption of sulfate by gibbsite, the anion accepts a proton from the positive site (M-OH_2^+) on the surface, and the monovalent species HSO_4^- is adsorbed by displacing the resulting OH^- ion without creating additional negative charges on the surface. On the other hand, Rajan (1977), in his work on sulfate adsorption by hydrous alumina, showed from the quantitative relationships between the sulfate adsorbed, the ligands displaced, and the changes in surface charge, that sulfate is most probably adsorbed by bridging across two adjacent Al surface atoms to form a 6-member ring. Parfitt and Russell (1977) also showed that sulfate is adsorbed on goethite as a binuclear bridging complex.

Several authors have shown that adsorbed anions affect the physico-chemical and engineering properties of soil clays (Mitchell, 1976; Sridharan *et al.*, 1981; Sreepada Rao, 1982). For example, fluoride and phos-

phate form complexes with Fe and Al ions extracted from the clay mineral structure at low pH (Wiklander, 1964). These compounds therefore act as cementing materials resulting in increased strength characteristics of the clay body. The adsorption of anions is known to bring about changes in surface charge (Bowden *et al.*, 1973). Thus, anion adsorption may cause either flocculation or dispersion of clay particles and may cause volume changes at the macrolevel. The percolation of water through some soil materials decreases the anion content to an appreciable degree (Reisenauer, 1967) and alters the material properties. A detailed knowledge of the mechanism of anion adsorption is therefore necessary to understand the properties and behavior of soils and soil materials.

The present work investigated the possible mechanisms of sulfate adsorption on kaolinite. Experimental investigations were carried out to determine the amount of sulfate adsorbed at different solution concentrations, the amount of OH^- ions released, and the variation of surface charge caused by sulfate adsorption.

MATERIALS AND METHODS

Materials

Kaolinite from Gujarat state, India, was used in the studies. Its X-ray powder diffraction pattern indicated a c-axis spacing of 7.15 Å. The aqueous cation-exchange capacity (CEC) of the kaolinite mineral, as determined by the pH equilibrium method of Jackson (1958), was 3.3 meq/100 g. The specific surface area as evaluated by the single-point water-vapor adsorption method was 24.56 m^2/g . Hydrometer analysis showed that about 30% of the sample fraction had particle size of $<2 \mu\text{m}$ and that the remaining material ranged in size between fine and medium silt. The CEC and surface area values are close to those reported (van

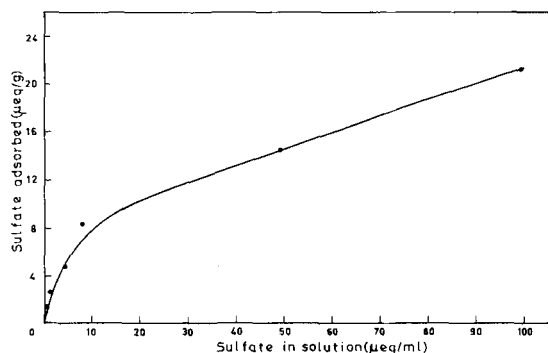


Figure 1. Adsorption of sulfate on kaolinite as a function of solution concentration.

Olphen and Fripiat, 1979) for a less well-crystallized kaolinite from Georgia, USA; however, a band at 3669 cm^{-1} in the infrared spectra of the sample indicated that the mineral is not extremely disordered. The bands at 2934 cm^{-1} and 2855 cm^{-1} , and at 798 cm^{-1} and 780 cm^{-1} , respectively, suggest the presence of diaspore and quartz as impurities (Van der Marel and Beutelspacher, 1976). The presence of diaspore was also revealed by a small peak in the XRD pattern of the sample at $21.9^{\circ}2\theta$ ($\text{CuK}\alpha$ radiation).

Methods

Adsorption of sulfate. Five grams of oven-dried kaolinite was equilibrated at 30°C with 50 ml of 0.1 N NaCl solution for about 24 hr at pH 6.0. The counterions Na^+ and Cl^- retained gave a measure of the negative and positive charge on the surface, respectively. The pH of the suspension was maintained by successive additions of dilute HCl over the 24-hr equilibration period. At the end of the period, 50 ml of sodium sulfate solution was added such that the final sulfate concentration in the slurries was between 0.5 and $100\text{ }\mu\text{eq/ml}$. The slurries were further allowed to stand for a period of 24 hr with intermittent shakings. The pH was maintained at 6.0 by successive acid additions from a microburette. Finally, the slurries were filtered through weighed sintered-glass crucibles. The loaded crucibles were weighed, dried overnight at 80°C , and reweighed to obtain the weight of the entrapped sulfate solution. The filtrates were analyzed for sulfate content by precipitation with BaCl_2 and subsequent gravimetric estimation. The amount of sulfate in the entrapped solutions were calculated from the experimentally determined concentrations in the final solutions. The amount of sulfate adsorbed was taken as the difference between the amount taken and that found in the filtrate on equilibration after making due corrections for the sulfate present in the entrapped solution and for the amount of acid added to the suspension.

All equilibrations were carried out in duplicate. The difference in the sulfate adsorption values between duplicate runs was about 4% for sulfate solution concentrations up to $1\text{ }\mu\text{eq/ml}$ and $\leq 2\%$ for higher solution concentrations. The averages of the values obtained from duplicate runs have been used.

OH⁻ release and surface charge. The OH^- released on sulfate adsorption was estimated from the amount of acid required to maintain the pH of the slurry at 6.0 during equilibration with the sulfate solution. The negative and positive charges of the kaolinite sample were determined by estimating the Na^+ and Cl^- ions retained by the clay mineral from NaCl and NaCl- Na_2SO_4 solution mixtures, following a procedure outlined by Rajan (1977). A 0.05 M $\text{Ca}(\text{NO}_3)_2$ solution was used as the extractant. Na^+ ions in the extract were determined by flame photometry. The chloride content was estimated indirectly from the amount of silver consumed using atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Adsorption isotherm

Figure 1 depicts the amount of sulfate adsorbed as a function of sulfate concentration in solution. The amount of adsorbed sulfate increased with increasing solution concentration, typical of Freundlich-type behavior. The sulfate ion apparently was adsorbed by ligand exchange as well as by retention as a counterion in the diffuse double layer. Rajan (1977), in his work on sulfate adsorption on hydrous alumina, observed that the maximum contribution from the latter mode of adsorption amounted to $25\text{ }\mu\text{eq/g}$, which corresponds to about 3% of his observed maximum sulfate adsorbed. We also found in the present work that this contribution was small and within the limits of experimental error; hence, it had little effect on the isotherm and was not considered.

Variation of surface charge

The variation of the positive and negative charges as a function of sulfate adsorbed is presented in Figure 2. The Na^+ adsorption value of $28\text{ }\mu\text{eq/g}$ for the untreated kaolinite corresponds to exchange of Na^+ ions with the counterions at the kaolinite surface. The observed plateau for the Na^+ adsorption on kaolinite at different levels of sulfate uptake suggests that the clay mineral did not develop negative charge on sulfate adsorption. The untreated kaolinite had a positive charge (σ^+) of $31.9\text{ }\mu\text{eq/g}$ which decreased with increasing sulfate adsorption to a value of $9.0\text{ }\mu\text{eq/g}$ at the experimental sulfate adsorption maximum of $21.3\text{ }\mu\text{eq/g}$.

Mechanism of sulfate adsorption

At the experimental pH (6.0) studied, the kaolinite edge carried positive sites, as suggested by the adsorp-

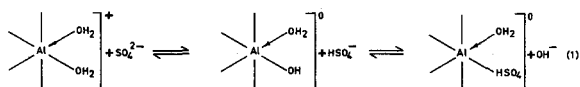
Table 1. Ligand exchange data for sulfate adsorption on kaolinite.

Sulfate adsorbed (S) (μeq/g)	OH ⁻ released (μeq/g)	OH ₂ released/ positive charge neutralized (μeq/g)	Total ligands displaced (L) Col. 2 + Col. 3 (μeq/g)	ξ ¹ Col. 3 / Col. 1	OH ⁻ released / sulfate adsorbed	L/S
1.5	0.3	2.7	3.0	1.80	0.20	2.0
2.5	1.0	4.0	5.0	1.60	0.40	2.0
4.9	2.5	7.1	9.6	1.45	0.51	1.96
8.4	4.6	11.2	15.8	1.33	0.55	1.88
14.4	8.6	17.8	26.4	1.24	0.60	1.83
21.3	14.4	22.9	37.3	1.075	0.68	1.75

$$^1 \xi = \frac{\text{positive charge neutralized}}{\text{unit amount of sulfate adsorbed}}$$

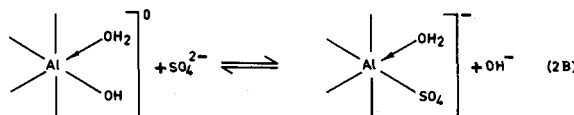
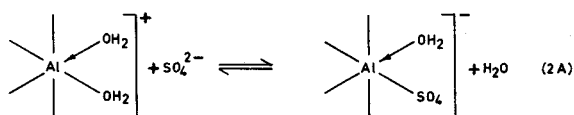
tion of Cl⁻ ions by the untreated kaolinite, and probably neutral sites. The existence of negative centers is unlikely because the amount of Na⁺ adsorbed did not exceed the aqueous CEC of the sample.

If the sulfate accepted a proton from the positive site on the edge surface, as proposed by Hingston *et al.* (1972), the adsorption of sulfate can be represented as:

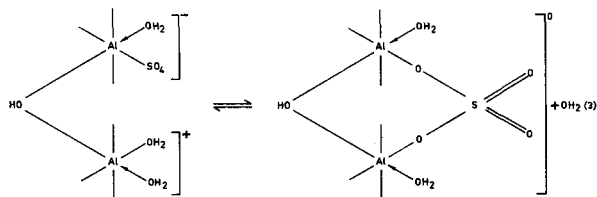


The above reaction requires an equal number of equivalents of the anion adsorbed and (1) the positive charge neutralized and (2) the OH⁻ ions released. The value of the positive charge neutralized $\sigma^+_0 - \sigma^+_s$ (σ^+_s = the positive charge on the sulfate-adsorbed sample) and the amounts of OH⁻ ions released at different sulfate saturations are presented in Table 1. It is seen that the equivalents of sulfate adsorbed equal neither those of the positive charge neutralized nor of the OH⁻ ions released.

The adsorption of sulfate according to the mechanism proposed by Rajan (1977) may be represented by:



In the absence of the development of a negative charge due to sulfate adsorption on the clay surface (Figure 2), it is presumed that the neutralization of the negative charge left on the surface from reactions (2A) and (2B) proceeded by the participation of a neighboring Al ion resulting in ring formation. This reaction may be depicted as:



If the neighboring Al was a neutral site, an OH⁻ would have been released on charge neutralization. Kafkafi *et al.* (1967), proposed a similar ring formation mechanism for phosphate fixation by kaolinite.

The values of the positive charge neutralized ($\sigma^+_0 - \sigma^+_s$) per unit amount of sulfate adsorbed, defined as ξ at various anion saturations, are presented in Table 1. The ξ value decreased from 1.8 at 1.5 μeq of sulfate adsorbed to 1.075 at 21.3 μeq of sulfate adsorbed, suggesting that at low concentrations sulfate was predominantly adsorbed on the positive sites. With the saturation of these sites, adsorption progressively occurred at the neutral sites. This relationship is also reflected in the increasing values of the ratio of OH⁻ released to sulfate adsorbed (Table 1).

The adsorption of sulfate as a binuclear bridging complex in accordance with reactions (2) and (3) requires that each equivalent of adsorbed sulfate displaced two equivalents of ligands. Assuming that the

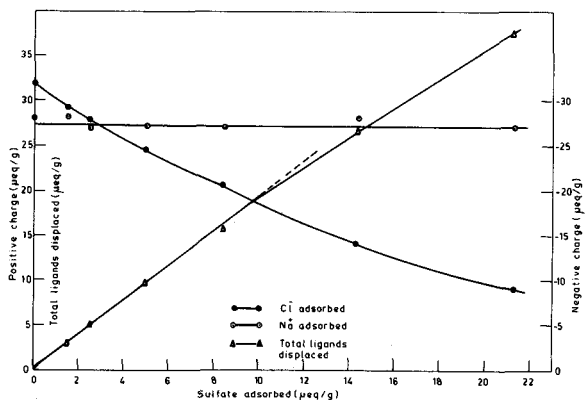


Figure 2. Total ligands displaced (OH⁻ + OH₂) and variation of surface charge as a function of sulfate adsorbed on kaolinite.

amount of aquo groups displaced was equivalent to the positive charge neutralized, the sum of OH^- and OH_2 groups released at each level of sulfate adsorbed was determined (Table 1). The ratio of sum of ligands displaced ($\text{OH}^- + \text{OH}_2$) to the sulfate adsorbed (L/S) should equal 2. Allowing a 5% variation in this value as experimental error, the ratio in Table 1 is fairly close to 2 for sulfate adsorption values as high as $8.4 \mu\text{eq/g}$. At higher levels of sulfate uptake, the ratio tends to be <2 . This variation of the L/S values with the sulfate saturation is also reflected in the plot of total ligands displaced vs. sulfate adsorbed (Figure 2) which showed a break in the linear relationship above $8.4 \mu\text{eq}$ of sulfate adsorbed. The initial segment has a slope of 1.94, and the latter portion has a value of 1.64. The above trend suggests that a 1:2 stoichiometry definitely existed between the sulfate adsorbed and the ligands displaced up to intermediate levels of sulfate uptake. The L/S ratio for higher anion saturations suggests that the sulfate probably formed both monodentate and bidentate complexes with the surface Al atoms. The monodentate ligand was presumably the monovalent ion HSO_4^- , as kaolinite did not develop negative charge on sulfate adsorption.

The above observations are in agreement with the model of Bowden *et al.* (1973, 1977) which predicts that at low anion saturation the higher positive charge of the surface favors the adsorption of divalent ions and that the decreased positive charge at the higher levels of anion adsorption results in an increased preference of the surface for monovalent ions. In his work on selenite adsorption on hydrous alumina, Rajan (1979) likewise observed that the preferential adsorption of multi- or monovalent ions takes place depending on the positive charge of the surface in concurrence with the model of Bowden *et al.* (1973, 1977). In addition, Rajan considered that at low surface saturations the decreased H^+ activity near the positive surface as compared to that in the bulk solution favors the existence of divalent ions and hence their adsorption. The decrease in positive charge and consequently the decrease in surface potential at the higher levels of anion adsorption resulted in the H^+ activity near the edge surface approaching that in the bulk solution. At the higher solution concentrations, this increase in the H^+ activity near the edge face probably resulted in a fraction of the sulfate ions existing as HSO_4^- and their being adsorbed as monodentate ligands.

CONCLUSIONS

At low anion saturations, sulfate was adsorbed on kaolinite as a divalent ion and presumably formed a binuclear bridging complex, displacing two ligands in the process. At the higher solution concentrations, the surface also favored the adsorption of monovalent ions, and the sulfate formed both monodentate and biden-

tate complexes displacing one and two ligands, respectively. Initially, sulfate ions were preferentially adsorbed at the positive sites. With the neutralization of these sites, the proportion of the anions being adsorbed at neutral sites increased.

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Резюме—Адсорбция сульфата каолинитом исследовалась для концентрации раствора между 0,7 мэкв/мл и 99 мэкв/мл при 30°C и pH = 6,0; были определены количество выделенных ионов OH⁻ и изменения поверхностного заряда. Сульфат адсорбировался на положительных и нейтральных местах путем вытеснения групп OH₂ и OH⁻, соответственно. Адсорбция сульфата происходила в главной мере на положительных местах при низких концентрациях раствора (0,7 мэкв/мл до 0,9 мэкв/мл), тогда как при больших концентрациях, пропорция сульфата адсорбированного на нейтральных местах увеличивалась, принимая значения от 51% для 4,9 мэкв/мл до 68% для 99 мэкв/мл. Тип связи сульфата зависел, вероятно, от уровня положительного заряда на поверхности глины. Большой положительный заряд при низких и промежуточных уровнях насыщения сульфатом приводил к адсорбции сульфата в виде двухвалентного аниона путем формирования 6-членного кольца с поверхностными атомами Al. При уменьшении положительного заряда на больших уровнях адсорбции, ион сульфата образовывал монозубчатые и двухзубчатые комплексы. [E.G.]

Resümee—Die Sulfatadsorption an Kaolinit wurde von 0,7 µÄquivalent/ml bis 99 µÄquivalent/ml Lösungskonzentration bei 30°C und pH 6,0 verfolgt, wobei die Menge der freigesetzten OH⁻-Ionen und die Veränderung der Oberflächenlagen bestimmt wurde. Das Sulfat wurde an positiven und neutralen Plätzen adsorbiert, wobei es OH₂- und OH⁻-Gruppen ersetzte. Die Sulfatadsorption erfolgte bei niedrigen Lösungskonzentrationen (0,7 µÄquivalent/ml bis 0,9 µÄquivalent/ml) vor allem an den positiven Plätzen, während bei höheren Lösungskonzentrationen der Anteil des Sulfats, das an neutralen Plätzen adsorbiert wird, zunahm, wobei er von 51% bei 4,9 µÄquivalent/ml bis 68% bei 99 µÄquivalent/ml variierte. Die Art der Sulfatbindung wurde offensichtlich durch die Höhe der positiven Lagen auf der Tonoberfläche reguliert. Eine höhere positive Ladung führte bei niedriger oder mittelmäßiger Sulfatsättigung zu der Adsorption von Sulfat in Form eines divalenten Anions, wobei ein 6-er Ring mit dem Oberflächen-Al gebildet wurde. Wenn die positive Ladung bei höherem Adsorptionsgrad abnahm, dann bildete das Sulfation sowohl einzählige als auch zweizählige Komplexe. [U.W.]

Résumé—On a suivi l'adsorption sulfate sur la kaolinite à des concentrations de solution de 0,7 µeq/ml à 99 µeq/ml à 30°C et au pH 6,0, et on a déterminé la quantité d'ions OH⁻ relâchés et le changement de charge de surface. La sulfate a été adsorbée à des sites positifs et neutres par déplacement de groupes OH₂ et OH⁻, respectivement. L'adsorption de sulfate s'est passée de façon prédominante à des sites positifs à des concentrations de solution basses (0,7 µeq/ml à 0,9 µeq/ml), tandis qu'à de plus hautes concentrations de solution, la proportion de sulfate adsorbée aux sites neutres a augmenté, variant de 51% à 4,9 µeq/ml à 68% à 99 µeq/ml. La forme de liaison de sulfate était apparemment gouvernée par le niveau de la charge positive sur la surface de l'argile. Une plus haute charge positive à des niveaux de saturation de sulfate bas et intermédiaires a résulté en l'adsorption de sulfate en tant qu'anion divalent par la formation d'un anneau à 6 membres avec l'Al de surface. Lors d'une diminution de charge positive à des niveaux d'adsorption plus élevés l'ion sulfate a formé à la fois des complexes monodentates et bidentates. [D.J.]