Charge Effects in the Adsorption of Polyacrylamides on Sodium Kaolinite and Its Flocculation

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SUMMARY

Adsorption of relatively high molecular weight non-ionic and anionic polyacrylamides on sodium kaolinite has been studied simultaneously with various flocculation responses (per cent solids settled, settling rate and supernatant clarity) under controlled conditions of ionic strength, temperature and agitation. Flocculation properties are correlated with polymer adsorption and particle zeta potential, and mechanisms of flocculation are examined as a function of the charge of the polymer and clay.

INTRODUCTION

Polymer adsorption has been widely investigated primarily because of its importance in the understanding of the flocculation mechanisms utilized in various industrial applications such as beneficiation of mineral fines [1, 2], waste water treatment [3] or papermaking [4]. Among the most frequently used flocculants, polyacrylamides have been extensively studied, but their flocculation behavior is not fully understood due to the complexity of the adsorption phenomena influenced by a number of polymer, mineral and solution properties.

Polymer type and molecular weight as well as concentration and dosage influence adsorption and impact on flocculation response [1, 2, 5 - 7]. Solution properties such as temperature, pH and ionic strength also play an important role in the adsorption [1, 2, 7, 8]. Interactions governing adsorption depend on the nature of the adsorbent as well as the polymer. For instance, salt added to control

ionic strength not only affects polymer–solvent interactions in the bulk and at the surface, but also adsorbs competitively on the solid surface [7, 9]. pH also shows complex effects on the adsorption of polymers, affecting both functional groups on polyacrylamide and charging properties of clay. Separate charging mechanisms for clay edges and faces can even result in opposite charges.

While polymer adsorption clearly governs flocculation, the effect it has depends on the response monitored [8]. Per cent solids settled and settling rate can show quite different trends from supernatant clarity. These flocculation properties reflect the different interactions that can occur, in a clay–polymer system [10]. For instance, settling rate is a measure of the size and density of the flocs and floc networks and finally of floc compressibility. Supernatant clarity reflects the size distribution of flocs and the ability of the polymer to attach to fine particles. A system could have a high settling rate and yet yield a turbid solution of suspended fines. In order to fully elucidate flocculation, it is important to simultaneously measure adsorption density and flocculation response and to monitor several responses.

The study examining flocculation responses of sodium kaolinite to the adsorption of non-ionic and anionic polyacrylamides is expanded in this work in order to ascertain any correlation between polymer adsorption, flocculation and zeta potential. Various flocculation responses (solids settled, settling rate, supernatant turbidity) to reagentizing time, polymer charge and to pH are monitored.

EXPERIMENTAL

Materials

A well-crystallized sample of Georgia kaolinite was obtained from the clay repository

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at the University of Missouri. The surface area of this sample, determined by the nitrogen adsorption technique (BET), is 9.94 cm^2/g. Particle size distribution of this sample has been determined by a Leeds and Northrup Microtrac Particle Size Analyzer to be 80% under 5 μm and 100% under 22 μm. A homo-ionic sample of this kaolinite was prepared using a standardized technique described earlier [11, 12].

The ^{14}C-labeled non-ionic polyacrylamide (PAM, 5.2 $\times$ 10^6 molecular weight) and 33% hydrolyzed polyacrylamide (HPAM, 6.6 $\times$ 10^5 molecular weight) used here were synthesized and characterized by American Cyanamid Company.

Fischer-certified HCl and NaOH were used to adjust the pH of the suspension. Amend Drug and Chemical Company reagent grade, 99.96% pure NaCl was used to adjust the ionic strength. All solutions were made in triply distilled water.

Methods

Flocculation procedure

The details of the flocculation experiments have been described elsewhere [8]. Important points include, 2 hours pre-conditioning of clay with salt solution before polymer is added. The final solid/liquid ratio is 0.025. For per cent solids settled, 100 cm^3 of suspension is suctioned out after 30 s settling and the two portions are filtered, dried and weighed. Settling rate is determined in a flat-bottomed graduated cylinder and turbidity is measured in the cylinder after 10 min of settling. A Zeta Meter is used to measure the electrophoretic mobility of clay particles from which the zeta potential is obtained.

RESULTS AND DISCUSSION

Monitoring the effect of reagentizing time on per cent solids settled and on polymer adsorption establishes that polymer adsorption (from a 25 ppm solution) is finished within 2 min, plateauing at 1 mg/g for both PAM and HPAM. Solids settled reaches its stable value after 10 min conditioning. Thus, 10 min conditioning with the polymer is used for the rest of the experiments.

Effect of polymer dose

The comparison of adsorption density and flocculation as reflected in settled solids is
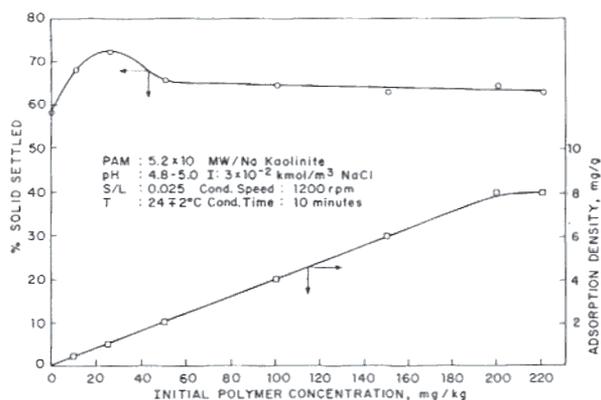
Fig. 1. Effect of initial polymer concentration of PAM on flocculation of sodium kaolinite.
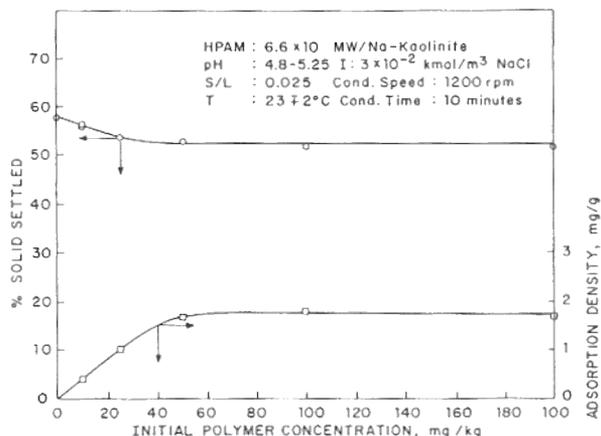
Fig. 2. Effect of initial polymer concentration of HPAM on flocculation of sodium kaolinite.

shown in Figs. 1 and 2 for PAM and HPAM at natural pH. Adsorption shows typical polymer isotherm behavior for both polymers, reaching plateau adsorption values of 8 mg/g for the non-ionic and only 1.7 mg/g for the anionic polymer. Whereas the plateau is not attained until 200 mg/kg for the non-ionic, it is reached at considerably lower dosage for the anionic polymer, 50 mg/kg. Clearly, charge—charge repulsion plays a governing role restricting adsorption of the negatively charged polymer. It is interesting, however, that the initial isotherm slope is steeper for the anionic than non-ionic polymer, suggesting stronger adsorption. Typically, PAM adsorption is thought to occur via hydrogen bonding; here, there is evidence that, for the hydrolyzed polymer, the charged functional group contributes to the adsorption step, probably at cation sites, until repulsive forces become predominant.

.The effects of the two polymers on the suspension stability are quite opposite; while the non-ionic polymer causes flocculation of the kaolinite at low dosage, the anionic polymer produces only dispersion, lower per cent solids settled, under the tested conditions in spite of adsorption.

Since per cent solids settled cannot be considered to be an absolute measure of flocculation of these types of suspensions, two other properties of the system, settling rate and supernatant transmittance have been measured. These are plotted in Figs. 3 and 4 as a function of adsorption density as well as surface coverage. Settling rate is calculated from the constant settling region, interface height *vs.* time. Settling experiments could be done only up to concentrations of 30 mg/kg addition for 33% hydrolyzed polyacrylamide since the slurry/supernatant interface is not visible at higher concentrations; complete dispersion of the sample results with the anionic polymer above 30 mg/kg polymer dosage.

It can be seen from Fig. 3 that both the settling rate and the supernatant transmittance are found to go through a maximum as a function of adsorption of the non-ionic polymer. The maxima in solids settled, settling rate and transmittance all occur at quite low adsorption density, 1 mg/g, corresponding to only 10% surface coverage. This suggests a bridging mechanism between particle–polymer/particle rather than between particle–polymer/polymer–particle. As the adsorption density increases, it begins hampering flocculation, as shown by the decrease in responses measured.

In contrast to this, Fig. 4 shows that the hydrolyzed polyacrylamide yielded a maximum solely in the case of settling rate. It produced only an increase in turbidity upon the addition of anionic polymer. Comparing Fig. 2 and 4 reveals that while adsorption does not enhance per cent solids settled, at very low dosage it can increase the settling rate but at the same time supernatant clarity worsens dramatically. In other words, what little adsorption contributes to flocculation only increases the rate of settling and fines are in fact stabilized by adsorbed polymer. The overall effect is negative.

The slope of the transmittance–time curve is a measure of the speed with which the suspension clears and is a parameter of practical
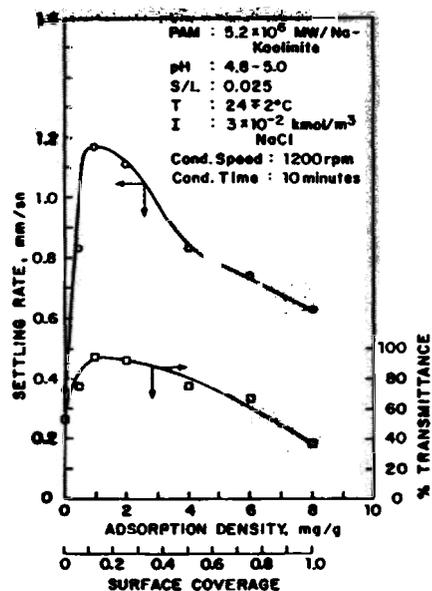
Fig. 3. Flocculation responses of sodium kaolinite as a function of surface coverage by PAM.
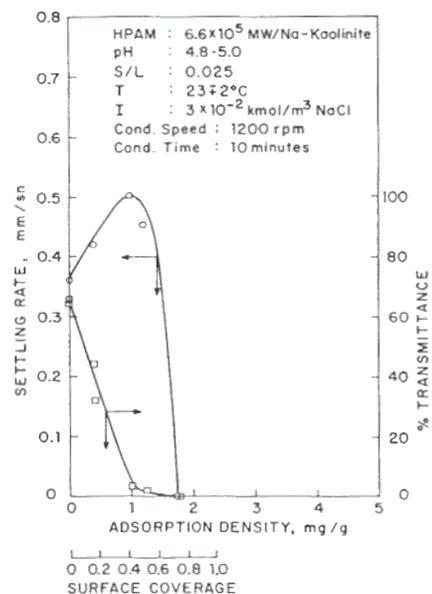
Fig. 4. Flocculation of response of sodium kaolinite as a function of surface coverage by 33% HPAM.

significance. This response can be seen in Figs. 5 and 6 for PAM and HPAM, respectively. The non-ionic polymer clarifies the suspension rapidly and reaches a high final clarity but only at low doses. Even though additional polymer enhances settling, the clarity suffers drastically, suggesting that a significant amount of the fine fraction of the slurry lags behind the settling mass and remains suspended. It is important to note that at the intermediate doses, even though
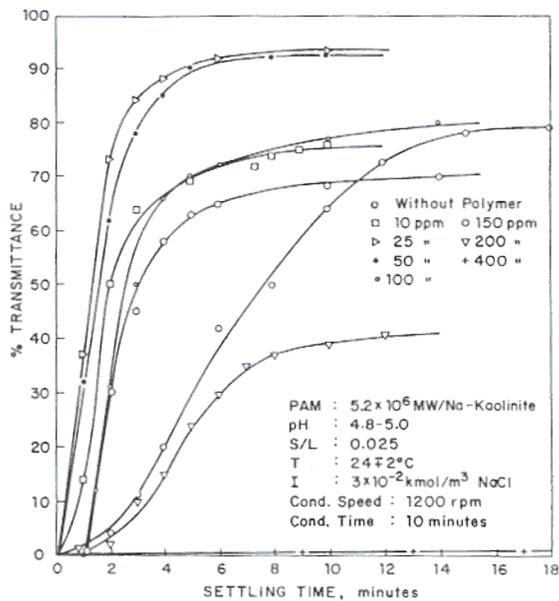
Fig. 5. Supernatant transmittance for PAM as a function of settling time.
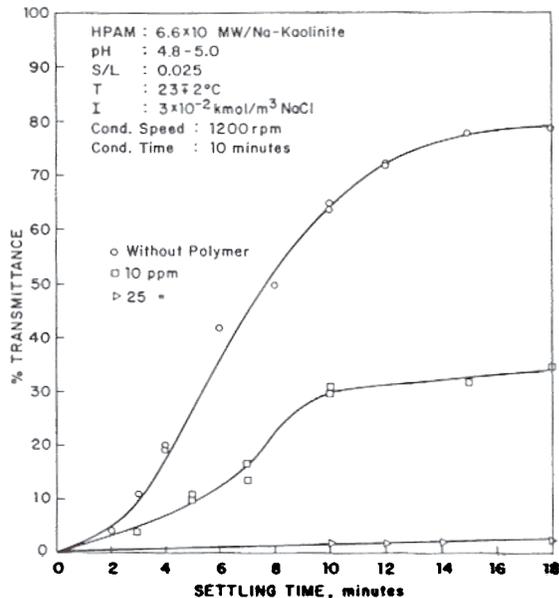
Fig. 6. Supernatant transmittance for HPAM as a function of settling time.

the suspension clarifies more rapidly than in the absence of the polymer, ultimate clarity is poor. In contrast to the non-ionic polymer, the ionic polymer makes the slurry supernatant more turbid at all tested dosages. For both polymers, the adsorbed layer can lead to steric stabilization of fine particles.

At low polymer doses, the sample with the non-ionic polymer is in a flocculated state with a clear supernatant, whereas the one with the anionic polymer is dispersed with a cloudy supernatant. At higher polymer doses, the non-ionic polymer continues to adsorb in increasing amounts, enhancing the settling but not the transmittance. In this concentration range, additional adsorption of the hydro-, lyzed polyacrylamide is prevented, presumably due to electrostatic repulsion from the adsorbed layer of anionic polymer. In the case of the non-ionic polymer, electrostatic forces are unimportant and solvation and hydrogen bonding forces predominate. Similar to results on solids settled, these properties show that maximum flocculation is obtained at fractional saturation coverages which are much smaller than the 0.5 which had been proposed in the past [13]. Apparently, particles do not flocculate in this case by particle–polymer to polymer–particle bridging. In fact, this interaction is repulsive. More importantly, the adsorbed anionic polymer molecules require a larger bare share of the particle surface. This is consistent with the idea that uncharged polymers tend to form coils in solution and charged polymers tend to be extended. Thus, when adsorbing, the former would require less area than the latter.

Effect of molecular weight

The effect of molecular weight may be seen by comparing these results with those using lower molecular weight polymers in an earlier phase of the work. Not surprisingly, increased molecular weight has no effect on non-ionic PAM adsorption density (on a weight basis) or settling rate. However, the smaller polymer resulted in plateau transmittance at 80% clarity, while the longer polymer yielded a maximum. Or, some steric stabilization is caused by the longer adsorbed loops in the latter case. Contrastingly, even a small increase in molecular weight of the anionic polymer impacts on flocculation response. Adsorption density is reduced, probably due to the increased anionicity per molecule, leading to earlier charge–charge repulsion while settling rate is not affected. Lower molecular weight HPAM shows a maximum in transmittance at very low adsorption density, but at the higher molecular weight, only dispersion is observed. Again, the longer chain could lead to a thicker adsorbed layer which leads to an apparent higher charge density in the adsorbed layer and this in turn to repulsion.

Effect of pH

The type of surface site is as important as the functional group of the polymer in adsorption. For sodium kaolinite, the charge characteristics of the surface will depend on the presence of electrolytes and particularly on the pH of the solution. Figure 7 shows the zeta potential of kaolinite in the absence and presence of the anionic polymer. The figure shows that the isoelectric point of this sample is 4.7 and does not change in the presence of HPAM. At low pH, the polymer reduces the zeta potential, masking surface charge. At high pH, within the scatter, the anionic polymer does not significantly affect the measured interfacial potential.

Fig. 8. Effect of pH on flocculation of sodium kaolinite in the absence and presence of HPAM.
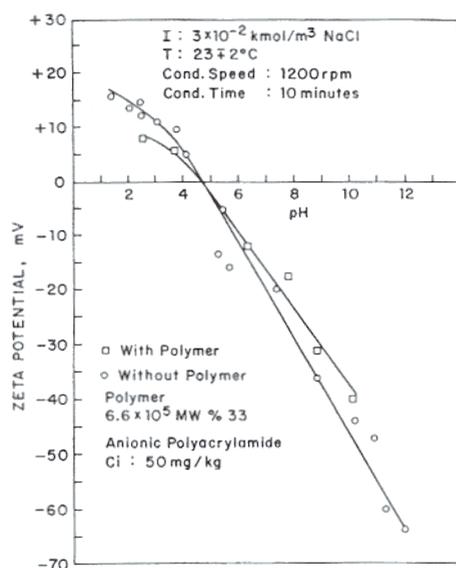
Fig. 7. Zeta potential of sodium kaolinite at various pH ranges in the absence and presence of HPAM.

Fig. 9. Effect of pH on flocculation of sodium kaolinite in the absence and presence of PAM.

Results obtained for flocculation and adsorption for the same sample are given as a function of pH for the anionic polyacrylamide in Fig. 8 and for the non-ionic in Fig. 9. Adsorption density of the anionic polymer can be seen from Fig. 8 to decrease with increase in pH, which is consistent with the lack of effect on zeta potential at higher pH. At low pH, where an effect on zeta potential was observed, some flocculation is obtained. This is due to bridging between the positively charged kaolinite and the adsorbed negative polymer molecules. The polymer causes no flocculation above pH 3 in spite of the fact that there is significant adsorption at pH 5. Near pH 5, the kaolinite particles report a

zero charge and the adsorbed anionic polymer does not contribute toward any bridging. If anything, there is already sufficient polymer on the surface to cause repulsion between adsorbed layers. Above pH 7, where the mineral is highly negatively charged, adsorption is insignificant and there is no flocculation.

Adsorption density is not affected by pH in the case of PAM even though a more concentrated solution leads to higher adsorption (Fig. 9); hydrogen bonding and solvation must be the predominant interactions. Interestingly, with the non-ionic polymer, increased flocculation is obtained with increase in pH but only at low initial concentration even though the adsorption density remains essentially unchanged as a function of

pH. Differences in conformation of adsorbed polymer, suggested by observed bulkier flocs, could be contributing to this effect. The reasons are not clear at present, but the results suggest a role in bridging played by the negative surface sites and adsorbed polymer layer as long as the layer is not so thick that it masks the surface leading to stabilization. At high polymer dosage, both the adsorption and flocculation remain approximately the same with increase in pH until pH 11, where the polymer has lost its flocculating power due to hydrolysis of the functional groups.

CONCLUSIONS

Adsorption, flocculation and zeta potential results suggest that kaolinite flocculation by polyacrylamides arises from a bridging mechanism in which two particles are linked by an adsorbed polymer molecule, or particle–polymer/particle interaction. As the adsorption density increases, it begins hampering flocculation. Once the adsorption is high enough, adsorbed polymer sees adsorbed polymer and repulsion or steric stabilization results. Particle–polymer/polymer–particle interaction leads to dispersion, as evidenced by high turbidity and slow settling in cases in which higher adsorption is measured.

In addition to hydrogen bonding forces, electrostatic forces play a role in the adsorption of polyacrylamides. At natural pH, non-ionic PAM adsorption is governed primarily by hydrogen bonding and solvation interactions, while clearly electrostatic forces are important for charged polymer. Very low does the non-ionic; however, the initial iso-pH (<5), but with even a slight increase in either of these, dispersion results. The anionic polymer adsorbs much less on kaolinite than those the non-ionic; however, the initial iso-therm slope is higher than that of the non-ionic. This suggests that although the net interfacial potential is zero, individual positive surface sites have a higher driving force for adsorption than adsorption by hydrogen bonding in the case of PAM. The negative charge quickly becomes detrimental as positive surface sites are saturated and/or chargen charge repulsion becomes predominant. Even a small increase in molecular weight of the charged polymer suppresses adsorption and leads to dispersion. Zeta potential results at natural pH do not reflect the effect of adsorbed anionic polymer which would have been expected to yield a more negative potential. However, this is a difficult region to make measurements and the effect may have been missed. Adsorbed polymer does reduce zeta potential at low pH, which is the region where flocculation is observed.

Low doses of non-ionic PAM yield a flocculated state with a clear supernatant. At higher adsorption, settling is enhanced but clarity worsens, which could be due to stabilization of the fine fraction by the adsorbed polymer. Although the adsorption density does not change, flocculation is enhanced at high pH. This is attributed to the formation of large bulky flocs in the basic pH region, which may also entrap additional material while settling. Conformational changes in adsorbed polymer layers are not well understood at present. There seems also to be some role played by negative surface sites in the bridging by the non-ionic polymer as seen by continued adsorption at high negative interfacial potential.

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