

Effects of the conformation of polyacrylic acid on the dispersion–flocculation of alumina and kaolinite fines

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Abstract—Conformational characteristics of polyacrylic acid (PAA) adsorbed on alumina were studied along with stability of its suspension in order to delineate the mechanism by which polymer conformation affects the stability of fines. Fluorescence spectroscopy, with pyrene as the probe, was used to monitor the conformation of the polymer at the solid–liquid interface. The stability of these fines with PAA in coiled, stretched and coiled-transformed-to-stretched conformations was investigated. With PAA in coiled and stretched forms, the suspensions were slightly flocculated. Under the coiled-to-stretched conditions, achieved through manipulation of polymer conformation, flocculation was drastically enhanced at lower polymer concentrations, while a stable dispersion was observed at higher polymer concentrations. This difference in dispersion–flocculation behavior is explained on the basis of a concentration-dependent conformational transition. Enhanced flocculation of kaolinite was also achieved by manipulation of polymer conformation.

1. INTRODUCTION

Colloidal stability is a key interfacial parameter that controls the efficiency of many industrial processes: printing, detergency, cosmetics, microelectronics, high performance ceramics, mineral processing, effluent treatment and food processing [1–5]. In most of these processes, dispersion or flocculation of particles is determined by macromolecular adsorption both in terms of the amount and the configuration of the adsorbed species [4–13]. Polymers can exist in different conformations depending on the physico-chemical conditions of the system (e.g. pH, ionic strength of the solution, type of solids and solubility). Stability of suspensions will therefore be influenced by these factors. Due to the non-existence of reliable *in situ* techniques to determine the conformation and orientation of adsorbed polymeric species, very little work has been done in the past to elucidate the mechanism by which polymer conformation controls suspension stability and to identify means for controlling polymer conformation to achieve flocculation or dispersion. As a result, colloidal stability has been interpreted mostly on the basis of polymer adsorption density and the surface charge properties of the particles.

Recently, we developed a multi-pronged approach involving simultaneous measurements of flocculation–dispersion responses, electrokinetic behavior of particles and configuration of adsorbed polymeric species using fluorescence technique and pyrene-labelled reagents [14,15]. The rationale behind the use of this technique

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is the observation that, in bulk solutions, the extent of excimer formation (i.e. association of a ground state pyrene with an excited state pyrene) depends strongly on the polymer conformation [16,17]. When a polymer is in a coiled conformation, there is a higher probability of intramolecular excimer formation between pyrene groups. Similarly, when a polymer is in a stretched conformation, there is a low probability of such excimer formation. The difference between the two conformations is discernible in the intensity of their fluorescence spectra at certain wavelengths. Here, the ratio of the intensity of the excimer (I_e) to the monomer peaks (I_m) is referred to as the 'coiling index' of the polymer. In the absence of significant intermolecular interactions, a high I_e/I_m value is obtained for a coiled conformation, while a low ratio is associated with a stretched conformation.

The aim of this investigation was to study the role played by the conformation of polyacrylic acid (PAA) in determining the stability of fines, in particular alumina, and to develop methods for controlling the stability of colloids through manipulation of polymer conformation. Configurational behavior of the adsorbed polymer was determined along with flocculation and zeta potential properties of the same samples. Use of the same samples for all measurements is considered important, since correlation of results from different tests can be misleading due to experimental artifacts. The effects of polymer concentration and conformation (coiled, stretched and coiled-to-stretched) on the stability response for alumina suspensions were studied. On the basis of information obtained from an alumina/PAA system, the approach of conformation manipulation was also applied to a kaolinite/PAA system.

2. EXPERIMENTAL

2.1. Materials

Linde Alumina (Union Carbide) of $0.3\ \mu\text{m}$ size was used in this study. The isoelectric point of the sample was pH 3.3. Another mineral used in this investigation was homoionic Georgia kaolinite obtained from the clay repository of the University of Missouri, and prepared using a standardized technique which involves repeated washing with distilled water and treatment with NaCl solutions to remove exchangeable ions, such as Ca^{2+} , and freeze-drying of the final product [8,18]. Particle size distribution of this sample was determined, using Microtrac Particle Size Analyzer, to be 80% under $5\ \mu\text{m}$ and 100% under $22\ \mu\text{m}$. The isoelectric point of the kaolinite sample was pH 4.5. A pyrene-labelled PAA sample of molecular weight 88 000 was used in this investigation [16,17], along with an unlabelled polyacrylic acid of molecular weight 90 000 purchased from Polysciences, Inc. To minimize intermolecular excimer formation at higher polymer concentrations, a mixture of pyrene-labelled PAA with pyrene-free PAA was used. Concentration of the pyrene-labelled polymer was maintained at 20 p.p.m. while that of the unlabelled polymer was varied. All polymer solutions were prepared in $0.03\ \text{kmol/m}^3$ NaCl solutions. Fisher-certified NaOH and HCl were used for pH adjustment, while constant ionic strength was maintained by the use of reagent grade NaCl.

2.2. Equipment

Emission spectra were obtained using a SPEX FLUOROLOG fluorescence spectrophotometer. The pH was measured with an Orion Research Digital Ionalyzer 501

To determine the electrokinetic properties of the suspension, a Zeta-Meter was used. Residual polymer concentration of supernatants was determined using a Dohrmann DC 90 Total Organic Carbon (TOC) analyzer.

2.3. Procedures

A 10 g mineral sample was equilibrated with 194 ml of 0.03 kmol/m³ NaCl solution for 45 min by stirring with a magnetic bar. After pH adjustment, the suspension was further equilibrated for 45 min. The magnetic bar was removed, a baffle with four 0.63 cm wide plates was inserted and the suspension was stirred for 3 min using a 2.5 cm diameter propeller, with three blades at 45° inclination, at 600 r.p.m. Using a Sage syringe pump, 6 ml of polymer solution was added to the suspension dropwise at a rate of 6 ml/min. The polymer-containing suspension was further stirred for 5 min before flocculation measurements were made. For the system in which pH adjustment was made after the polymer was added, an additional 5 min of stirring was done. Aliquots for emission spectra and zeta potential determinations were collected from the same sample.

2.4. Flocculation tests

After allowing the suspension to settle for 45 s, the upper-half of the suspension was removed by suction and the percent solids settled was estimated by measuring the solid content of the lower half. It is to be noted that flocculation tests have been performed for both the system containing pyrene-labelled PAA and that containing unlabelled PAA. The results showed no measurable difference between the flocculation responses obtained using them, suggesting that the pyrene labelling had no effect on the flocculation behavior itself.

2.5. Adsorption tests

Supernatant solutions were removed from these samples, centrifuged and analyzed for residual concentration using the TOC analyzer. Under all conditions, PAA was completely adsorbed and no residual concentration could be detected in the supernatant.

3. RESULTS AND DISCUSSION

Figure 1 shows the excimer-to-monomer ratio (I_c/I_m) of the adsorbed PAA* at the alumina-liquid interface as a function of PAA concentration at pH 4.4 and 10.5. It can be seen from Fig. 1 that I_c/I_m , and hence the degree of coiling, is higher at pH 4.4 than at pH 10.5. This can be attributed to the low degree of ionization of the polymer at pH 4.4 (pK_a of PAA = 4.5; refs 10 and 19) which will result in diminished intramolecular electrostatic repulsion. A significant reduction is observed in the zeta potential of alumina due to adsorbed PAA (Fig. 2). Even though the reduction in charge led to agglomeration and some settling of fines,

* For the two systems studied, under all the experimental conditions there was complete adsorption of the polymer so that the fluorescence signal was entirely from the adsorbed polymer.

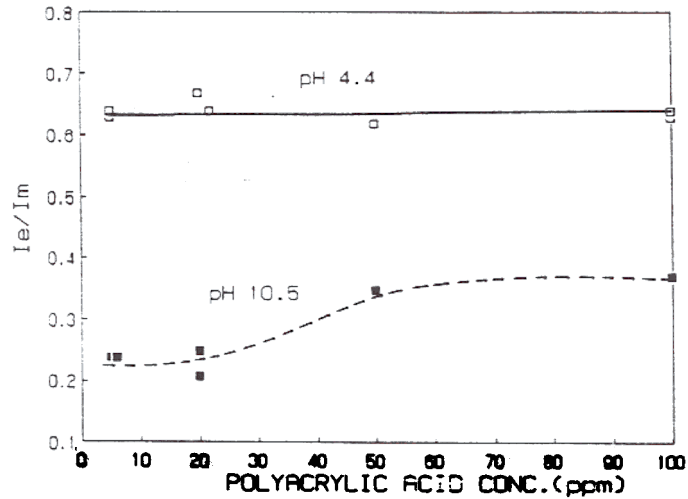


Figure 1. Excimer-to-monomer ratio, I_e/I_m , of PAA at the alumina-liquid interface as a function of PAA concentration at pH 4.4 and 10.5 ($IS = 0.03 \text{ kmol/m}^3 \text{ NaCl}$, $S/L = 10 \text{ g/200 ml}$).

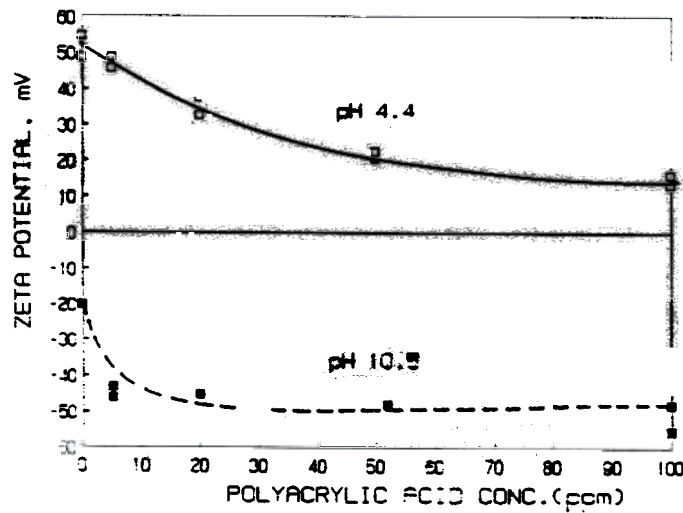


Figure 2. Zeta potential of alumina suspension as a function of PAA concentration at pH 4.4 and 10.5 ($IS = 0.03 \text{ kmol/m}^3 \text{ NaCl}$, $S/L = 10 \text{ g/200 ml}$).

adsorbed PAA in the coiled conformation was apparently not able to bridge these agglomerated fines and affect the percent solids settled (Fig. 3). From this study it is clear that PAA in coiled conformation does not have any significant effect on the flocculation and sedimentation of alumina under the tested conditions.

At pH 10.5, the values of I_e/I_m are lower than that obtained at pH 4.4 which indicates that the polymer is adsorbed in a relatively stretched conformation (Fig. 1). This can be attributed to the higher charge density of the polymer (due to ionization of carboxylic acid groups) at pH 10.5, compared with that at pH 4.4, and this will cause enhanced intramolecular repulsion. In contrast to the behavior at pH 4.4, at pH 10.5 the conformation of polyacrylic acid depends on the concentration of the

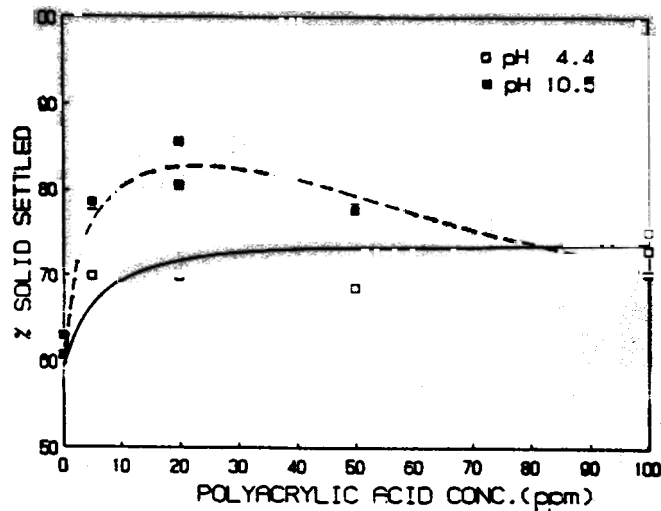


Figure 3. Percent solid settled of alumina suspension as a function of PAA at pH 4.4 and 10.5 (IS = 0.03 kmol/m³ NaCl, S/L = 10 g/200 ml).

polymer. At lower polymer concentrations, the adsorbed chains appear to be more stretched ($I_e/I_m = 0.25$). As the concentration of the polymer is increased, the polymer assumes a less stretched conformation ($I_e/I_m = 0.35$), apparently due to the crowding of polymer chains on the particles. Stability tests, as presented in Fig. 3, however, did not show similar concentration-dependent behavior. The amount of solids settled passes through a maximum at 20 p.p.m. Simultaneous examination of I_e/I_m (Fig. 1) shows that at this concentration (20 p.p.m.) the I_e/I_m increases suggesting that the more stretched polymer conformation causes enhanced flocculation in this case. This inference is also supported by the fact that the amount of solids settled at pH 10.5 when the polymer is stretched is higher than that at pH 4.4.

A relatively low value of I_e/I_m at pH 10.5 would only indicate that the polymer is in a stretched conformation. It does not provide any information as to whether or not the stretched polymer is lying flat on the surface or dangling into the liquid. The flocculation results, however, suggest that the stretched polymer is likely to be dangling into liquid since enhanced flocculation by bridging, compared to when the polymer is coiled, is possible under this condition. The proposed conformation is also consistent with the fact that both the polymer and the surface are negatively charged and it is unlikely that the polymer would lie flat on the surface under this condition, as such a conformation would require a large number of attachment points between the polymer and the surface. However, adsorption can still occur (as also determined experimentally) since even at pH 10.5 there will be sufficient number of unionized carboxylic acid groups ($-\text{COOH}$) which can attach to the surface through hydrogen bonding.

The results discussed above clearly show that the conformation of PAA has a major effect on the stability of alumina suspensions. The percent settled solid was higher with the stretched polymer chains which effectively bridged the fines to produce large flocs. In an attempt to control the stability of alumina with PAA, a scheme involving pH changes after polymer adsorption was investigated. In this case, PAA was first adsorbed on alumina at pH 4 and then the pH was raised to 10

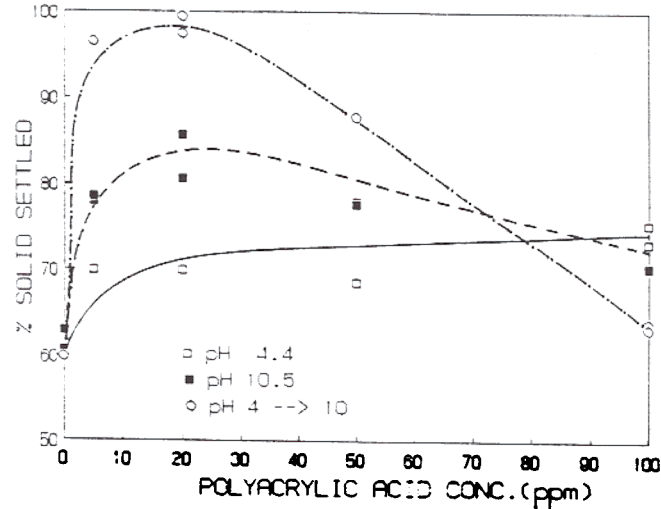


Figure 4. Percent solid settled of alumina suspension as a function of PAA concentration at pH 4.4 and pH 10.5, and under Shifted pH Conditions (from pH 4 to 10) ($IS = 0.3 \text{ kmol/m}^3$, $S/L = 10 \text{ g}/200 \text{ ml}$)

(shifted pH condition). As shown in Fig. 4, a marked increase in flocculation is obtained at lower polymer concentrations when the pH was raised. The system was better flocculated under shifted pH conditions than either at pH 4.4 or at 10. At higher concentrations, the alumina suspensions were highly dispersed.

Zeta potential behavior of alumina particles in PAA solution alone cannot explain the observed flocculation–dispersion behavior under shifted pH condition. It must be noted that no residual polymer could be detected in the supernatant solutions under these conditions even when the pH was raised, confirming the absence of desorption.

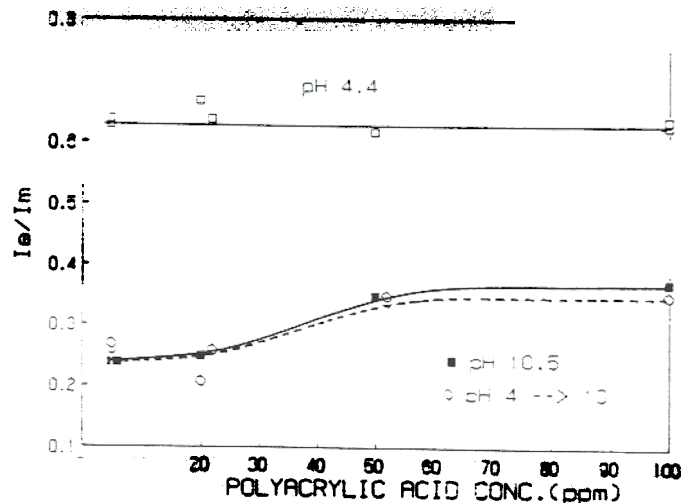


Figure 5. Excimer-to-monomer ratio, L_e/L_m , of PAA at the alumina-liquid interface as a function of PAA concentration at pH 10.5 and under shifted pH conditions (from pH 4 to 10) ($IS = 0.03 \text{ kmol/m}^3$ NaCl, $S/L = 10 \text{ g}/200 \text{ ml}$).

Changes in the conformation of adsorbed PAA due to pH increase are illustrated in Fig. 5. Adsorbing PAA first in coiled form at pH 4 (high I_c/I_m), and then raising the pH to 10, causes the conformation of polyacrylic acid to change from coiled to stretched form (lower I_c/I_m). However, the adsorbed polyacrylic acid is more stretched at low concentrations than at higher concentrations. The marked increase in flocculation at low concentrations (see Fig. 4) is interpreted on the basis of the changes in the polymer conformation from coiled to stretched upon pH increase. When PAA adsorbs initially on alumina suspension at pH 4, fines are aggregated into small floccs (*microflocs*); with increase in pH to the intermediate pH range (pH 5–7), the adsorbed polymer chains are extended, due to ionization, possibly causing aggregation of the *microflocs* into *macroflocs*. Any further increase in pH above 7 results in further stretching of the polymer causing aggregation of *macroflocs* into *superflocs* and, thus, enhancing flocculation and sedimentation [15]. At higher concentrations, when the pH of the alumina/PAA system is raised from 4 to 10, adsorbed PAA is apparently unable to stretch to the same extent as at lower concentrations due to the crowding of these chains at the solid-liquid interface. Because of repulsion among the adsorbed polymer chains, the suspension is dispersed under these conditions.

The effects of pH shifting on the stability of the suspension can also be seen in Fig. 6, in which the percent settled is plotted as a function of PAA concentration at pH 4.3, pH 10.4 and under shifted pH conditions (i.e. from pH 4 to 10). Under fixed pH conditions (pH 4.3 and 10.4), the percent settled solids shows a maximum at 5 p.p.m. PAA and the effects of the conformation of the polymer on the flocculation behavior are noticeable at these pH values. Kaolinite suspension is better flocculated at pH 10.4 when PAA is in the stretched conformation. However, adsorption of PAA on kaolinite at pH 4 followed by raising of the pH to 10 results in a drastic increase in flocculation at lower polymer concentrations. While 20 p.p.m. PAA addition did not enhance percent settled solids (only 55%) under fixed pH condition (pH 4.3), under shifted pH conditions almost complete

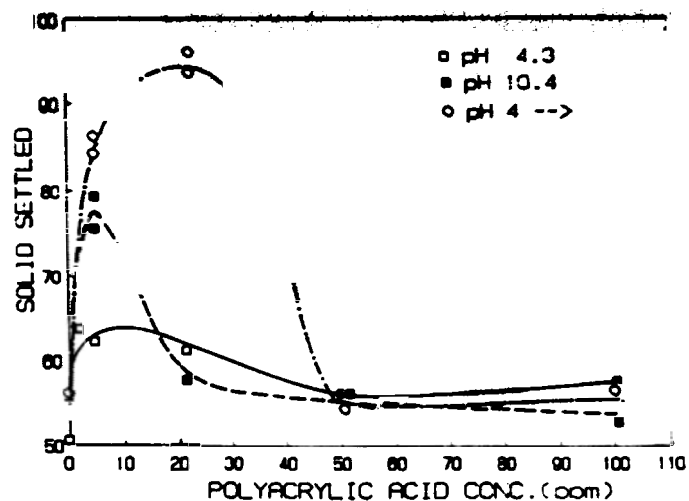


Figure 6. Percent solid settled of kaolinite as a function of PAA concentration at pH 4.3 and 10.4, and under shifted pH conditions (from pH 4 to 10) ($IS = 0.03 \text{ kmol/m}^3$, $S.L = 10 \text{ g/200 ml}$).

flocculation is observed (~95% solids settled). At higher polymer concentrations, pH shifting does not seem to affect the stability of kaolinite.

CONCLUSIONS

It is evident that the conformation of the polymeric species is a major controlling factor in determining the stability of alumina and kaolinite suspensions. pH shifting offers a new means of controlling the conformation of the polymer in the adsorbed state and thus the stability of suspensions. At low dosages, PAA conformational changes from coiled to stretched, due to pH increase, lead to excellent flocculation of alumina and kaolinite suspensions, while dispersion is enhanced at higher polymer dosages.

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