Adsorption of Polyacrylamides on Kaolinite and Its Flocculation and Stabilization

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Adsorption of nonionic and anionic polyacrylamides on kaolinite clay is studied together with various flocculation properties (settling rate, sediment volume, supernatant clarity and suspension viscosity) under controlled conditions of pH, ionic strength and agitation. Adsorption and flocculation data obtained simultaneously for selected systems were correlated to obtain information on the dependence of flocculation on the surface coverage. Interestingly, optimum polymer concentration and type vary depending upon the flocculation response that is monitored. This is discussed in terms of the different properties of the flocs and the floc network that control different flocculation responses. Flocculation itself is examined as the cumulative result of many subprocesses that can depend differently on system properties.

The nature of the flocculation of fines obtained in polymer solutions is dependent upon a number of factors including polymer characteristics, solid and solvent properties as well as the hydrodynamic conditions used during the flocculation and pre-flocculation stages. Understanding the role of factors is important for achieving the desired flocculation state of fines, particularly of mineral dispersions which are not easily processed (1,2). It is noted here that different properties of the flocculated systems can be the determining criterion in different processes. For example, whereas supernatant clarity will be important when water is to be recycled, it can be the sediment volume or the settling rate that will be important in effluent treatment. Different polymers can have different effects on the above-named properties of a flocculating system, and a simultaneous study of these effects can provide useful information about the mechanism of interaction between polymers and particles as...
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well as between the polymer-coated particles. In this study, the effect of polymer properties, such as charge density, on selected flocculation parameters, such as settling rate, sediment volume, and supernatant clarity, is studied for kaolinite fines. The flocculation of kaolinite has been studied extensively in the past (3-9). However, the results have been contradictory, for example, in the case of the polymer charge density required for optimum flocculation. While the discrepancies might be owing partly to the different methods used to measure flocculation, they also could have resulted from uncertainties in the measured properties of kaolinite caused by aging or ion exchange, in the properties of polymer due to the use of different commercial samples, or in the properties of the solution owing to variations in pH, ionic strength etc. An accurate understanding of the flocculation and dispersion of clays is, however, of much importance since clays are universally present in ore deposits, oil reservoirs, and marine and agricultural systems and markedly influence various processes involving them.

Flocculation is indeed dependent on polymer adsorption, and there are hypotheses correlating the two phenomena, but often these have been put forth without detailed measurement of the two phenomena simultaneously (10-13). In this paper, flocculation is investigated as a function of polymer and solution properties and hydrodynamic conditions by measuring different properties of the system, including adsorption, using well characterized kaolinite and polymer samples prepared specifically for this purpose. Also, the role of concentration and charge density of polyacrylamide and polyacrylamide-polyacrylic acid co-polymers in determining kaolinite flocculation is examined under controlled hydrodynamic conditions.

**Experimental**

**Materials.** Na-Kaolinite: A homoionic sample of kaolinite was prepared from a well-crystallized sample purchased from Source Clays, University of Missouri, using a standardized technique (14) which involved repeated washing with distilled water and by treatment with NaCl solutions to remove exchangeable ions such as Ca, and freeze-drying of the final product. Nitrogen specific surface area of this kaolinite was estimated to be 9.4 m²/g and X-ray analysis showed the characteristic pattern of kaolinite.

Polymers: Polyacrylamide and hydrolyzed polyacrylamide were prepared by the American Cyanamid Company specifically for this project, starting with ¹⁴C labelled monomer. The radioactivity level of the monomer was kept below 0.20 mCi/g in order to avoid significant spontaneous polymerization, utilizing a copper inhibitor. The homopolymer was synthesized by free radical solution polymerization in water at 40°C, using monomer recrystallized from chloroform, an ammonium persulfate-sodium metabisulfite catalyst system, and isopropanol as a chain transfer agent. Sodium
ethylene diamine tetraacetate was included in the recipe to sequester residual copper inhibitor in the labelled monomer. In order to avoid broadening the molecular weight distribution, the polymerization reaction was not carried to completion. Residual monomer was extracted with methanol-water mixtures and with methanol until it was less than 0.5 wt. % of the polymer. The final product was stored as the freeze-dried material. Polycrylamides of different anionicities were prepared by hydrolyzing dilute aqueous solutions of the homopolymer to the desired level with sodium hydroxide at 43°-46°C, in the presence of 2 wt. % isopropanol. These products also were stored as freeze-dried materials.

The intrinsic viscosity of the homopolymer was found to be 1.8 dl/g in 1 M NaCl at 30°C, using a 75 Cannon-Ubbelohde viscometer. Using the Mark-Houck equation \( \eta = K M^a \) with \( K = 3.73 \times 10^{-4} \) and \( a = 0.66 \), the viscosity average molecular weight is estimated to be 0.4 x 10^6 daltons (15). The carboxyl levels of the hydrolyzed polycrylamides were analyzed by infrared absorption spectroscopy, and were reported to be 9 \pm 2, 21 \pm 2, and 33 \pm 2 mole %. The polycrylamides are designated as PAM or as HPAM to indicate the homopolymer or a hydrolyzed product. Two numbers are added after the letters, the first indicating the molecular weight in units of a million, and the second the extent of hydrolysis (e.g., HPAM 0.4-33 has a molecular weight of 0.4 x 10^6 daltons and is hydrolyzed to the extent of 33 mole %).

Procedure. For each test, a 5 gram sample of Na-kaolinite was first conditioned in 150 ml of 3 x 10^{-2} kmol/m^3 NaCl solution in teflon bottles for two hours using a wrist-action shaker set for maximum agitation of the suspension. It was then stirred for desired intervals using a 1" propeller (three 2.54 cm diameter blades at 45° inclination) at 1200 rpm in a 250 ml 6.3 cm diameter beaker fitted with four 0.63 cm wide baffle plates (16) with 50 ml of polymer solution added in the beginning while the suspension was being stirred. Time of conditioning of the suspension with the polymer is indicated in each figure. Samples were then removed from this for various measurements.

Percent solid settled: In tests where adsorption and flocculation were determined simultaneously, the 200 ml sample was allowed to settle for 30 seconds and then 100 ml of the supernatant was removed using a suction device and after centrifugation analyzed for residual polymer concentration. The minimum level of detection was at 0.5 to 1 ppm and the reproducibility of the adsorption measurements was 2-3%. The settled 100 ml portion was analyzed for solid content. Flocculation due to polymer addition is measured by noting % solid settled as a function of polymer concentration.

Settling rate: For determining the settling rate, the 200 ml sample was transferred to a 250 ml flat bottomed graduated cylinder and 4 ml of supernatant was used for polymer analysis. The original solution was made up with an equal volume of electrolyte solution and then mixed manually and over end. The settling rate was determined by measuring the descent of the solid/solution interface as a function of time and by estimating the slope of the linear region.
Sediment volume: The sample used for measurements of settling rate was allowed to subside overnight for 16 to 24 hours and the sediment volume was read on the graduated cylinder.

Supernatant clarity: After subsidence, the sample was remixed manually and allowed to settle for 3 minutes. Supernatant clarity was measured using a Brinkman probe colorimeter PC 1600 by dipping the probe to just below the surface of the liquid.

Viscosity: A 16 ml sample of the suspension removed after remixing was used for torque measurements using a Brookfield viscometer (Model: LVTD) with a UL adapter. Initial torque readings were used for estimating viscosity in order to avoid problems arising from any settling of the kaolinite in the viscometer during the measurements.

Results

Simultaneous Adsorption/Flocculation Tests. Results obtained for adsorption and flocculation (as measured by the amount of solid settled) for the same samples are given as a function of concentration of the nonionic polyacrylamide in Figure 1 and the 33% hydrolyzed polymer in Figure 2. Flocculation as measured by settling rate is given in Figure 3 for the case of the nonionic polyacrylamide. In these tests both polymers were completely depleted from solution up to about 100 mg/kg addition. As far as flocculation is concerned, the nonionic polymer is found to increase both the percent solid settled and the settling rate which go through maxima at about 25 mg/kg addition. While polymer addition had no measurable effect on percent solid settled even at higher polymer concentrations, at all levels of addition, the settling rate is higher than that obtained in the absence of the polymer. It is clear from a comparison of the polymer effect on these two flocculation responses that a single parameter cannot be used to characterize flocculation. Even though the settling rate is often a more sensitive parameter, as in the present case, it is often necessary—particularly in the case of selective flocculation—to also measure percent solid settled to a given level and to analyze the settled mass for mineralogical composition. It is noted that while the nonionic polymer enhanced the amount of solid settled, the anionic polymer had no measurable effect on this response even though its adsorption was comparable to that of the former. More important is the observed lack of the proposed correlations between the extent of polymer coverage and flocculation. This is further seen when the effect of time of stirring of the mineral with the polymer solution is examined (see Figure 4). While adsorption reached its maximum value within 2 minutes, flocculation decreased for at least 20 minutes upon continued stirring. Evidently the amount of polymer adsorbed cannot be considered to be the sole factor governing the flocculation.

Polymer Concentration. The effect of polymer dosage on additional flocculation responses was measured together with adsorption
Figure 1. Adsorption and flocculation obtained with Na-kaolinite at pH 4.5 as a function of dosage of polyacrylamide (PAM 0.4-0).

Figure 2. Adsorption and flocculation obtained with Na-kaolinite at pH 4.5 as a function of dosage of 33% hydrolyzed polyacrylamide (HPAM 0.4-33).
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Figure 3. Settling rate of Na-kaolinite suspension at pH 4.5 as a function of polyacrylamide (PAM 0.4-0) dosage.

Figure 4. Diagram illustrating kinetics of adsorption and flocculation for Na-kaolinite/polyacrylamide (PAM 0.4-0) system.
for both the nonionic and the anionic polymer. Conditioning was done in these tests at 1200 rpm for 10 minutes. On the basis of the results given in Figure 4, adsorption can be considered to have attained equilibrium during this time for these systems.

Results obtained for various floculation responses are given in Figures 5 and 6 for the nonionic and the anionic polymer respectively. It is seen from Figure 5 that while the settling rate goes through a maximum as a function of PAM concentration, the transmittance of the supernatant increases from 38% at 0 mg/kg to 80% at 25 mg/kg and then remains at that level till at least 50 mg/kg. The sediment volume does not vary to any significant extent. Adsorption of the polymer on the other hand is found to increase continuously in the complete concentration range of 0 to 100 mg/kg. In contrast, with the 33% hydrolyzed polyacrylamide, while the adsorption reaches its maximum value at about 50 mg/kg, both the settling rate and the supernatant transmittance are found to go through a maximum in the 10–25 mg/kg ranges. Also in this case the sediment volume is affected by the polymer addition. It is to be noted that the maximum effect is seen at different polymer concentrations for different responses. Viscosity of the suspension also responds to the PAMA addition, but again the polymer concentration required for this effect is different from those for changes in other responses.

These differences in the effect of polymers on various floculation responses have important theoretical and practical implications and can be explained in terms of various characteristics of flocs and floc-aggregates. Polymer adsorption or attachment of particles to polymer can occur in any number of configurations, and as a result the aggregation of particles also can take place in many ways, leading to different floc and suspension structures which will respond differently to different tests. Thus, a wide size distribution of floc can yield both a turbid supernatant and a relatively high settling rate. Viscosity and sediment volume will also depend on floc structure, but more importantly on possible interfloc aggregation to form network structures (17–19). They also can be directly affected if the polymer adsorbs with long loops and tails and by alterations in the structure of the fluid medium in the vicinity of the adsorbed species. Indeed, such alterations in the fluid structure and attachments of ultrafines and colloids to the polymer can be expected to depend on the charges of both the particle and the polymer. Thus, at 50 mg/kg polymer addition, even though both types of polymer adsorb to the same extent, the sample containing the nonionic polymer is in a flocculated state with a clear supernatant whereas the one containing the anionic polymer is dispersed and the supernatant is totally turbid. The anionic polymer has adsorbed to saturation at this level of addition, but under these conditions aggregation between the particles can be prevented by the electrostatic repulsion between them. However,
Figure 5. Various flocculation responses together with adsorption obtained with Na-kaolinite at pH 4.5 as a function of polyacrylamide (PAM 0.4-0) dosage.
Figure 6. Various flocculation responses together with adsorption obtained with Na-kaolinite at pH 4.5 as a function of 33% hydrolyzed polyacrylamide (HPAM 0.4-33) dosage.
While particle/polymer-polymer/particle aggregation will be prevented by such repulsion, particle/polymer-particle aggregation conceivably could occur since the particles are not completely covered by the anionic polymer under such conditions (the nonionic polymer adsorbs to a greater extent than the anionic polymer at polymer additions higher than 50 mg/kg, and there is no apparent reason for a larger surface coverage per molecule by the anionic polymer). Evidently the electrostatic repulsion is sufficient to prevent even particle/polymer-particle aggregation. Whether or not the entropy changes in this system are sufficient to produce such stabilization of the suspension is not clear at present.

**Polymer Charge Density.** The effect of polymer charge density is illustrated in detail in Figure 7. For reference purposes, values obtained in the absence of the polymer are 0.4 mm/s, 38%, 25 cm$^3$ and 1.56 cp for settling rate, supernatant transmittance, sediment volume and viscosity, respectively. While all the responses are sensitive to the polymer charge density, it is clearly seen that a maximum effect is obtained at different levels of anionicity for different responses. Settling rate and sediment volume are sensitive in the 0 to 20% hydrolysis range, whereas viscosity and supernatant transmittance become sensitive at higher anionicities. Discrepancies in the literature regarding the optimum charge density for flocculation might partly be the result of use of different techniques to monitor flocculation. It is to be noted that the values obtained for the optimum charge density can be dependent on the polymer dosage, solution properties--such as pH and ionic strength--and hydrodynamic conditions.

**Discussion**

The results of this study clearly show the complex dependence of the flocculation process on polymer dosage and charge density. It is seen that the form of dependence varies markedly among the responses monitored. In addition to the factors studied here, it can also be expected to depend upon several other physico-chemical conditions of the system, including the type of mixing. The final state of flocculation achieved by a mineral/polymer system will depend upon many interactions in the system as determined by various chemical and hydrodynamic properties of the particles, polymer, dissolved organics and the fluids. These include electrostatic interaction between the particles and interaction of particles with the fluid governed by their wettability, morphology and density (17-19); the extent of adsorption of the polymer and its influence on the interaction of particles, the orientation or configuration of the adsorbed polymers (and surfactant when it is present) and resultant interaction of adsorbed layers; the hydrodynamic state of the system and its influence on the interaction of flocs themselves.
Figure 7. Diagram illustrating the effect of polymer charge density on various flocculation responses of Na-kaolinite at pH 4.5.
Among the properties measured here, the settling rate is mainly a measure of the size of the flocs and in later stages the compressibility of flocs and floc networks, and the supernatant clarity is a measure of the size distribution of flocs and size dependent capture of the particles and flocs by the polymer. The sediment volume and the pulp viscosity on the other hand, are direct measures, not only of floc size and structure but also of adsorbed polymer layers. It is to be noted in this regard that it is this latter aspect which makes it possible to estimate the thickness of adsorbed polymer layers by measuring the viscosity of the medium and the suspension in the presence of polymers (20,21). This combination of effects is another reason one cannot always expect correlation between various flocculation responses.

In order to generate information on the mechanism of flocculation by polymers it is, however, necessary to correlate flocculation with various system properties, particularly adsorption. Thus, if particle/polymer-polymer/particle contact is the aggregation mechanism, the flocculation responses should be expected to continuously increase with surface coverage. On the other hand, if particle/polymer-particle contact is predominant and if the polymer adsorption is essentially irreversible, maximum flocculation might be expected under submonolayer conditions. In order to determine the nature of this relationship for the present systems, selected flocculation responses are plotted in Figures 8 and 9 as a function of surface coverage for the nonionic and the anionic polymer respectively. The assumptions involved in the computation of the surface coverage are to be noted at this point: 1. Saturation adsorption corresponds to monolayer formation; 2. Configuration of the adsorbed species remains unaltered from low to high concentrations. Indeed, these assumptions cannot be considered valid for polymer adsorption particularly if it is possible for the adsorbed polymer to move from a flat configuration to one with loops and trains (22,23). In spite of these difficulties, it can be safely stated that the flocculation response exhibits a maximum with respect to surface coverage, the optimum surface coverage being about 0.1 for the nonionic polymer and 0.1 to 0.2 for the anionic, depending on the flocculation response measured. It is seen from Figure 9 that full surface coverage leads to dispersion, suggesting that particle/polymer-polymer/particle aggregation is not the predominant mechanism in this case. Also, the 0.5 coverage criterion proposed in the past (13) appears not to be valid for the present system under the tested conditions. Evidently, in this case, flocculation is favored when a major fraction of the surface remains bare and available for aggregation by bridging. Indeed, such bridging should be influenced both by the electrostatic properties of the polymer and the mineral and by the polymer configuration, which in turn will depend upon molecular weight, charge density, pH and ionic strength. While the nonionic polyacrylamide can be
Figure 8. Flocculation of Na-kaolinite at pH 4.5 as measured by settling rate and supernatant clarity as a function of particle surface coverage by polyacrylamide (PAM 0.4-0).
Figure 9. Flocculation of Na-kaolinite at pH 4.5 as measured by the settling rate and the supernatant clarity as a function of particle surface coverage by 33% hydrolyzed polyacrylamide (HPAM 0.4-33).
expected to be in a coiled form, the 33% hydrolyzed polymer will be more extended at pH 4.5 since about half of the carboxylate groups will be in dissociated anionic carboxylate form. The higher viscosity obtained for the anionic polymers supports the above consideration. Such expansion of the polymer due to charge repulsion can facilitate bridging due to increased polymer length but can also retard it via electrostatic repulsion between the polymer and the similarly charged faces of the kaolinite particle. The net effect of these competing phenomena will actually determine the flocculation power of the hydrolyzed polyacrylamide. In the present study, reduced flocculation was obtained upon increasing the charge density of the polyacrylamide, suggesting the predominating contribution of the electrostatic repulsion. The higher sediment volume obtained with hydrolyzed polyacrylamides can also be attributed to such changes in configuration of the polymer upon hydrolysis: The charged polymer can produce voluminous flocs due to both its expanded configuration and to longer loops owing to the fewer contact points expected between the similarly charged polymer and mineral particles. Indeed, some additional contacts can occur between the polymer and the edges of the kaolinite particles.

The presence of excess salt, particularly of bivalent inorganics can reduce the electrostatic repulsion between the anionic polymer and the kaolinite particles and enhance flocculation (24,25). The optimum flocculation of fine coal and coal refuse (which contained 13 to 65% clays) obtained by Lewellyn and Wang (24) with hydrolyzed polyacrylamide containing 70% acrylate in fact might have resulted from the use of recycled water which contained 55 ppm Ca and 30 ppm Mg. Other works in literature have reported maximum flocculation of kaolinite to occur with 30% hydrolyzed polyacrylamide (5,6,10,26,27). Such differences in reported results could easily result from variations in water chemistry, originating either with the water used or with dissolved organics released by the mineral itself.

Summary

Flocculation using polyacrylamide and hydrolyzed polyacrylamides was investigated by studying a number of flocculation responses of Na-kaolinite under controlled chemical and hydrodynamic conditions.

The flocculation responses studied are settling rate, percent solid settled, supernatant clarity, sediment volume and slurry viscosity. The polymer concentration and polymer anionicity required for maximum flocculation were seen clearly to depend on the response studied. Both the settling rate and the supernatant clarity with the nonionic polyacrylamide floculent showed at pH 4.5 a marked increase to a maximum at about 25 mg/kg, whereas with the anionic polymer settling rate and supernatant clarity showed maxima at 10-25 mg/kg, but the system was totally
dispersed at higher concentrations. Sediment volume did not show any measurable change over the entire concentration range of nonionic polymer. In contrast, with the anionic polyacrylamide (33% hydrolyzed) both the sediment volume and the slurry viscosity showed increases with polymer concentration in the 0 to 50 and 25 to 50 mg/kg ranges respectively. Viscosity and sediment volume, however, remained at the highest levels up to the highest tested concentrations of anionic polymer. The different effects of polymers on the above responses are discussed in terms of various characteristics of flocs and floc-aggregates. While settling rate and percent solid settled can be expected to be governed essentially by the coarser region of the particle size distribution, by the density and compressive strength of the flocs, and by the structure of any three dimensional networks that can trap the fluid, the supernatant clarity will depend on any shift in the fine region of the size distribution and on the ability of the polymers and the network to capture the ultra-fines and colloids. Sediment volume and slurry viscosity on the other hand can depend on, in addition to the floc size distribution and the compressive strength of the flocs, also the thickness of the adsorbed layers of the polymer on the particles.

All the measured responses were sensitive to the anionicity of the polymer used as the flocculent. Settling rate showed a maximum with 0% hydrolysis and the supernatant clarity exhibited a maximum in the 0-20% hydrolysis range. While the anionicity did not have a significant effect on the viscosity in the 0-20% range, further increases in anionicity produced a measurable decrease in viscosity. These effects are accounted for in terms of electrostatic interactions between the polymer layers on the particles and alterations in the configuration of the adsorbed polymers due to the presence of the charged groups.

Flocculation was correlated with both adsorption density and estimated surface coverage for the nonionic and 33% hydrolyzed polyacrylamides. Maximum settling rate was obtained with the nonionic flocculent at 0.1 and with the hydrolyzed sample at 0.2 surface coverage. Supernatant clarity showed a maximum at a surface coverage of Na-kaolinite by the hydrolyzed polyacrylamide of 0.1. At higher surface coverages (such as 0.5) considered in the past to be optimum for flocculation, complete dispersion was obtained with both the nonionic and the anionic polymer.

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