Correlation of Alumina Flocculation with Adsorbed Polyacrylic Acid Conformation

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ABSTRACT

Conformation of polyacrylic acid (PAA) adsorbed on alumina is studied here simultaneously with various flocculation properties of the same systems. Conformational characteristics of pyrene-labelled PAA is monitored using fluorescence spectroscopic technique. Among flocculation properties, the percent solid settled and the settling rate are measured by CAT scan. Our results show that polymer conformation is indeed a controlling factor of flocculation process even though the role of coiling is different from the traditional postulates. Under fixed pH conditions, the stretched polymer (which stands up at the solid/liquid interface) gives better flocculation than the coiled polymer (which sits at the interface). Under changing pH conditions, polymer adsorption in coiled form followed by partial transformation to stretched form results in the best flocculation performance. A two-stage flocculation mechanism is proposed to interpret our observation.

INTRODUCTION

Polymer conformation, considered to play a major role in flocculation processes, has never been delineated as to which conformation or series of conformation is best. The study of the conformation of polymers in various solvents [1,2] and on different substrates [3] have recently been made possible by the synthesis of pyrene-labelled macromolecules and the use of fluorescence spectroscopy techniques. Fluorescence spectroscopy involves the measuring of the monomer (Im) and excimer (Ie) emission intensities. The ratio of the excimer intensity (Ie) to the monomer intensity (Im) is related to the coiling/stretching of the polymer. In the absence of significant intermolecular interactions, a high Ie/Im ratio can be considered to be the result of a coiled conformation, while a low ratio is associated with a stretched one.
Lack of information on the conformational behavior of polymer (in the bulk and on the substrate), suspension stability, and the extent of polymer adsorption for the same system has made it difficult to relate these phenomena. In the present work, the effect of polyacrylic acid (PAA) conformation on alumina suspension was investigated under fixed and changing pH conditions. Correlation was made between the in-situ conformation of the polymer, changes in suspension stability as well as the effect of the adsorbed polymer on the charge of the mineral for the same test samples.

EXPERIMENTAL

Materials: Linde Alumina of 0.3 micron purchased from Union Carbide was used. In order to break up aggregated particles, the alumina sample was ultrasonicated in 0.03 M NaCl solution for 2 minutes. The point of zero charge (pzc) of this sample is 8.3. A pyrene-labelled polyacrylic acid of molecular weight 88000, prepared according to the method of Turro and Arora [2], was used in this investigation. All polymer solutions were prepared in 0.03 M NaCl solutions. Polymer solutions were stored in a refrigerator between use and solutions older than a week were not used. Fisher certified NaOH and HCl were used for pH adjustment, while constant ionic strength was maintained by the use of reagent grade NaCl.

Equipments: Recordings of the emission spectra were made with SPEX FLUOROLOG fluorescence spectrophotometer. The pH was measured with the Orion Research Digital Ionalyzer 501. The percent solid settled and the settling rate were measured by a CAT scan (EMI scanner CT5005, EMI Medical Limited, Slough, U.K.). Supernatant clarity measurements, in % transmittance, were made with a Brinkman PC 600 Colorimeter. To determine the electrostatic properties of the suspension, a Zeta-Meter was used.

Procedures: Ten grams of ultrasonicated alumina sample were equilibrated with 194 ml of 0.03 M NaCl solution in a 250-ml beaker for 45 minutes by stirring with a magnetic bar. Then, after pH adjustment, the suspension was further equilibrated for 45 minutes. The magnetic bar was removed and a baffle with four 0.63 cm wide plates was inserted and stirred for 3 minutes using a 1"-diameter propeller (with three 2.54 cm-diameter blades at 45° inclination) at 600 rpm. Using a Sage syringe pump, 6 ml of polymer solution was added to the suspension dropwise at the rate of 6ml/min. The polymer-contained suspension was further stirred for 5 minutes, before transfer into a 250-ml flat-bottom graduated cylinder for flocculation tests. For the system in which pH adjustment was made also after the polymer was added, an additional 5 minutes of equilibration was employed. It is to be noted that samples for emission spectra and zeta potential determinations for a given experiment were collected from the same cylinder.

Flocculation tests: Percent transmittance measurement was measured by dipping the Brinkman probe to just below the surface of the liquid at designated time intervals, while sediment volume was read on the graduated cylinder after 12 hours. Both the percent solid settled and the settling rate were measured by a CAT scan. After being remixed manually end over end, the graduated cylinder was mounted in the center of the CAT scan X-ray gantry [4]. X-ray scans were taken at designated time intervals. Solid-concentration profiles along the center line of the cylinder were evaluated from the raw CAT scan data and then both upper (supernatant/suspension) and lower (suspension/sediment) interfaces were determined. From the plot of solids concentration versus cylinder height, percent solid settled was calculated by dividing the area below
the lower interface by the total area. The settling rate was taken as the initial slope of the upper interface as a function of time. The CAT scan is used here to determine the settling rate because, in these alumina flocculant systems, highly cloudy supernatants are often observed which make it impossible to identify the supernatant/suspension interface by naked eye.

RESULTS AND DISCUSSION

Fixed pH Conditions:

Figures 1 and 2 show that aggregation of alumina particles without polymer is controlled by the electrostatic interaction because all sensitive measurements (percent solid settled, settling rate, and supernatant clarity) point to a maximum at pzc, at which the electrostatic repulsion between particles is minimum. Flocculation of alumina with PAA, however, is predominantly controlled by the conformation of adsorbed polymer rather than the electrostatic force. Both the percent solid settled and the settling rate (in Fig. 3) show that the stretched polymer (low Ie/Im in Fig. 4) resulted in better flocculation than the coiled polymer (high Ie/Im in Fig. 4) regardless of the electrostatic interaction (see zeta potential data in Fig. 2). Supernatant clarity (in Fig. 3) shows a slightly higher transmittance at low pH than that at high pH. By considering that the supernatant clarity is simply a measure of the supernatant regime, this trend cannot be considered to represent the overall flocculation behavior but it only indicates that less fine particles remained in supernatant at low pH. In both cases, sediment volume did not show any significant trend (Figs. 1 and 3).

Changing pH Conditions:

In order to investigate the effects of the in-situ conformational changes of the adsorbed polymer on flocculation performance, PAA was adsorbed on alumina and then the pH of the system was changed. In these systems, PAA was added to the alumina suspension that was equilibrated at the same pH as the polymer. After conditioning for 5 minutes, the pH of the suspension with the adsorbed polymer was changed. As can be seen from Fig. 5, excellent flocculation performance was observed in the case of pH 4→10, i.e., the polymer was added to the suspension at pH 4 and then pH was raised to 10 five minutes later. Its performance was even better than that under fixed high pH conditions (see pH 10 data in Fig. 3). While in the opposite case of pH 10→4 (Fig. 5), the behavior was as bad as that found at fixed pH 4 (Fig. 3). Figures 4 and 6 show the variation in the adsorbed polymer conformation under changing pH conditions. It is clear that coiled polymer, adsorbed on solid/liquid interface at low pH, stretched out when pH was raised; while the initially-stretched polymer adsorbed at high pH remained in the stretched form when the pH was lowered.

Based on the above observation and the fact that pzc of alumina = 8.3 and pKa of PAA = 4.5 [5], the variation of polymer conformation at the solid/liquid interface can be schematically represented as shown in Fig. 6. Starting from pH 4, the coiled polymer in solution (coiled because it was nonionic, no intrapolymer electrostatic repulsion) adsorbed and remained in the same coiled conformation on the positively-charged alumina surface (Fig. 6(a)). When the pH was raised to the intermediate neutral range (−5–7), ionization of PAA generated some negative charges in the polymer chain and reduced the extent of coiling. Polymer was still strongly adsorbed on the surface because of the electrostatic attraction between the negative charges on the polymer and the positive charges on the solid (Fig. 6(b)). By raising the pH above the point
of zero charge of alumina, the solid particles became negatively charged like the polymer and under these conditions the electrostatic repulsion would cause the polymer to be displaced away from the particles and to stand up on them (pH 10, Fig. 6(c)). In contrast to the above, when the suspension was first treated with the polymer at pH 10, the stretched polymer adsorbed possibly due to hydrogen bonding on the negatively-charged alumina particles (Fig. 6(d)). By reducing the pH below the pzc, alumina particles underwent charge reversal to positive values causing polymer chains to be pulled down and to be adsorbed wholly in the flat configuration (Fig. 6(e)). Further reduction of pH across pKa did not cause the polymer to coil although it lost charges (Fig. 6(f)).

In order to explain the unique, excellent flocculation behavior in the case of pH 4→10, a two-stage flocculation mechanism is proposed as follows. For the first stage of flocculation of primary particles to small flocs, the coiled polymer is better than the stretched polymer as supported by supernatant clarity data (in Fig. 3) which indicated less fine particles found in supernatant in the presence of coiled polymer. For the second stage of flocculation of small flocs to larger ones, the stretched polymer chain (which stands up on the solid surface) is better because the long chain is necessary for establishing bridges between flocs. Thus, in the case of pH 4→10, after the coiled polymer has successfully brought primary particles to form small flocs at low pH, they stretch outward to play a subsequent role in bridging small flocs to larger superflocs at high pH. This combination apparently yields the best flocculation behavior. On the other hand, in the case of pH 10→4, vertical configuration transforming to horizontal adsorption of the polymer is apparently a poor sequence for flocculation. As a result, it is significantly worse than the stretched unperturbed polymer alone (fixed pH 10, Fig. 3) and it is as bad as the coiled unperturbed polymer alone (fixed pH 4, Fig. 3). It can be already seen from this study that it is desirable to have a combination of appropriate configuration of the adsorbed polymer produced either by perturbation of the system conditions or possibly by even sequential addition of different polymers under different conditions.

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REFERENCES

Fig. 1. Various flocculation responses as a function of pH for alumina alone. (I.S. = 0.03M NaCl, S/L = 10g/200ml.)

Fig. 2. Zeta potential of alumina as a function of pH. (I.S. = 0.03M NaCl.)
Fig. 3. Various flocculation responses as a function of pH for alumina with 20ppm PAA (Polyacrylic acid). (I.S. = 0.03M NaCl, S/L = 10g/200ml.)

Fig. 4. Excimer to monomer ratio, Ie/Im, as a function of (final) pH for alumina with 20ppm PAA. (I.S. = 0.03M NaCl, S/L = 10g/200ml.)
Fig. 5. Various flocculation responses for alumina with 20ppm PAA as a function of final pH under changing pH conditions. (Hollow symbols: pH 4→10; filled symbols: pH 10→4; I.S. = 0.03M NaCl; S/L = 10g/200ml.)

(a) low pH, 4
(b) medium pH, 5~7
(c) high pH, 10

(f) low pH, 4
(e) medium pH, 5~7
(d) high pH, 10

Fig. 6. Schematic representation of the variation of polymer conformation at the solid/liquid interface under changing pH conditions.