

Role of Polymer Conformation in Interparticle-Bridging Dominated Flocculation

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Flocculation of alumina with a dual polymer combination (polydiallyl dimethyl ammonium chloride and polyacrylic acid) is compared in this study with individual polymers. Zeta potential and conformational characteristics of the system are studied in order to determine the role of these properties in determining flocculation. The dual polymer system is shown to yield markedly better flocculation than either single polymer. Analysis of flocculation results along with the zeta potential measurements under corresponding conditions showed polydiallyl dimethyl ammonium chloride flocculation of alumina to be mainly electrostatic while polyacrylic acid flocculation to be polymer bridging at high pH and charge neutralization at low pH. The role of polymer conformation was found to be very important upon isolating the electrostatic effect by comparing the flocculation results under constant zeta potential. Polymer conformation in solution as well as at the solid-liquid interface can be altered by changing solution conditions and complexation with another polymer. It was shown that by manipulating polymer conformation, the flocculation can be greatly enhanced even at very low polymer dosage. In the specific case studied, the stretched and strongly adsorbed polymer was found to give excellent flocculation. © 1996 Academic Press, Inc.

Key Words: flocculation; polymer combinations; polymer conformation; polymer complexation; zeta potential; alumina; polyacrylic acid; polydiallyl dimethyl ammonium chloride.

INTRODUCTION

Polymers are increasingly used as flocculants in solid-liquid separation and sludge dewatering processes (1). In many cases, use of two or more polymers has been found to enhance the flocculation markedly. However, while the effect of charge density, chemical structure, and dosage of polymers has been studied in the past, not much attention has been given to understanding the mechanisms of dual or multipolymer flocculation (2, 3). Polymer-polymer interaction in solution or at the solid-liquid interface depends on the nature of polymers and solid surface, solution chemistry, and the interaction can profoundly change the charge properties of polymers and more vitally the conformation of poly-

mers, both of which are ascertained to be main controlling factors in flocculation with polymeric flocculants (4).

Our previous studies have discussed the importance of polymer conformation in flocculation of alumina suspension with polyacrylic acid and a method using pH shifting to manipulate the conformation to achieve enhanced flocculation or dispersion as desired (5). Recently, we have obtained markedly better flocculation using a combination of polymers (6). The aim of this work is to elucidate the mechanisms involved in such flocculation. The electrostatic force was isolated by comparing the dual polymer performance at one pH with that of single polymer at a pH where the zeta potential is identical.

EXPERIMENTAL

Materials

Linde A alumina powder used in this study was purchased from Union Carbide Corp. and had an average size of 0.3 μm and BET surface area of $\sim 14 \text{ m}^2/\text{g}$. Polyacrylic acid (PAA) of molecular weight 100,000 and polydiallyl dimethyl ammonium chloride (PDADMAC) of molecular weight 240,000 were purchased from Polysciences Inc. ACS certified grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) solution from Fisher Scientific Inc. were used as pH modifiers. Ionic strength was kept constant by using 0.03 mol/liter NaCl solution in all the experiments.

Methods

Flocculation tests. For each test, a 5 g sample of alumina was stirred in 190 ml of 0.03 mol/liter NaCl in a 250 ml beaker with a magnetic stirrer for 30 min. The pH of the suspension was then adjusted to the desired values and the suspension was further conditioned for 30 min. The beaker was then fitted with four $\frac{1}{4}$ -in. wide baffle plates and a 1-in. diameter propeller for better mixing and stirred with the desired amount of polymer stock solution for 1 min at 600 rpm. In the case of the dual polymer systems, the second polymer was added 1 min after stirring with the first polymer. The sample was stirred for an additional 4 min at 300 rpm.

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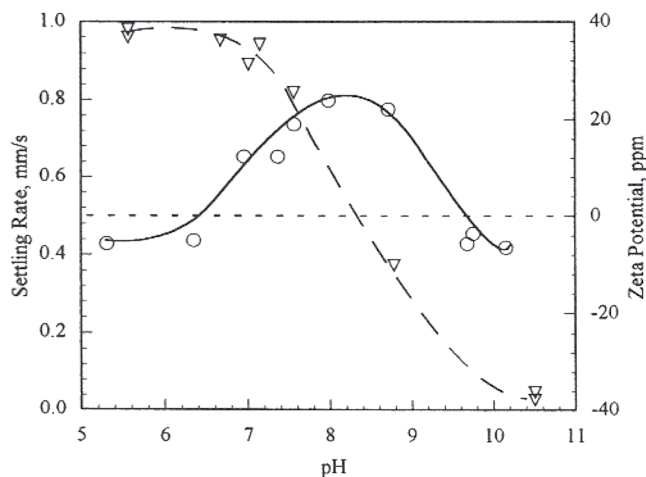


FIG. 1. Effect of pH on the zeta potential and flocculation of alumina particles (○ Settling rate, ▽ Zeta potential).

The slurry was then transferred into a 250 ml graduated cylinder for settling rate measurement.

Zeta potential measurements. The zeta potential was measured using a laser zee meter (Pen Kem Model 501). After the flocculation test was completed, flocs were ultrasonicated for 30 s to break them to small particles and diluted with supernatant in order to obtain a suitable dilute sample.

Polymer adsorption tests. Polymer adsorption on alumina was estimated by determining its depletion from the solution. The samples were treated in a fashion similar to that used for the flocculation tests and supernatants were then separated from sediments by centrifugation at 3000 rpm for 15 min. Polymer concentration was measured using a Dohrmann total organic carbon analyzer. Blank tests with polymer or polymer mixture solutions at the same concentrations without alumina were carried out to ensure that adsorption results were not affected by any precipitation.

RESULTS AND DISCUSSION

Electrostatic Flocculation

Flocculation is considered to be governed by two major mechanisms, the electrical double layer compression or charge neutralization and interparticle polymer bridging. However, the latter has not been as well understood as the former mainly because of the lack of a reliable technique to determine polymer conformation. In order to understand the bridging effect, it is necessary to isolate electrostatic forces. Alumina flocculation without polymer was done as a function of pH as a reference for comparison since it is dependent only on the electrostatic force between particles (see Fig. 1). It can be seen that flocculation results correlate well with the zeta potential of alumina particles. The maximum settling occurs at the isoelectric point (IEP) of alumina. Results

obtained for flocculation of alumina at pH 10.5 with polydiallyl dimethyl ammonia chloride are shown in Fig. 2 along with the zeta potential. It can be seen that the optimum flocculation (maximum settling) was obtained when the zeta potential was close to zero, which suggests that the flocculation in this case is controlled primarily by electrostatic forces. Adsorption results also show the positively charged polymer to adsorb completely on the negatively charged alumina at pH 10.5 in the concentration range studied. It is noted that the settling obtained with polymer at IEP is slightly different from that obtained without polymer at IEP. This suggests that apart from charge neutralization polymer bridging also plays a role in the flocculation. But, it is surprising that this bridging effect is minor even though the molecular weight of the polymer is high enough to cause good bridging.

Flocculation with Combined Mechanism

Flocculation of alumina with polyacrylic acid is shown in Fig. 3 as a function of pH along with the zeta potential. It can be seen that with the addition of PAA, maximum flocculation is obtained still close to pH 8 in comparison to pH 8.5 without PAA, which is close to the IEP of alumina after PAA adsorption. This suggests that the electrostatic effect is the governing factor in this flocculation also. However, it should be noted that the alumina suspension is flocculated with PAA even when both the polymer and the particles are similarly negatively charged at high pH. It has been suggested (6) that polyacrylic acid can adsorb on alumina either by electrostatic force at pH lower than IEP or via hydrogen bonding at high pH. The flocculation obtained here at pH below IEP is attributed to electrostatic adsorption of PAA resulting in interparticle bridging and charge neutralization. When pH is above the IEP, the polymer molecules

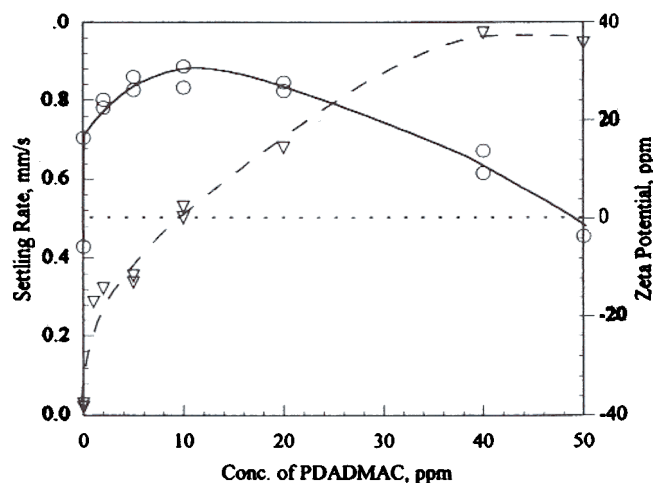


FIG. 2. Flocculation of alumina with polydiallyl dimethyl ammonium chloride at pH 10.5 (○ Settling rate, ▽ Zeta potential).

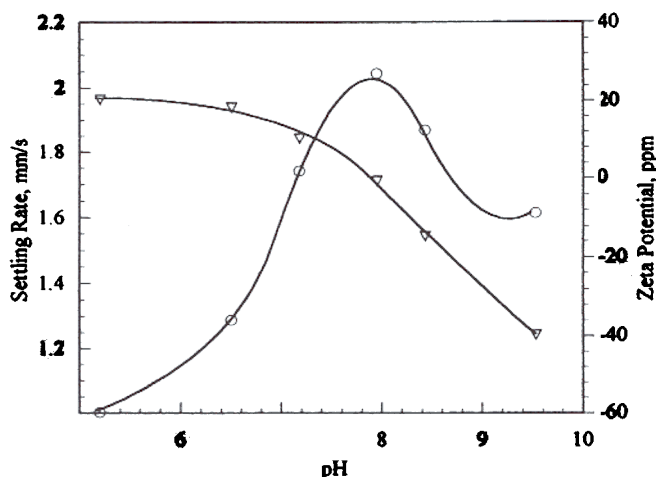


FIG. 3. Flocculation of alumina suspension with 20 ppm polyacrylic acid as a function of pH (○ Settling rate, ▽ Zeta potential).

adsorb via hydrogen bonding and inducing interparticle bridging causing flocculation even when the zeta potential of alumina particles is high.

Flocculation of Alumina Dispersion with Dual Polymers

Flocculation results obtained with the sequential addition of polydiallyl dimethyl ammonium chloride and polyacrylic acid are given in Fig. 4. It can be seen that the flocculation is markedly enhanced by the subsequential addition of PAA after the cationic polymer preadsorption. This is attributed to the efficient interparticle bridging by polyacrylic acid which was added subsequent to the adsorption of the oppositely charged PDADMAC molecules. Zeta potential measurements showed that PAA addition to the system does not affect the surface charge of alumina particles significantly.

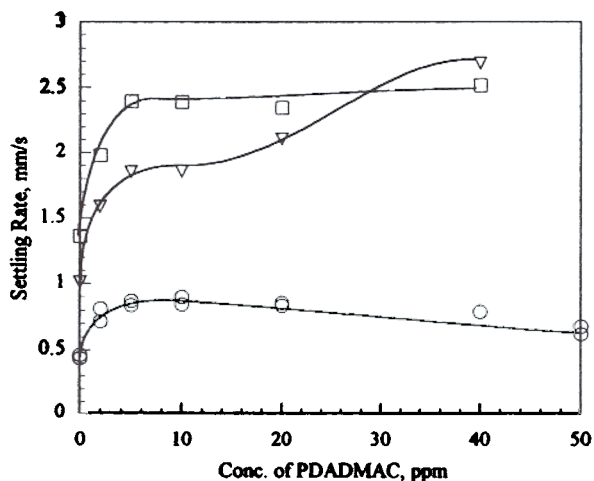


FIG. 4. Flocculation of alumina suspension with PDADMAC and PAA (○ PDADMAC alone, ▽ PDADMAC + 2 ppm PAA, □ PDADMAC + 5 ppm PAA).

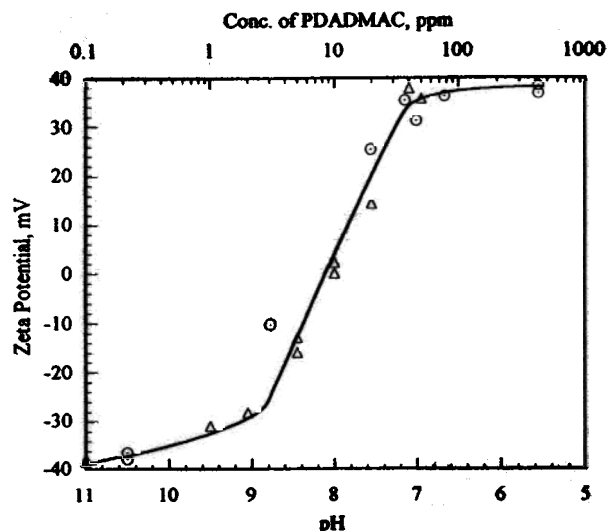


FIG. 5. Comparison of the zeta potential of alumina particles as a function of pH (Δ) and concentration of PDADMAC (○).

This is possibly due to the low dosage of polyacrylic acid used in comparison to polydiallyl dimethyl ammonium chloride. Adsorption results show the PDADMAC to strongly interact with alumina with no polymer left in the supernatant in the concentration range studied. PAA was also shown to completely adsorb on the alumina surface for all experiments.

Unlike in the case of single polymer systems, there is no longer a definite correlation between zeta potential and flocculation, indicating that electrostatic force is no longer the only governing factor for this flocculation.

Comparison of Flocculation with Single and Dual Polymer Systems

In order to isolate the electrostatic effect, the zeta potential of alumina is plotted together in Fig. 5 as a function of pH and as a function of PDADMAC concentration. By choosing the proper scale, both curves are made to overlap, so that zeta potentials at a given concentration of PDADMAC are identical to that at a specific pH. Flocculation of alumina with PAA at different pH conditions and PDADMAC adsorptions are compared in Fig. 6 using the same scale as in Fig. 5. Since the zeta potential of particles along the x axis on both curves is identical, the property that could have yielded different is proposed to be interparticle bridging that is dependent upon the polymer conformation at interface. It can be clearly seen that the flocculation response with dual polymers is better than that obtained with either polymer alone with the difference being particularly marked at low pH values.

Change of PAA Conformation in Solution

Polyacrylic acid, with carboxyl groups along the backbone, can be expected to possess different conformations at

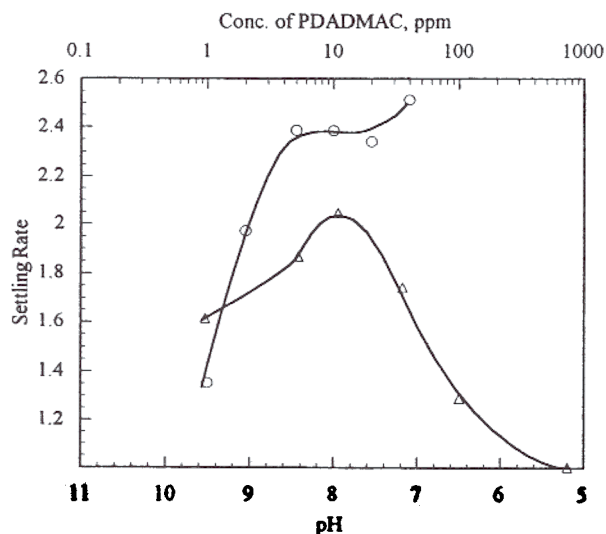


FIG. 6. Comparison of flocculation response as a function of pH (Δ) and concentration of PDADMAC (\circ).

different pH due to the pH dependent ionization ratio of COOH groups and interactions of these groups with other ions in the system and functional groups on other polymers. The fluorescence spectroscopic technique was used here to determine conformation of pyrene labeled polyacrylic acid. The conformation of PyPAA in alumina supernatant is shown in Fig. 7 as a function of pH. It can be seen that the polymer chain becomes stretched out with increase in pH due to the increasing intramolecular electrostatic repulsion caused by the ionization of $-\text{COOH}$ groups. The change in conformation of PAA upon the addition of the cationic polymer is also shown in Fig. 7. The coiling index shows an increase followed by a decrease with the addition of the

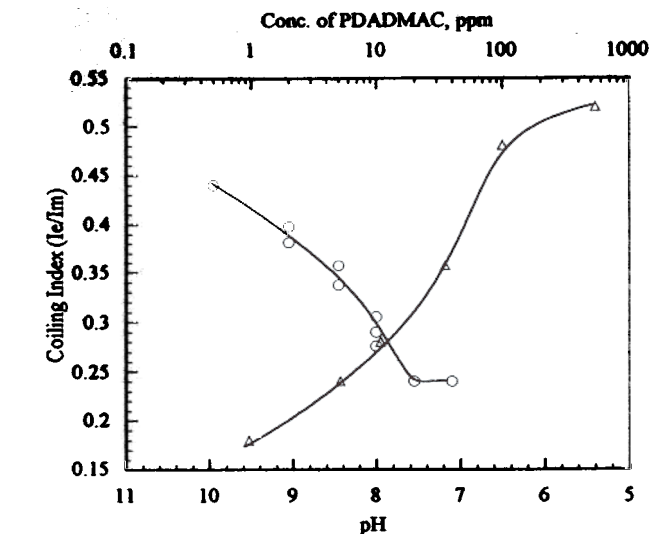


FIG. 8. Conformation change of PAA at the solid-liquid interface as a function of pH (Δ) and concentration of PDADMAC (\circ).

cationic polymer. Coiling of polyacrylic acid with PDADMAC at low dosage is attributed to the charge neutralization of the acrylate groups by the oppositely charged cationic polymer. With further addition of the cationic polymer, the polymer complex could become positively charged with resultant restretching.

The change of PAA conformation with the addition of PDADMAC clearly shows complexation between these two oppositely charged polymers. Such complexation is also confirmed by the observation that higher adsorption density of polyacrylic acid is obtained on alumina with PDADMAC preadsorption than that on bare alumina at any pH conditions.

Correlation of Flocculation Response with Polymer Conformation

Results obtained for conformation of PAA at the solid-liquid interface under corresponding conditions are given in Fig. 8. Interestingly, the effect of PDADMAC on the conformation of PAA is very different from that in solution. The coiling index of PAA is found to continuously decrease with the addition of PDADMAC. In the case of flocculation with polyacrylic acid alone, good flocculation could not be achieved because at low pH adsorption of the polymer in the coiled form is unable to cause good bridging and at high pH the stretched polymer is unable to interact strongly with the solid surface due to the electrostatic repulsion. In flocculation with dual polymers, unlike that with PAA alone, alumina particles are subjected to charge neutralization and reversal with PDADMAC preadsorption. While the zeta potential of alumina changes from -30 to $+40$ mV due to the adsorption of the cationic polymer, the PAA molecules remain in the same stretched conformation since the solution

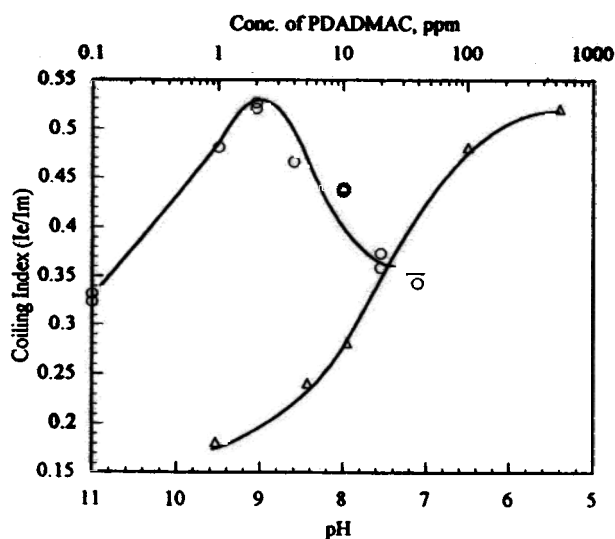


FIG. 7. Conformation change of PAA in solution as a function of pH (Δ) and concentration of PDADMAC (\circ).

pH remains unchanged. The negatively charged stretched PAA adsorbs on particles via interaction with preadsorbed PDADMAC on alumina surface and provides better interparticle bridging and thus excellent flocculation.

CONCLUSIONS

1. Conformation of the adsorbed polymer molecules at the solid-liquid interface can be altered drastically by the addition of a secondary polymer as well as other changes in solution conditions such as pH.
2. Polymer-polymer complexation in the solution and at the interface can lead to coadsorption of one polymer which otherwise does not adsorb.
3. Use of dual polymer systems can markedly enhance flocculation at a much lower dosage.
4. In addition to adsorption density, polymer conformation plays a predominant role in flocculation. In the case studied here, the stretched anionic polymer provides better

interparticle bridging when adsorbed on particles with preadsorbed polymer of cationic charge.

ACKNOWLEDGMENT

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