

Polyelectrolyte Adsorption by Kaolinite

A. S. MICHAELS AND O. MORELOS

Massachusetts Institute of Technology, Cambridge, Mass.

OVER the past few years, considerable interest has developed in the use of certain polyelectrolytes as flocculating agents for finely divided solids in aqueous suspension and as aggregating agents for soils, so-called soil conditioners. These compounds, when added in concentrations as low as 0.01% of the weight of the solid to be treated, can under proper conditions agglomerate particles very rapidly and produce stable aggregates (14, 16).

The mechanism by which these polymers cause flocculation is not yet clearly defined. Pertinent facts relating to the types of compounds that are effective flocculants and the conditions under which flocculation occurs are as follows:

1. Cationic polyelectrolytes and certain nonionic water soluble gums are effective flocculants for many solid suspensions over wide ranges of pH and electrolyte concentration in solution (15, 18).

2. Anionic polyelectrolytes are effective flocculants for clays which normally carry negative charges in water only when the polymer also contains nonionic polar groups—e.g., hydroxyl or amide—and/or the anion is carboxyl (COO^-). Purely polycarboxylic polymers—e.g., sodium poly(methyl methacrylate)—or sulfonate polymers—e.g., sodium polystyrene sulfonate—do not flocculate these solids (9, 19).

3. Anionic polyelectrolytes such as hydrolyzed polyacrylonitrile, hydrolyzed polyacrylamide, and poly (calcium maleate *co* vinyl acetate) are effective flocculants for clays and soils in neutral or slightly acid solution. In solutions made alkaline with caustic soda, flocculation does not occur. In solutions made alkaline with lime, flocculation does take place (13).

4. With caustic-hydrolyzed polyacrylamide, maximum flocculation effectiveness is found to occur when the extent of hydrolysis is about 30% (7).

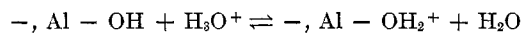
5. Despite their poor flocculating ability, purely carboxylic polymers such as sodium poly(methyl methacrylate) adsorb on the surface of clays such as kaolinite in neutral solution. Adsorption is increased by addition of electrolyte (NaCl) to the solution (19).

Generally researchers in this field agree that flocculation occurs by a process of adsorption of polymers on, and of bridging of polymer chains between solid particles. With cationic polymers, adsorption on negatively charged solid particles and consequent flocculation occur by simple electrostatic attraction. With nonionic polymers (such as the starches) it has been proposed (15) that adsorption and flocculation occur via hydrogen bonding between the solid surfaces and the hydroxyl groups on the polymer. However, the fact that anionic—i.e., carboxylic—polyelectrolytes adsorb on and flocculate negatively charged solids such as clays is more difficult to explain, since it would be expected that electrostatic repulsion between the similarly charged solid and polymer would prevent adsorption.

KAOLINITE STRUCTURE AND PROPERTIES

Kaolinite is a naturally occurring two-layer aluminosilicate whose composition, crystallographic structure, and physical properties are well defined. The pure mineral has a low but measurable cation exchange capacity and, thus, evidently contains a number of negatively charged sites on its surface, the exact nature or location of which is in dispute. Some evidence (10) indicates that these sites are located on the fractured edges of the crystals and are due to surface ionization brought about by unbalanced electrical forces. It has also been postulated (4) that exchange sites develop on the planar surfaces due to ionization of OH groups attached to the weakly acidic aluminum or silicon.

The cation exchange capacity of kaolinite is quite variable depending on the source of the mineral, its particle size, and the pH of the environment in which ion exchange is measured. The exchange capacity increases with increasing specific surface area—i.e., decreasing particle size—and also with increasing pH of the solution in which the clay is suspended, because both alumina and silica behave as weak acids whose degree of ionization is favored by reduction in hydrogen ion concentration. However, even in rather strongly acid solutions, pH 3 to 4, cation exchange can occur, indicating that some of the anionic sites on the particle surfaces behave as rather strong acids. However, in very strongly acidic solutions, pH = 2 or below, kaolinite adsorbs or exchanges anions (21). This is believed to be caused by the amphoteric nature of alumina, which will coordinate with hydronium ions rather than hydroxyl ions in strongly acid solution



Schofield (21) has postulated that cationic sites of this nature are present on the edges of kaolinite particles even at a relatively high pH, 9.0 or less, although the evidence supporting this is not complete.

Natural kaolinite, containing exchangeable calcium, magnesium, or other foreign cations, can be converted to the so-called hydrogen form by electrodialysis of the mineral (in aqueous suspension) against distilled water. This hydrogen-clay is quite free of foreign ions and uncontaminated by adsorbed leaching components. Such kaolinite forms fairly acidic suspensions, pH = 4.5 and can be titrated with standard bases as a weak acid. Hydrogen kaolinite, when titrated with caustic soda to a pH of 7.0, will usually exhibit a cation exchange capacity of from 0 to 5 meq. per 100 grams.

Considerable evidence (21) supports the belief that a hydrogen kaolinite is not merely a form of the mineral in which the anionic exchange sites are satisfied by hydrogen ion, but that such a clay contains significant quantities of aluminum ion (extracted from the crystal edges, presumably), adsorbed on the particle surfaces. This aluminum can be removed from the clay by leaching with acidic salt solutions, pH = 3. The precise manner in which this aluminum is held to the mineral is not clear, but it might be coordinated with hydroxyl groups on the surface or edges of the particles. Whether this extractable aluminum should be considered a normal constituent of the crystal structure or a foreign cation remains open to question.

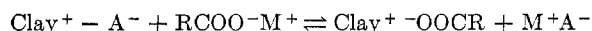
As a consequence of these surface properties, kaolinite behaves in aqueous suspension as an electrocratic colloidal system. At a high pH and in the presence of highly hydrated monovalent cations, the particles carry a high net negative charge and are surrounded by a large diffuse double layer of balancing cations. At a relatively low pH or in the presence of polyvalent cations such as calcium, the net negative surface charge is low, and the double layer of counterbalancing cations is thin. The magnitude of the surface charge on kaolinite exerts an important influence on the state of aggregation of the particles in water; when this charge is high, electrostatic repulsion between particles causes the mineral to disperse readily and form stable suspensions, while when the charge is low, the particles agglomerate in stable flocs which separate rapidly from suspension. While the role of surface charge on the state of aggregation of kaolinite and other similar solids has been well demonstrated and clarified,

the reason why anionic polyelectrolytes cause flocculation of clays remains obscure. It is to explain this phenomenon in the light of the known facts about clay structure and properties that this research has been undertaken.

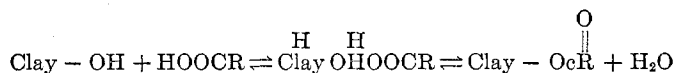
PROPOSED MECHANISMS FOR FLOCCULATION BY POLYANIONS

To explain the flocculation of clays by polyanions, it is inferred from the work of Ruehrwein and Ward (19) that adsorption of polymer occurs by a process of anion interchange with clay (kaolinite), wherein the carboxylate ions replace adsorbed anions (presumably OH^-) on the clay surface. In contrast, it has also been proposed (15) that adsorption of polyanions on clay occurs by hydrogen bonding (between the solid and hydroxyl, amide, or un-ionized carboxyl groups of the polymer) as with polysaccharides, the sole function of the ionic groups on the polymer being to extend the polymer chain. A third possibility is that polyvalent cations (e.g., Ca^{++}) usually present in clays may act as electrostatic bridges between the solid surface and the polyanion.

If the anion-interchange mechanism is correct, then the reaction



should be favored by a high concentration of carboxylate ion—i.e., adsorption should increase with increasing pH. If, on the other hand, the hydrogen bonding mechanism is correct, then the reaction



should be favored by a high concentration of un-ionized carboxylate—i.e., adsorption should decrease with increasing pH. If, finally, adsorption takes place by polyvalent cation bridging, then no adsorption should take place in a system devoid of such ions.

The object of this investigation has been to attempt to clarify the mechanism of adsorption of selected carboxylic polyelectrolytes by examining the adsorption of these polymers on purified—i.e., polyvalent cation-free—hydrogen kaolinite under conditions of varying hydrogen ion concentration. By measuring simultaneously the extent of flocculation of the clay to these polymers, an attempt has been made to relate the flocculating ability of these compounds to their extent of adsorption.

The polymers studied in this work were sodium polyacrylate, and partially caustic-hydrolyzed polyacrylamide. The former was prepared by the polymerization of acrylic acid, followed by neutralization with sodium hydroxide. The latter was prepared by the polymerization of acrylamide, followed by controlled hydrolysis of the polymer with sodium hydroxide. Sodium polyacrylate is not active as a flocculant for clay, whereas hydrolyzed polyacrylamide is quite effective; it was, therefore, desirable to determine whether there are significant differences in the adsorption of these two polymers by clay which might account for their differences in flocculating ability.

The clay used in this work was a refined kaolinite, Edgar Plastic Kaolin (2), which was converted to the pure hydrogen form by exhaustive electrodialysis. The pH of this hydrogen kaolinite in aqueous suspension is about 4.5. By addition of controlled quantities of caustic soda to this clay, a series of aqueous kaolinite suspensions was prepared varying in pH from 4.5 to 10. To these suspensions, in which the only cations present were sodium and hydrogen, were added measured quantities of the polyelectrolytes, and the extent of polymer adsorption and the change in state of aggregation of the clay were measured.

These measurements and their interpretation permit a more thorough understanding of the nature of carboxylic polymer adsorption and of the cause of flocculation by such compounds.

PROCEDURE

Electrodialysis. Kaolinite, which usually exhibits a base exchange capacity of about 1 to 5 milliequivalents per 100 grams, is found in nature predominantly in the calcium form. This clay can most satisfactorily be converted to the hydrogen form by dispersing the mineral in water, and submitting the suspension to electrodialysis against distilled water for a period of about one week. During this process, the exchangeable calcium ions on the clay are replaced by hydrogen ions from the water, and essentially all soluble electrolytes are removed. A standard procedure developed by the Ceramics Laboratory of the Massachusetts Institute of Technology (2, 11) was employed.

The suspension of kaolinite so electrodialyzed was filtered, and the solid dried in an oven at 110°C . for about 16 hours and then pulverized in a mortar.

Synthesis of Sodium Polyacrylate (SPA). Approximately 10 ml. of glacial acrylic acid (B. F. Goodrich Chemical Co.) was diluted to 100 ml. with distilled water which had been degassed by boiling, and the solution was stripped of residual oxygen by bubbling with nitrogen. To this solution was added 0.081 gram (0.355 mole) of ammonium persulfate catalyst and 0.088 gram (0.355 mole) of sodium thiosulfate activator to produce a redox system—monomer mole ratio of approximately 1/200. This mixture was allowed to polymerize at room temperature (25°C .) for 5 days. The final solution was quite turbid in appearance and of relatively low viscosity.

A 10-ml. aliquot of this polymer solution was diluted to approximately 100 ml. with distilled water and titrated with standardized sodium hydroxide solution to a phenolphthalein end point: 14.1 meq. of caustic were required for this titration. Inasmuch as the color change for phenolphthalein occurs at a pH of 8.3 (18), it was assumed that complete neutralization of the acid was accomplished under these conditions; hence the concentration of polyacrylic acid in the original solution was 1.41N.

To a 10-ml. aliquot of the polymer solution was added the stoichiometric equivalent quantity (14.1 meq.) of 1.345N caustic soda and the solution diluted to 1410 ml. to produce a stock solution containing 0.01 meq. of sodium polyacrylate per ml. The pH of this stock solution was 9.0.

The intrinsic viscosity of this stock solution determined with an Ostwald pipet was $[\eta] = 3.83$ at pH of 9.0.

Synthesis of Hydrolyzed Polyacrylamide (PAM). Exactly 10.00 grams (140.6 meq.) of crystalline acrylamide (American Cyanamid Co.) was dissolved in distilled water that had been degassed by boiling, and the solution (100 ml. in volume) was stripped of residual dissolved oxygen by bubbling with nitrogen. To this solution was added 0.1604 gram (0.703 mole) ammonium persulfate and 0.1745 gram (0.703 mole) sodium thiosulfate. This mixture was allowed to polymerize at room temperature (25°C .) for 24 hours. The final solution was perfectly clear and of very high viscosity. The solution was then diluted to exactly 500 ml.

To a 50-ml. aliquot of this solution (containing 14.06 meq. of acrylamide as the polymer) was added 14.58 ml. of 0.9650N sodium hydroxide solution, this quantity of caustic being stoichiometrically equivalent to the amide present in the solution. The mixture was allowed to stand for 23 hours and was then diluted to exactly 500 ml. A 50-ml. aliquot (containing before hydrolysis 1.406 meq. of amide) was titrated with standard 0.1N hydrochloric acid to a methyl orange end point. The quantity of acid required for this titration was 1.695 meq. The extent of hydrolysis of the polyacrylamide was determined by the relation used by Gardner and Montemayor (7)

$$\% \text{ Hydrolysis} = \frac{\text{meq. HCl} - \text{meq. NaOH}}{\text{meq. initial amide}} = \frac{1.695 - 1.406}{1.406} = 20.6\%$$

To another 200 ml. of the hydrolyzed solution was added an amount of standard hydrochloric acid solution equivalent to the residual unconsumed caustic present and diluted to 562.5 ml. to produce a stock solution 0.01*N* in total acrylic constituent. The pH of this solution as determined electrometrically was 6.7.

The intrinsic viscosities (concentration expressed in grams/liter) of both the 0.01*N* hydrolyzed polyacrylamide solution and a solution of unhydrolyzed polymer of the same concentration were determined. The values thus measured were

Table I. Intrinsic Viscosities

	$[\eta]$
Unhydrolyzed polyacrylamide	0.382
20.6% Hydrolyzed polyacrylamide	3.25 at pH 8.1
20.6% Hydrolyzed polyacrylamide	2.70 at pH 6.7

In the synthesis of these polymers, an attempt was made to prepare compounds of approximately the same molecular weight by using the same concentrations of monomer and catalyst in each case and by carrying out the polymerization reactions at the same temperature. The only evidence indicating the similarity of molecular weight of the two polymers is the intrinsic viscosity measurements. Unfortunately, for polyelectrolytes the intrinsic viscosity is controlled not only by molecular weight but also by degree of ionization; therefore, direct comparison of the viscosities of two different polymers as a means of indicating relative molecular weights is questionable. However, in alkaline solutions, pH 8 and above, when both polymers are essentially completely ionized, the intrinsic viscosities differ by only about 17%; this may be interpreted as indicating that the two polymers are of at least comparable chain lengths.

Electrometric Titration of Kaolinite. A weighed quantity (approximately 10 grams) of dry electrolyzed kaolinite was suspended in 50 ml. of distilled water in a flask, a measured volume of standard sodium hydroxide solution added with agitation, and the total volume brought to about 80 ml. After a 15- to 30-minute aging, the pH of the suspension was measured with a pH meter (Beckman Model H2), using glass-calomel electrodes.

The suspension was transferred from the flask to a 100-ml. graduate, the graduate was stoppered and allowed to stand for approximately 24 hours. The volume occupied by the sedimented clay was measured, as was the pH of the supernatant. The contents of the graduate was shaken to resuspend the clay, and the pH of the suspension was measured once again.

This procedure was repeated with eight 10-gram kaolinite samples, using different quantities of caustic soda solution, to permit the determination of a titration curve for the kaolinite over a wide pH range and simultaneously to prepare suspensions for the polymer adsorption tests.

Turbidimetric Determination of Polymer Concentration in Solution. To determine the concentration of the polyelectrolytes present in the extremely dilute solutions employed in this work advantage was taken of the fact that polyanions react with either fatty cations—e.g., fatty quaternary ammonium salts—or cationic polyelectrolytes to produce insoluble complexes that remain colloidal suspended in solution and give rise to turbidity (6). In the presence of excess complexing cation, the turbidity is a measure of the polyanion concentration.

The complexing agent used for this purpose was Hyamine 1622 (Rohm and Haas *p*-diisobutyl phenoxy ethoxy ethyl benzyl dimethyl ammonium chloride, a high purity fatty quaternary ammonium salt). This compound was dissolved in distilled water to produce a 3.5% stock solution.

A series of dilute solutions containing known concentrations (ranging from 0.1 to 1.0 meq. per liter) of the two polyelectrolytes studied were prepared by dilution of the 0.01*N* stock solutions.

To 10 ml. of these solutions were added excess quantities of Hyamine 1622 (3 drops of the 3.5% solution), and the resulting turbidity was measured with a Fisher electrophotometer using a blue filter (5). The turbidity of these solutions changed somewhat with time, reaching a fairly constant value after about a 20-minute aging. A calibration curve of optical density versus polymer concentration for each polyelectrolyte was, therefore, prepared based on measurements of solutions that had been allowed to age for 20 minutes after the Hyamine addition.

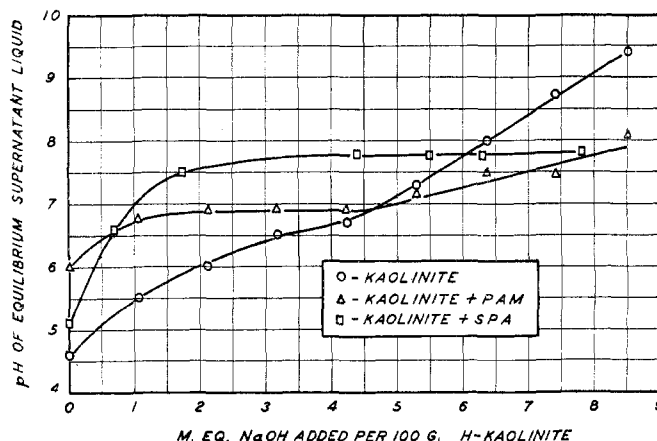


Figure 1. Titration curves for kaolinite suspensions

Polymer Adsorption and Sediment Volume Measurements. To each 10-gram sample of kaolinite suspended in water and containing a known quantity of sodium hydroxide was added exactly 6.0 ml. of the 0.01*N* polymer stock solution—0.60 meq. of polymer per 100 grams clay is very nearly equal to 0.05% by weight of polymer—this concentration has previously been found (6) to be close to the optimum polyelectrolyte concentration for maximum flocculation of clays. Also, Ruehrwein and Ward (19) found that the amount of sodium poly(methyl methacrylate) adsorbed by kaolinite was about 0.3 meq. per 100 grams of clay. The volume of the suspension, after polyelectrolyte addition, was brought to exactly 100 ml. by addition of distilled water; the graduates were shaken gently, and the suspension was allowed to stand without disturbance for about 24 hours. The volume occupied by the sedimented clay was measured, and a sample of the supernatant solution was removed for polymer analysis and pH determination. To minimize the effect of pH on the turbidimetric determinations, all solutions were adjusted to a constant pH value (about 6.4 for polyacrylamide and about 7.8 for sodium polyacrylate) before addition of Hyamine. These pH's correspond nearly to the pH of the standard solutions employed in the calibration.

In some instances, a small quantity of finely divided clay remained in the supernatant liquid; this was removed as completely as possible by centrifugation. To the supernatant liquid samples (10 ml. in volume) were added 3 drops of Hyamine 1622 solution, and the turbidity was measured with the electrophotometer immediately, and also after the 20-minute aging. The polymer concentration was found by reference to the electrophotometer calibration plot for the corresponding polyelectrolyte using the average of the two readings noted.

RESULTS

The results of this investigation, showing the titration of hydrogen kaolinite with sodium hydroxide and the effect of polyanion addition on solution pH, polyanion adsorption by kaolinite as a function of supernatant solution pH at equilibrium, and specific sediment volume of kaolinite before and after treatment with polyanions as a function of sodium hydroxide content are shown in Table II and Figures 1 to 5.

DISCUSSION OF RESULTS

Reproducibility of Electrodialyzed Kaolinite Samples. The procedure for the preparation of the hydrogen kaolinite by electro-dialysis entails, as a final step, oven-drying and grinding of the dried clay. Because of the difficulty of controlling the grinding conditions, the various clay samples differed appreciably in initial state of aggregation, as evidenced by differences in the volume of sediment produced after settling from distilled water. In clay sample A, Table II, this difference amounted to 25% with respect to sample B. When suspended in alkaline solution, however, all the kaolinite samples formed sediments of about equal volumes, indicating further that the initial differences in bulk density were due primarily to variations in degree of aggregate breakdown rather than in structure or composition of the clay. Nevertheless, the sediment volume data obtained with clay sample A (items 1, and 2 in Table II) which have been adjusted to agree with the data obtained with subsequent clay samples, may be as much as $\pm 25\%$ in error.

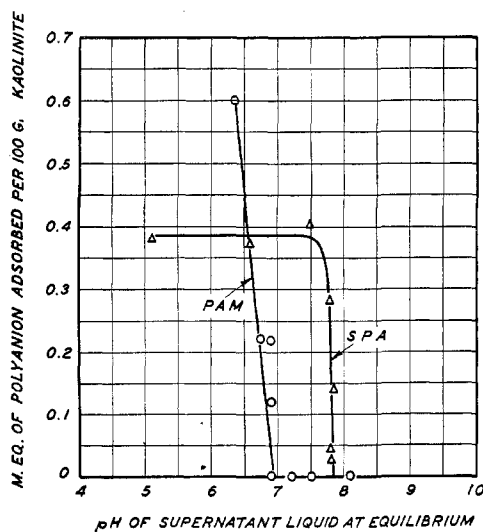


Figure 2. Effect of pH on adsorption of polyelectrolytes by kaolinite

Polymer Adsorption Measurements. The photometric analysis for the polyelectrolytes showed excellent reproducibility ($\pm 2\%$) for duplicate samples of the same polymer solution and for most of the adsorption data reported; the values are accurate to $\pm 2\%$. With the very alkaline clay suspensions, however, it was almost impossible to remove the last traces of suspended kaolinite from the solutions by centrifuging, and, consequently, it was necessary to apply an appreciable correction factor to the photometer readings to account for the initial turbidity of the sample. For this reason, the polymer absorption values obtained at a high pH are likely to be in error to the extent of $\pm 30\%$.

Sediment Volume Measurements. With two duplicate clay samples from the same batch of kaolinite, under the same conditions, the sediment volumes were reproducible to within 10%.

Analytical Measurements and pH Determination. The measurement of the quantities of reagents used (monomers, sodium hydroxide, hydrochloric acid, weights of kaolinite, and volumes of solutions) was conducted with standard analytical apparatus, so that the errors introduced during these operations were negligible relative to the sources of error described. The pH measurements were reproducible (for duplicate samples of the same solution) to within ± 0.1 pH unit.

Sodium Ion Exchange Characteristics of Hydrogen Kaolinite.

Figure 1 presents the results of the electrometric titration of electro-dialyzed kaolinite with sodium hydroxide. This clay exhibits a characteristic buffer action; the titration curve shows

an inflection point at a pH of approximately 6.5, at which point the clay contains 3.5 meq. sodium per 100 grams. At neutrality, pH = 7, Figure 1 shows that the sodium ion content of the kaolinite is 5.0 meq. per 100 grams. This amount agrees with the reported exchange capacity of this kaolinite (17), which is customarily determined in essentially neutral solution.

Effect of Sodium Content and pH on the Degree of Dispersion of Kaolinite. The treatment of aqueous suspension of hydrogen kaolinite with sodium hydroxide is accompanied by significant changes in the state of aggregation of the clay particles. This is evidenced by the change in the volume occupied by a given weight of clay after sedimentation from suspension, as shown in Table II and Figure 3. The higher the density of the sediment or the lower the specific sediment volume the greater the extent of deflocculation, since in the deflocculated state individual particles are free to settle and pack with maximum efficiency.

The sediment volume of the kaolinite first increases with rising pH and added sodium hydroxide, until a pH of 5.5 is reached at which point the clay contains 1.0 meq. of sodium per 100 grams. From a pH 5.5 to 6.5, the sediment volume decreases rapidly to an asymptotic low value, in the neighborhood of 1.0 to 1.3 cc. per gram.

At a high suspension pH above 6.5, an appreciable fraction of the clay present—of the order of 10 to 20%—remained suspended in the liquid phase even after prolonged standing. The contribution that this suspended clay would have made to the total sediment volume could not be determined, but because of its much smaller apparent particle size relative to that which settled the increase in volume would probably have been small. Consequently, the volume of the sediment was assumed to be equal to the volume occupied by the total quantity of clay (10 grams) present in the container, had it settled completely.

The decrease in sediment volume and attendant deflocculation of the clay above pH = 6.5 is evidently caused by replacement of hydrogen by sodium in the diffuse double layer surrounding the clay particles with an accompanying increase in electrokinetic potential. The critical deflocculating condition appears to be at a pH of approximately 6.5; the clay then contains 3.5 meq. of sodium per 100 grams.

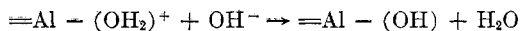
The observed increase in sediment volume as the pH of the clay suspension is increased by sodium hydroxide addition from 4.5 to 5.5 was unexpected. The flocculation of the clay during this process can best be explained by the existence, in the electro-dialyzed acid clay, of cationic sites ($=\text{Al} - (\text{OH}_2)^+$ probably) which give rise to electrostatic repulsive forces between particles.

Table II. Adsorption and Flocculation Data

NaOH/10 Grams Clay, Meq.	pH of Equil. Supernatant Solution		Polymer Adsorbed, Meq./100 Grams Clay	Sediment Volume of Kaolinite after 24 Hr., Ml./Gram	
	Without polymer	With polymer		Without polymer	With polymer
Kaolinite A with Sodium Polyacrylate					
0.0	4.6	5.1	0.38	2.3 ^a (1.7)	2.0 ^a (1.5)
0.635	5.3	6.6	0.37	2.4 ^a (1.8)	2.2 ^a (1.6)
1.75	5.9	7.5	0.40	2.3	2.0
4.4	6.8	7.8	0.28	1.45	1.55
5.5	7.4	7.8	0.03	1.40	1.50
6.3	8.0	7.8	0.04	1.35	1.45
7.8	9.0	7.85	0.14 (?)	1.20	1.30
Kaolinite B with Polyacrylamide					
0.0	4.6	6.0	0.60	2.3	2.25
1.06	5.5	6.8	0.22	2.8	3.85
2.12	6.0	6.9	0.22	2.35	3.60
3.18	6.5	6.9	0.12	0.95 (?)	3.75
4.24	6.7	6.9	0.0	1.10	3.60
5.30	7.3	7.2	0.0	1.05	3.20
6.36	8.0	7.5	0.0	0.95	2.20
7.42	8.7	7.5	0.0	1.30	1.75
8.48	9.4	8.1	0.0	1.20	1.40

^a These values adjusted to compare with those obtained with clay sample B; measured sediment volumes are in parentheses. Differences appear to be caused by variations in grinding dry hydrogen clay.

As the pH is raised, these cationic sites are neutralized by the reaction



with consequent discharge of the clay particles and accompanying flocculation.

Physicochemical Properties of Sodium Polyacrylate (SPA). Examination of the effect of the addition of SPA on the pH of kaolinite suspensions, as presented in Table II and Figure 1, shows that this compound exerts a strong buffering action at a pH of very nearly 7.8. Since in these solutions, the concentration of polymer is constant at 6×10^{-4} meq. per ml., provided no adsorption of the polymer occurs, it is possible from these data to calculate the ionization constant for polyacrylic acid

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

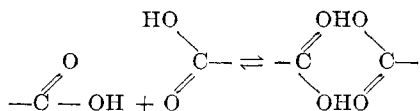
$$\frac{(RCOO^-)(H^+)}{RCOOH} = K_H = 1.5 \times 10^{-5}$$

This value is essentially the same as that reported in the literature (8) for the majority of the monobasic aliphatic carboxylic acids, but is considerably smaller than that of glutaric (pentanedioic) acid for which $K = 4.75 \times 10^{-5}$ (22), with which polyacrylic acid might most properly be compared. This lower-than-expected base strength is probably caused by the high concentration of anions along the polymer chain which renders ionization thermodynamically less favorable than for the simple dibasic acid.

The intrinsic viscosity of a polymer solution is a convenient and fairly reliable measure of the size of the polymer molecules in solution, or perhaps more correctly, of the volume occupied by a polymer molecule. If the polymer molecule involved is a flexible chain, the intrinsic viscosity should be directly proportional to the molecular weight of the polymer and hence its chain length (20).

In the case of a polyelectrolyte, the apparent chain length in aqueous solution, as measured by its intrinsic viscosity, is profoundly influenced by the hydratability of the polymer and its degree of ionization. If the polymer is poorly hydrated and essentially not ionized, the chains will tend to exist in a tightly coiled state, exposing as little surface to the surrounding water as possible. If the polymer is highly hydrated and/or highly ionized, the chains will be greatly extended and will occupy a relatively large volume in solution. In the case of sodium polyacrylate, both the extent of ionization and degree of hydration of the polymer are markedly influenced by the pH of the solution. At a low pH, where the polymer is essentially not in the ionized acid form, dilute solutions of the compound have viscosities not detectably different from that of water and exhibit appreciable turbidity showing the presence of distinct colloidal-sized particles composed, probably, of masses of coiled chains. At a high pH these solutions are very viscous and optically clear. The variation in intrinsic viscosity with pH for the sodium polyacrylate (0.01N solution) prepared in this study is very marked, rising from a value of essentially zero at a pH of 4 to a value of 3.83 at a pH of 9.0. The actual percentage increase in viscosity over this pH range could not be determined but is probably greater than 1000-fold; hence it must be concluded that the change in configuration of SPA molecules with changing pH is very great indeed.

The intramolecular coiling which probably accompanies a reduction in ionization of sodium polyacrylate is undoubtedly brought about by strong hydrogen bonding between carboxyl groups



Hydrogen bonding between carboxyl groups is particularly strong evidently because of the high electronegativity of the oxygen atom bonded to the carboxyl group and because of the convenient six-membered ring formed in the chelate.

Hence, there are two factors which appear to be responsible for the unique physical behavior of sodium polyacrylate in aqueous solution

1. The relatively low ionization constant of polyacrylic acid
2. The very great tendency of the un-ionized carboxyl groups to associate by hydrogen bonding.

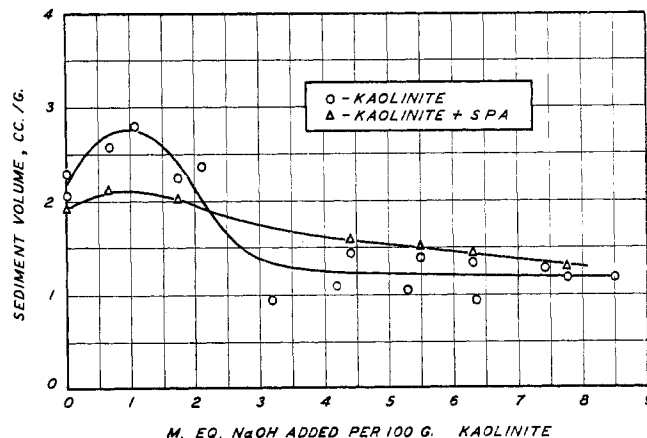
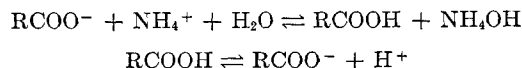


Figure 3. Effect of sodium polyacrylate on kaolinite aggregation as a function of kaolinite sodium ion content

Physicochemical Properties of Hydrolyzed Polyacrylamide (PAM). Examination of the effect of polyacrylamide on the pH of kaolinite suspensions shows this compound to exert a small but detectable buffering action at about pH 6.9. This observation is corroborated by a direct titration curve of the polymer in solution which shows an inflection point at pH 6.9. Since this polymer contains 0.206 meq. carboxylate per meq. of initial amide constituent (20.6% hydrolyzed), and since the polymer also contains a quantity of ammonia (as NH_4^+ and NH_4OH) stoichiometrically equivalent to the carboxylate, the ionization constant for the carboxylic acid in the polymer can be readily calculated



$$K_{NH_4OH} = \frac{(NH_4^+)(OH^-)}{(NH_4OH)} = 1.8 \times 10^{-5} \quad (21) \quad (1)$$

$$K'_H = \frac{(RCOO^-)(H^+)}{RCOOH} = 2.9 \times 10^{-5}$$

The carboxylic acid present in polyacrylamide, therefore, appears to be slightly stronger than that in polyacrylic acid.

The viscosity characteristics of aqueous polyacrylamide solutions as a function of pH are markedly different from those of sodium polyacrylate. Unhydrolyzed polyacrylamide dissolves in water to produce dilute solutions of appreciable viscosity. When hydrolyzed (20.6%) the viscosity of such a solution increases significantly and varies somewhat with pH. Intrinsic viscosity values measured in this study are shown in Table I.

It is thus apparent that the extent of coiling or of intramolecular association of polyacrylamide is much less marked than that of polyacrylic acid, and the effect of pH on coiling of hydrolyzed polyacrylamide is much less than on that of sodium polyacrylate. Two factors appear to be responsible for these differences

1. In hydrolyzed polyacrylamide, the frequency of occurrence of carboxyl groups along the molecular chain is far lower

than with sodium polyacrylate—roughly one per five mer units versus one per mer unit in sodium polyacrylate.

2. With polyacrylamide intramolecular association via hydrogen bonding is of a lower order than with polyacrylic acid.

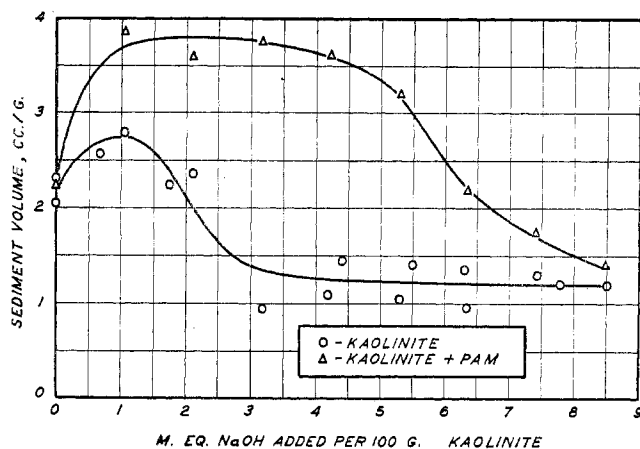


Figure 4. Effect of polyacrylamide on kaolinite aggregation as a function of kaolinite sodium ion content

With regard to the first factor, a reduction in number of ionizable carboxyl groups along the chain would be expected to reduce the influence of the degree of ionization of these groups on the configuration of the molecule; this explains the small (relative to sodium polyacrylate) influence of pH on intrinsic viscosity and apparent chain length of polyacrylamide. With regard to the second factor, hydrogen bonding, and hence intra- or intermolecular association of amides, is very likely of a lower order than that of carboxyls because the electronegativity of nitrogen in the amide linkage is lower than that of oxygen in carboxyl; it is probably closer to that of oxygen in hydroxyl. This explains why polyacrylamide is water soluble, and why the extent of coiling or association in aqueous solution is less than that of polyacrylic acid.

Adsorption of Sodium Polyacrylate and Polyacrylamide by Kaolinite. The most important features of the adsorption by kaolinite of the two polyelectrolytes studied, as deduced from the results shown in Table II and Figures 2, 3, 4 are

1. Above an initial supernatant pH of about 7.7, sodium polyacrylate does not adsorb on kaolinite. As the pH is reduced from 7.7, the adsorption of polymer increases rapidly, reaching a maximum and essentially constant value of 0.40 meq. per 100 grams at a pH of 6.0. Under these conditions, the maximum adsorption is about $\frac{2}{3}$ of the quantity of sodium polyacrylate added.

2. Above an initial supernatant pH of about 6.7, polyacrylamide does not adsorb on kaolinite. As the pH is reduced from 6.7, the adsorption of polymer increases rapidly, reaching a value of 0.60 meq. per 100 grams (100% of the polymer added) at a pH of 4.6—i.e., with pure hydrogen kaolinite.

Inasmuch as the kaolinite is present in suspension in a highly dispersed condition over most of the pH range (6.1 to 7.7) within which adsorption of both polyelectrolytes occurs, it appears reasonable to postulate that the adsorption is controlled primarily by the effect of pH on the properties of the polyelectrolyte molecules, and only to a lesser extent to the effect of pH on the properties of the kaolinite. This postulation seems further justified by the fact that adsorption of both polyelectrolytes ceases at a pH value corresponding to the buffer pH of the polymer present.

The variations in polymer adsorption with pH can be interpreted as indicating that the adsorption of polymer varies inversely with the extent of ionization of the polyelectrolyte molecule. As the pH of the suspending medium is reduced, the proportion of the carboxylate groups in both sodium polyacrylate and polyacrylamide present as un-ionized carboxylic acid increases rap-

idly and the anionic charge density per unit length of polymer chain decreases at the same rate. In the pH range over which polymer adsorption takes place, the kaolinite undoubtedly possesses a high negative surface charge density due to the relatively high sodium ion content of the double layer. Thus, when the polyelectrolytes are highly ionized, close approach of the polymer molecules to the clay surface is prevented by electrostatic repulsion. As the pH is reduced, the attendant reduction in polymer charge density permits the polymer molecule to approach the solid surface and adsorb thereon.

Since the ionization constants of both sodium polyacrylate and polyacrylamide have been determined, it is possible to estimate the relative proportions of ionized to un-ionized carboxyl groups on the molecules as a function of pH, and also to estimate the ion density per unit length of chain. These calculations are presented in Table III.

Table III. Effect of pH on Polymer Ionization

pH	SPA		PAM, 20.6% Hydrolyzed	
	COO ⁻ COOH	Anions Mer unit	COO ⁻ COOH	Anions Mer unit
8	1500	1.0	2900	0.20
7	150	0.99	290	0.20
6	15	0.94	29	0.19
5	1.5	0.60	2.9	0.15
4	0.15	0.13	0.29	0.05

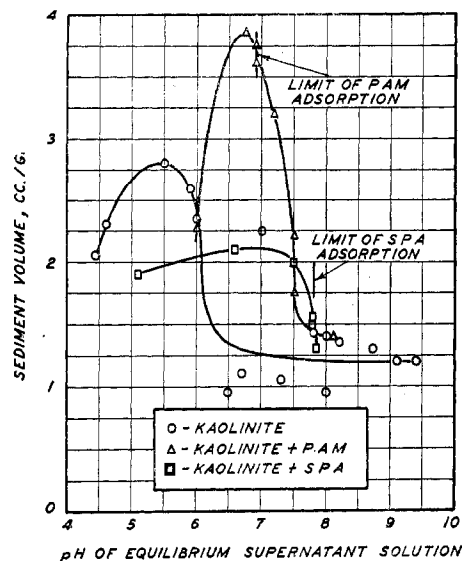


Figure 5. Effect of pH on aggregation of kaolinite

At any specified pH sodium polyacrylate has about 5 times the anion density as polyacrylamide, solely because the latter contains one fifth as many carboxyl groups. The extent of ionization of both polymers is essentially complete above a pH of 6.0. Since adsorption of both polymers takes place above this pH, it would seem difficult to defend the argument that adsorption is controlled by the extent of ionization.

However, kaolinite suspended in water behaves as an electrostatic colloid; each particle in suspension is surrounded by an ionic atmosphere, or double layer, in which the local cation concentration (Na^+ and H^+) is far higher than in the ambient solution. The difference between the hydrogen ion concentration in the neighborhood of the solid surface and that in the suspending medium can be roughly estimated as follows:

The specific surface area of kaolinite, as determined by many investigators, lies in the neighborhood of 20 square meters per gram (3). If it is assumed that the total ion exchange capacity

of the kaolinite used in this work is 5.0 meq. per 100 grams, and that the effective thickness of the ionic atmosphere around the clay particles is 200 Å. (12), the total cation concentration in the double layer can be calculated; this value is 0.14 meq. per ml.

When the pH of a kaolinite suspension is 6.5, roughly 3.5 meq. anionic sites on the clay per 100 grams are balanced by sodium—i.e., the double layer is approximately 0.09N in sodium. Inasmuch as the residual unneutralized acidic groups on the clay surface totaling roughly 1.5 meq. per 100 grams are very weakly ionized—of the order of 0.1%—the hydrogen ion concentration in the double layer should be of the order of 5.0×10^{-5} N, corresponding to about a pH of 4.3. The pH in the immediate vicinity of the clay particle surfaces would be expected to be about 2.2 units lower than that in the ambient solution. Table IV shows how this fact may affect the degree of ionization of the polymers.

These calculations may explain why these polyelectrolytes adsorb on kaolinite under conditions where they are essentially completely ionized in the suspending solution.

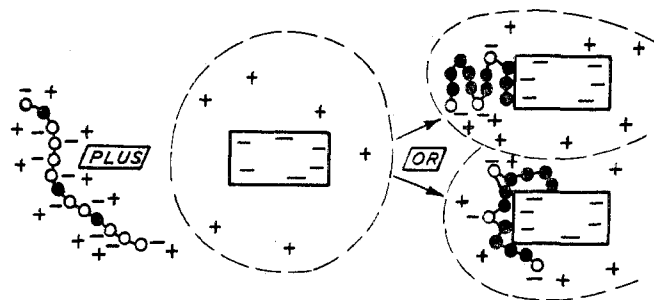
If electrostatic forces acting between the clay surface and the polymer molecules serve to prevent adsorption, it must follow that adsorption, when it does occur, is brought about by some nonionic binding process. It appears reasonable to postulate that hydrogen bonding between hydrogen-donor groups on the polymer (carboxyl or amide) and oxygen acceptor groups on the aluminosilicate surface is responsible. Recalling that COOH groups appear to undergo stronger hydrogen bonding than CONH₂ groups, this can explain why sodium polyacrylate is adsorbed on kaolinite at a higher pH and, therefore, in a more highly ionized state than polyacrylamide. In other words, the extent of adsorption is controlled by a balance between the magnitude of electrostatic repulsion and the magnitude of hydrogen bond strength. In the case of sodium polyacrylate, the number of hydrogen bonding groups increases at the same rate as the number of ionized groups decreases, while with polyacrylamide, the number of hydrogen bonding groups remains relatively constant as the number of ionized groups is reduced. This observation would explain why the adsorption of sodium polyacrylate is more sensitive to changes in pH than that of polyacrylamide.

Table IV. pH at the Clay Surface and Anionic Density

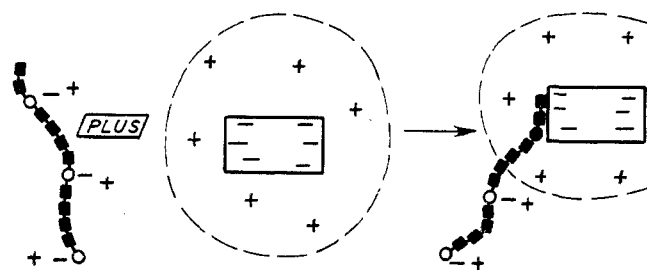
pH in Solution	pH at Clay Surface, Est.	Anions/Mer Unit at Est. Surface pH	
		SPA	PAM
8.2	6	0.94	0.19
7.2	5	0.60	0.13
6.2	4	0.13	0.03
5.2	3	0.02	0.004

The reason why polyacrylamide is adsorbed almost quantitatively by kaolinite as the pH is reduced while only about 2/3 of the sodium polyacrylate is adsorbed as a maximum remains to be explained. This difference can be accounted for in terms of the relative hydrogen bonding forces and intramolecular association tendencies—i.e., coiling—of the two molecular species. In the case of sodium polyacrylate, neighboring carboxyl groups formed during reduction of pH are probably more likely to associate with one another with consequent loss of two potential bonding sites than to bond to the clay surface. As long as the pH is fairly high and the number of un-ionized carboxyl groups per unit length of chain relatively low, the situation is somewhat more favorable for particle-to-polymer bonding than for intramolecular bonding. As the pH is reduced to progressively lower values, however, an increasing fraction of the carboxyl groups can undergo intramolecular association, and a smaller number of carboxyl groups per molecule are left available for bonding to the solid surfaces. In a sufficiently acidic environment, therefore, intramolecular or, quite possibly, also intermolecular car-

boxyl group association is so great that polymer molecules still in solution no longer have sufficient free carboxyl groups available to provide firm bonding to the solid surface. With sodium polyacrylate, this condition apparently obtains at a solution pH of about 7.2, corresponding to a double layer pH of about 5.0.



(a) ADSORPTION OF SPA BY KAOLINITE



(b) ADSORPTION OF PAM BY KAOLINITE

Figure 6. Mechanism of adsorption of polyelectrolytes on kaolinite schematic

● = Carboxyl (COOH)
○ = Carboxylate ion (COO⁻)
■ = Amide (CONH₂)

In the case of polyacrylamide the degree of intramolecular association is much less marked, and the dependence of intramolecular association of pH is of a lower order than that of sodium polyacrylate. Consequently, a reduction in pH serves mainly to reduce the polymer charge density without materially reducing the number of groups available for hydrogen bonding to the solid surfaces. This means that, even at a low pH, there are sufficient exposed amide groups present on the polymer molecules to provide firm polymer-to-particle bonding.

Flocculation of Kaolinite by Sodium Polyacrylate and Polyacrylamide. Table II and Figures 3, 4, and 5, show the effect of the two polyelectrolytes studied on the volume occupied by the kaolinite after sedimentation. The important features of these observations are

1. For a kaolinite suspension whose pH lies in the range 4.6 to 6.1, sodium polyacrylate causes a reduction in sediment volume, indicating that this compound exerts a deflocculating effect on the clay. In the pH range 6.1 to 8, the polymer causes a slight increase in sediment volume, and hence appears to exert a small flocculating effect. Above a pH of 8, this compound has little effect upon the state of aggregation of the clay.

2. With the pure hydrogen kaolinite, pH 4.6, polyacrylamide exhibits no influence on the state of aggregation. As the pH is raised by sodium hydroxide addition to 5.5, the sediment volume of the clay after polyacrylamide addition rises very rapidly to a maximum value of 3.85 cc. per gram. Further increase in suspension pH is accompanied by a rapid drop in sediment volume until, above a pH of about 9.4 corresponding to a clay sodium content of 8.5 meq. per 100 grams, the polymer appears to have no significant effect on sediment volume.

3. With both polyelectrolytes, polymer addition causes sig-

nificant changes in sediment volume at a pH where no adsorption of polymer by the clay is detected.

4. In the case of polyacrylamide, maximum flocculation occurs at suspension pH of 5.5, where only 37% of the added polymer, 0.22 meq. per 100 grams, is adsorbed by the clay.

If polymers flocculate, as believed, by adsorption and interparticle bridging, it is likely that the flocculating ability of a polymer will be determined by the firmness with which it bonds to the particles, and the distance which the molecule spans in solution.

With sodium polyacrylate, reduction in pH favors both adsorption of the polymer and intramolecular association or coiling of the polymer chain. Hence under the pH conditions where sodium polyacrylate adsorbs on kaolinite, the polymer chains become so greatly foreshortened that interparticle bridging is very improbable. It is also possible that these chains may adsorb with their long axes parallel to the plane of the surface. The fact that sodium polyacrylate actually appears to cause deflocculation of kaolinite when adsorbed may be caused by a somewhat increased surface charge density near the solid surface due to residual ionized carboxylate groups on the polymer. A schematic representation of this process is shown in Figure 6a.

With polyacrylamide at a pH where adsorption on kaolinite occurs, the chains are still sufficiently extended to permit the molecules to bridge between particles, and cause flocculation. This is shown schematically in Figure 6b. At a relatively low pH, there is evidently sufficient molecular coiling of polyacrylamide that the extent of interparticle bridging and hence the flocculating effectiveness is reduced.

In essence adsorption of anionic polyelectrolytes by kaolinite and the ability of anionic polyelectrolytes to flocculate this clay are two basically different processes; the former is controlled by the chemical constitution of the polymer and the electrostatic forces between polymer and solid, while the latter is determined by the configuration of the molecule during or after adsorption.

The observation that both sodium polyacrylate and polyacrylamide, when added to kaolinite suspensions at pH above which polymer adsorption occurs, cause flocculation of the clay needs to be resolved. Two factors appear to be responsible for this phenomenon. First, both polymers act as acid buffers at a pH above which adsorption does not occur. This means that the pH of the clay suspension is reduced by polymer addition, and as Figure 5 shows, a reduction in pH of the pure kaolinite suspension in the range 4.5 to 6 is accompanied by an increase in sediment volume. Second, addition of the polymers to suspensions at a higher pH is equivalent to adding a simple electrolyte; in the case of sodium polyacrylate, addition of 0.06 meq. of polymer renders the suspending liquid approximately $6 \times 10^{-4}N$ in sodium ion, while with polyacrylamide, which contains besides the polyelectrolyte itself sodium chloride, the suspending medium becomes about $6 \times 10^{-4}N$ in sodium ion as NaCl, and about $1.2 \times 10^{-4}N$ in ammonium ion as carboxylate salt. The combined effects of pH reduction, which reduces the kaolinite surface charge density, and introduction of monovalent cations, which compresses the electrical double layer around the clay particles, can sufficiently reduce the electrokinetic potential of the kaolinite to cause what may be called normal electrolytic flocculation of the clay. In other words, the clay flocculation produced by the polyelectrolytes in the pH range of 6.7 to 8.5 should be no different from that which would be produced by the addition of strong acid and a sodium salt (NaCl) to the suspension.

When, however, the kaolinite suspensions are brought to a relatively high pH (8.5 and above), the electrokinetic potential of the particles is raised to a value so high that addition of small quantities of sodium salts or acid is insufficient to cause flocculation. This would explain why, at a high pH, neither sodium polyacrylate nor polyacrylamide has any appreciable effect on clay sediment volume.

The fact that maximum flocculation of kaolinite by polyacryl-

amide occurs under conditions where only 37% (0.22 meq. per 100 grams clay) of the polymer added is adsorbed is interesting. If it is assumed that the primary clay platelets measure $1 \times 1 \times 0.1$ micron, and that the polymer molecules consist of 1000 mer units, calculation of this adsorption is about 350 molecules per solid particle. If every polymer molecule is shared by two particles, then the surface concentration of molecules is only one per 340,000 A.², an extraordinary low value relative to the cross-sectional area of the polymer chain, probably less than 100 A.²

CONCLUSIONS

The conclusions drawn from this work are

1. Adsorption of anionic polyelectrolytes such as sodium polyacrylate and polyacrylamide on kaolinite in all probability occurs via hydrogen bonding between the un-ionized carboxyl or amide groups on the polymer chains and oxygen atoms on the solid surface. Adsorption is hindered by electrostatic repulsion between the negatively charged clay surfaces and the ionized carboxyl groups on the polymer, so that adsorption of polymer is favored by the reduction in degree of carboxylate ionization which occurs on reduction of pH.

2. Intramolecular association between hydrogen bonding groups on a polymer chain evidently is competitive with the adsorption of these groups by kaolinite. With polymers rich in very active hydrogen bonding groups as in sodium polyacrylate, the intramolecular association tendency is so great that the opportunity for adsorption is significantly reduced. With polymers containing less active hydrogen bonding groups as polyacrylamide, the extent of intramolecular association is less marked, and hence the adsorption of such compounds by kaolinite is limited primarily by the number of active bonding sites on the solid surface.

3. Adsorption of anionic polyelectrolytes by kaolinite is not necessarily accompanied by flocculation. Flocculation is caused by the bridging of solid particles by polymer molecules and is controlled by the configuration of the molecule in the adsorbed state; for polyelectrolytes molecular configuration is determined by the degree of intramolecular association which favors chain coiling and extent of ionization which favors chain extension. The high flocculating ability of polyacrylamide appears, therefore, to be due to its relatively high degree of chain extension even at low extent of ionization.

4. Under conditions—e.g., at high pH—where no polymer adsorption by kaolinite occurs, anionic polyelectrolytes can nevertheless cause flocculation of the clay by the same ionic mechanism as that of simple electrolytes.

ACKNOWLEDGMENT

This article is a contribution of the M.I.T. Soil Stabilization Laboratory, and is part of a broad program of fundamental research sponsored by industrial contributions. The cooperation of T. W. Lambe, R. T. Martin, and G. E. Murray of the laboratory staff in reviewing and criticizing the manuscript is gratefully acknowledged.

REFERENCES

- (1) American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N. Y., "New Product Bulletin," vol. 28, 1952.
- (2) "Ceramic Data Book," Industrial Publications, Inc., Chicago, 1953-4.
- (3) Cornell University, Ithaca, N. Y., Final Report, Soil Stabilization Research, vol. II, 1951.
- (4) Dean, I. A., and Rubins, E. J., *Soil Sci.*, 63, 377-86 (1947).
- (5) Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pa., "Colorimetric Analysis with AC Model Fisher Electrophotometer," 1951.
- (6) Fuoss, R. M., and Sadek, N., *Science*, 110, 552-4 (1949).
- (7) Gardner, W. M., and Montemayor, L. W., M.I.T., B.S. thesis, May 1953.
- (8) Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, 1941.
- (9) Hedrick, R. M., and Mowry, D. T. (to Monsanto Chemical Co.), U. S. Patent 2,625,471 (Jan. 13, 1953).
- (10) Hendricks, S. B., *IND. ENG. CHEM.*, 37, 625 (1945).
- (11) Johnson, A. L., and Norton, F. H., *J. Am. Ceramic Soc.*, 24, 26 (1941).

- (12) Kruyt, H. R., "Colloid Science," vol. I, p. 131, Elsevier Publishing Co., New York, 1952.
- (13) Massachusetts Institute of Technology, Soil Stabilization Laboratory, Cambridge, Mass., unpublished data, 1952.
- (14) Michaels, A. S., "Altering Soil-Water Relationships by Chemical Means," Proc. Conference on Soil Stabilization, M.I.T., June 18-20, 1952.
- (15) Michaels, A. S., *IND. ENG. CHEM.*, **46**, 1485 (1954).
- (16) Michaels, A. S., and Lambe, T. W., *J. Agr. Food Chem.*, **1**, 835 (1953).
- (17) Norton, F. H., "Elements of Ceramics," pp. 28-30, Addison-Wesley Press, Inc., Cambridge, Mass., 1952.
- (18) Quastel, T. H., *Soil Sci.*, **73**, 419-55 (1952).

- (19) Ruehrwein, R. A., and Ward, D. W., *Ibid.*, **73**, 485 (1952).
- (20) Schmidt, A. X., and Marlies, C. A., "Principles of High Polymer Theory and Practice," p. 250, McGraw-Hill, New York, 1948.
- (21) Schofield, R. K., and Samson, H. R., *Clay Mineral Bull.*, **2**, No. 9, 45-51 (July 1953).
- (22) Wertheim, E., "Textbook of Organic Chemistry," p. 246, Blakiston, Philadelphia, 1939.

RECEIVED for review November 11, 1954.

ACCEPTED March 17, 1955.

Experimental results are from the M.S. thesis of O. Morelos submitted to the Department of Chemical Engineering, Massachusetts Institute of Technology, 1954.

Adsorption of Elastomers on Carbon Black

GERARD KRAUS AND JOSEPH DUGONE

Research Division, Phillips Petroleum Co., Bartlesville, Okla.

DURING the past 3 years considerable progress has been made in the study of adsorption of high polymers on the surfaces of solids from solution. A number of experimental investigations (11-14) have established that linear polymers are adsorbed at a number of segments along the molecular chain and that an apparent saturation value of the adsorption is reached with increasing concentration, leading to isotherms that exhibit considerable similarity with the classical Langmuir isotherm (11, 12, 22). Kolthoff and others (13, 14) have shown that poor solvents favor adsorption and that fractions of high molecular weight are adsorbed preferentially. Polymer of low molecular weight is adsorbed more rapidly but is eventually replaced by fractions of higher molecular weight. Kolthoff and Gutmacher (13) also observed some evidence of adsorption hysteresis in rubber-carbon black systems. Preferential adsorption effects have also been described by Goldfinger and others (2, 10), who, in addition, furnished an estimate of the thickness of the adsorbed layer (1). Theoretical explanation for many of these effects has recently come from a detailed statistical mechanical treatment of polymer adsorption by Frisch, Simha, and Eirich (8, 9, 17).

It is somewhat surprising that the adsorption of elastomers on reinforcing fillers from solution has received so little attention as a possible tool for the investigation of the polymer-filler interaction responsible for reinforcement. The reason for this appears to lie in the emphasis placed by many workers on the incomplete desorption effect observed when mill-mixed, unvulcanized stocks are extracted with solvents. The well known "bound rubber" phenomenon observed in this instance (5, 18-20) is large and shows some correlation with reinforcement, mainly because the effect is surface area-dependent (4, 16, 19). The fact that adsorption from solution is small when compared to bound rubber, particularly when a good solvent is used, has led some authors to consider the two effects as essentially separate phenomena (20) and to dismiss solution adsorption as without interest in reinforcement.

The present investigation was undertaken with the twofold objective of determining if adsorption isotherms of elastomeric molecules of carbon black are capable of detecting an "activity" effect, divorced from the influence of surface development, which would show correlation with reinforcement, and secondly of establishing the interrelation between adsorption and desorption—i.e., bound rubber. The carbon blacks selected for this research (Table I) represent a fairly complete cross section of rubber carbons as to both type and particle size. *n*-Heptane

was chosen for all adsorption experiments, for the reason that a relatively poor solvent, which would favor large adsorption for all three rubbers, was desired.

Table I. Surface Area of Carbon Blacks

Carbon Black Type	Surface Area	
	N ₂ adsorption (BET), sq. m./g.	Electron microscope, sq. m./g.
FT	13.7	17
SRF	27.6	35
PEF-I	45.6	65
PEF-II	47.8	65
Acetylene	56.0	65
HAF	75.1	94
Graphon	93.7	113
EPC	114.2	89
SAF-I	142.6	138
SAF-II	153.4	129
SAF-III	184.2	123

EXPERIMENTAL

Carbon Blacks. The electron microscope and nitrogen adsorption surface areas of the carbon blacks are listed in Table I. These values were obtained on the identical lots of black used in the present investigation. Preliminary adsorption experiments established the necessity for removal of adsorbed tars from the carbon blacks as a means for improving reproducibility of results. All carbons were, therefore, extracted with benzene for 72 hours in Soxhlet extractors, except the SRF and FT blacks, which were extracted 96 and 144 hours, respectively. The extracted blacks were dried at 70° C. in vacuo and stored in a vacuum desiccator over Drierite. All carbon blacks were in pelleted form with the exception of FT, SRF, acetylene, and SAF II and III.

Polymers. The cold rubber employed (X-672) was a 75/25 butadiene-styrene copolymer of 48 Mooney prepared in a sugar-free recipe at 41° F. The polymer was purified by Soxhlet extraction with the azeotropic mixture of ethyl alcohol and toluene. After drying, the extracted rubber was dissolved in toluene, reprecipitated with an excess of methanol, and vacuum-dried to constant weight at 50° C. The purified copolymer had an inherent viscosity in benzene of 1.86. The butyl rubber (GR-I-18) was purified in similar fashion, except that it was dissolved in benzene rather than toluene. Inherent viscosity in benzene was 0.86. The natural rubber sample was prepared by extracting masticated No. 1 smoked sheet with acetone for 72 hours, vacuum drying at 40° C., dissolving in benzene, precipitating with methanol, and again drying at 40° C. in vacuo. The inherent viscosity of the purified rubber was 2.38. All purified polymers were stored in the dark in a vacuum desiccator.