Behavior of Colloidal Suspensions of Zinc Carbonate in the Presence of Copolymers Designed for Selective Flocculation

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The flocculation/dispersion behavior of smithsonite fines in the presence of copolymers tailor-made for selective flocculation is investigated. Three copolymers of ethylene glycol methacrylate ethylene dioxybenzoate (EGMEDB) with acrylic acid (BE-39, EGMEDB 20%; BE-44, EGMEDB 10%) and methacrylic acid (BE-48, EGMEDB 10%) are used. BE-44 and BE-48 showed entirely opposite effects on the colloidal stability of smithsonite suspensions though their chain length and copolymer compositions were identical. At high pH values an increase in the dispersion power of the copolymer is observed and this is attributed to electrosteric stabilization of the fines by the polyelectrolytes. The measured zeta potential of the colloidal particles fails to explain the different effects of copolymers on smithsonite suspensions. Fluorescence spectroscopic investigations showed these copolymers to have a hypercoiled conformational state at low pH values due to intramolecular association of the hydrophobic groups on the polymer chain. At pH 7 and above, the acrylic acid copolymer, BE-44, unfolds and exists as an extended chain. However, an increase in the catecholic group (EGMEDB) content on the polymer chain, as in the case of BE-39, increases the association of the hydrophobic groups and its conformational properties are similar to those of methacrylic acid copolymer. The copolymers which flocculated smithsonite suspensions showed the presence of hydrophobic microdomains in the adsorbed layers of copolymers. The difference in the behavior of colloidal suspensions in the presence of structurally identical copolymers, BE-44 and BE-48, is attributed to such differences in the conformational states of the copolymers. © 1991 Academic Press, Inc.

INTRODUCTION

The economic as well as the environmental problems associated with the recovery of mineral fines provide the impetus for devising efficient processes for the treatment of fine particles. Selective flocculation is a promising technique (1-3) for the beneficiation of ultrafine minerals. Selectivity is achieved through interactions between mineral surface species and specific functional groups of the reagents. The choice of proper selective flocculants is usually made on an empirical basis from commercial polymers of natural or synthetic origin. In most cases the selectivity in-

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dicated from a combination of tests with pure minerals is not confirmed by tests with mineral mixtures or raw ore (4). The traditional mechanism of molecular bridging is insufficient to explain this flocculation behavior and it is necessary to take into account the interactions of the dissolved mineral species with polymer and the resultant conformation of polymer molecules at the interface and its effect on selectivity.

There have been very few theoretical investigations of problems related to the morphology of polymeric flocculants. Recently, a simplified theoretical model of the structure of tailor-made polymeric flocculants has been proposed (5). This is based on structural parameters that can be optimized for each mineral and correspond to three different chemical

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functions that must be present on the polymers. The three parameters of interest are:

(1) a functional group that can selectively interact with the mineral particle,

(2) pH-sensitive hydrophilic groups which control solubility as well as the overall conformation of the polymer chains, and

(3) a random distribution of functional groups which assures uniform composition of the polymer chain.

In the present work, the flocculation/dispersion of smithsonite fines in the presence of copolymers tailor-made for selective flocculation is investigated. Based on the characterization of the adsorbed polymer layers and the electrokinetic properties of the particles, an attempt is made to explain the behavior of smithsonite suspensions in the presence of structurally similar copolymers. A fluorescent probe which reports the micropolarity of its environment is used to obtain information on the conformational states of the copolymers in the bulk as well as the adsorbed layer.

EXPERIMENTAL

Pure smithsonite mineral from the Lamping deposit, China, was wet-ground in a porcelain mill and the minus $15-\mu m$ fraction was used for all experiments. Copolymers and homopolymers were prepared by Professor V. Bertini and co-workers at the Organic and Macromolecular Chemistry Laboratory of the University of Calabria, Italy. The random copolymers were synthesized from homogeneous mixtures of monomers using azobisisobutyronitrile as the initiator. The procedure is described in detail elsewhere (5). The catecholic-functional-group-containing monomer is ethylene glycol methacrylate ethylene dioxybenzoate (EGMEDB) and the comonomer is either acrylic acid (AA) or methacrylic acid (MA).

The copolymers after fractionation were characterized by IR and NMR spectroscopy. MA/10 (MA/EGMEDB 10%) is a copolymer containing about 90% methacrylic acid groups while AA/20 (AA/EGMEDB 20%) and AA/ 10 (AA/EGMEDB 10%) are copolymers with about 80 and 90% acrylic acid groups, respectively, on the polymer chains. The exact copolymer compositions and degree of polymerizations are listed in Table I.

The sedimentation tests carried out were similar to those reported earlier (6). The flocculating power (F) or dispersing power (D) of each copolymer was calculated with respect to pure smithsonite in the absence of the polymer under identical experimental conditions.

The zeta potential was measured using a Rank Bros. Mark II apparatus with a flat cell and platinum electrodes.

Micropolarity tests were done with pyrenecontaining (ca. 2×10^{-7} mol/liter) polymer solutions and polymer/smithsonite suspensions using the steady-state fluorescence emission method (7). Test samples were prepared by adding aqueous saturated solutions of pyrene to polymer stock solutions or smithsonite suspensions. One-half gram of smithsonite was equilibrated for 24 h with 10 ml copolymer/ pyrene solution. The concentration of the copolymer was adjusted to 100 ppm. The suspension was centrifuged and the supernatant removed. The steady-state fluorescence emission spectra of pyrene were recorded on a Spex Fluorolog spectrofluorometer. Spectra for slurry samples were measured as emissions from the front face of the cell at an angle of 22.5° from the incident light. The two monomer emission bands of interest in the fluorescence emission spectra were at 373 nm (I_1)

TABLE I

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Polymer designation	Copolymer composition (% of EGMEDB)	Degree of polymerization
AA/10 (EGMEDB/AA)	10.10	2100
AA/20 (EGMEDB/AA)	20.20	7100
MA/10 (EGMEDB/MA)	9.93	2200
PAA (homopolymer)		2100
PMA (homopolymer)		1800

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and 384 nm (I_3) . Ratios of their intensities, I_3/I_1 , were calculated from the spectra.

Triple-distilled water or high purity water from a Millipore water system, Milli Q, was used for all the experiments. Polymer solutions and smithsonite suspensions were prepared in 10^{-3} M NaCl solutions.

RESULTS AND DISCUSSIONS

Sedimentation results obtained for tests with smithsonite suspensions containing 50 ppm copolymers or homopolymers at pH 7 and 9 are presented in Table II. Low pH solutions caused dissolution of the zinc carbonate and have therefore been avoided. As can be seen from the table, both acrylic acid and methacrylic acid homopolymers have a weak dispersing effect on smithsonite. The copolymers had the same catecholic functional groups (EGMEDB) randomly distributed on the polymer chains. The copolymers BE-44 (acrylic acid copolymer) and BE-48 (methacrylic acid copolymer) were of comparable degrees of polymerization and also had the same copolymer compositions (EGMEDB 10%). Most interestingly, their effects on the colloidal stability of smithsonite suspensions are entirely opposite those on each other. The copolymer with 10% acrylic acid has a dispersing effect while the copolymer with 10% methacrylic acid has a flocculating effect. At pH 9 the polymers in general increase the dispersing power or decrease the flocculating power.

TABLE II

Flocculation/Dispersion Behavior of Smithsonite Suspensions in the Presence of 50 ppm Homopolymer or Copolymer

Name of the polymer	Flocculating (F) or dispersing (D) power	
	pH 7.0	pH 9.0
PAA	D 8.50	D 11.50
PMA	D 36.0	
AA/10	D 63.6	D 100
AA/20	F 55.3	
MA/10	F 81.8	F 51.78



FIG. 1. The zeta potential of smithsonite as a function of concentration of the copolymer.

The choice of the specific functional group that interacts with the mineral particle was made on the basis of published data (8, 9) on the thermodynamic stability of the complexes between various known ligands and metallic ions of interest. The efficiency of catecholic groups as selectively interacting functional groups has been tested and found satisfactory for various minerals such as chalcocite, rutile, quartz, and calcite (5). In the case of smithsonite also, the specific interaction of catecholic groups with mineral particles is evident from the observed effect on the dispersing and flocculating powers of the copolymers in comparison with those of the homopolymers. The flocculating/dispersing effect of homopolymers on the mineral is not very significant as these polymers contain only the functional groups which interact mainly with the solvent. On the other hand, the copolymers behave as good flocculants or dispersants due to the specific interactions of the catecholic functional groups with the mineral particles.

Zeta-potential values obtained for smithsonite in the presence of BE-44 and BE-48 are plotted in Fig. 1 as a function of polymer concentration at pH 7. Even at a very low concentration of 10 ppm, adsorption of the copolymers on the positively charged mineral surface results in its charge reversal and suggests chemisorption of the copolymer molecules through forces that are nonelectrostatic

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in nature. Because of the dissociation of carboxylic acid groups of acrylic and methacrylic acids, the particles covered with the polymer molecules are negatively charged at neutral and alkaline pH conditions.

Figure 2 shows the effect of pH on the zeta potential of pure smithsonite and smithsonite treated with copolymers. Pure smithsonite has a positive zeta potential (+40 mV) at pH 7 and is an isoelectric point of pH 8.6. At pH 7, smithsonite treated with BE-44 is highly negative (-32 mV), whereas smithsonite treated with BE-48 is less negative (-16 mV). It has been reported (10) that flocculation by interparticle bridging is possible up to a zeta potential of 15 to 20 mV and hence, the flocculation behavior of a smithsonite suspension with BE-48 is expected. As the pH of the suspension is increased, both copolymers further increase the negative potentials of the particles and the zeta potentials become identical at pH 9 (-35 mV). However, no drastic change in the flocculation/dispersion response of colloidal suspensions is observed, suggesting that the electrokinetic properties alone cannot explain this behavior. At pH 9, the copolymertreated colloidal suspensions become more dispersing. This is attributed to electrosteric stabilization (11) which is a combination of electrostatic and steric stabilization as the co-



FIG. 2. The zeta potential of smithsonite in the presence and the absence of copolymers as a function of pH (copolymer concentration, 200 ppm).

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polymers used are basically polyelectrolytes. The dissociation of carboxylic acid groups increases the electrostatic repulsions between the particles covered with polymers and also enhances the steric stabilization due to the increased hydrophilicity of carboxyl groups at higher pH.

Since the electrokinetic properties of the particles failed to explain the conflicting features of the colloidal suspensions in the presence of two structurally identical copolymers, it became clear that the conformational characteristics of the copolymers at the interface must play an important role in these systems. To determine this role, we obtained a description of conformation of these copolymers at the interface as well as in the bulk.

Synthetic polyelectrolytes possessing pendant hydrophobic groups often show a marked pH-induced conformational transition. This behavior in bulk solutions has been extensively studied and confirmed for poly(methacrylic acid) and its copolymers (12, 13). The polymer molecule exists in a compact form at low pH and in a more expanded conformation at high pH. In aqueous solutions, the hydrophobic interactions among the methyl groups of the polymer lead to the intramolecular association of methyl groups and the resulting hydrophobic microdomains stabilize the compact polymer structure. As the pH is increased coulombic repulsions between the ionized acid groups overcome the forces which stabilize the compact form of the macromolecule and the system undergoes a conformational transition. Though poly(acrylic acid) does not show a similar behavior, some of its copolymers having pendant hydrophobic groups do exhibit pH-dependent conformational changes (12). The stability of hydrophobic microdomains and the pH at which the conformational transition occurs in such systems are functions of their copolymer compositions.

Information on the conformational states of the copolymers is obtained by monitoring incorporation of a fluorescent probe into their hydrophobic microdomains. Pyrene is a probe that prefers to be in hydrophobic environments and its spectral characteristics are dependent on its microenvironment. As the pyrene molecule experiences a change in its environment, the relative intensities of the third and first vibrational bands of the monomer emission are affected. The ratio, I_3/I_1 , is a measure of the effective polarity of the medium around the pyrene molecule.

The pyrene fluorescence parameter, I_3/I_1 , is plotted in Fig. 3 as a function of pH for solutions (200 ppm) of various copolymers. The value for pyrene in pure water is 0.56 and is unaffected by changes in pH. At lower pH (pH < 7), all three copolymers have high $I_3/$ I_1 values, indicating the presence of hydrophobic microdomains on the chains. The copolymer molecules exist in a hypercoiled conformational state due to the intramolecular association of the hydrophobic groups. As the pH is increased, the I_3/I_1 value decreases and this decrease is a consequence of the unfolding of the copolymer chain, which reduces the number of hydrophobic sites. BE-44, which has comparatively lower I_3/I_1 values, shows no hydrophobicity at pH 7 and above (the $I_3/$ I_1 values are the same as those in water). On the other hand, BE-48 is strongly hydrophobic at pH 7 and shows the presence of hydrophobic guest sites for pyrene even at pH 9. Only at pH 11 the I_3/I_1 value corresponds to that of pyrene in water. BE-39, the acrylic acid co-



FIG. 3. The characteristic fluorescence parameter, I_3/I_1 , of pyrene in the presence of copolymers in solution (200 ppm).

TABLE III

The Ratio, I_3/I_1 , of Pyrene in the Adsorbed Layers of Copolymers at the Interface (Copolymer Concentration, 100 ppm)

Copolymer	I_3/I_1 of pyrene in the adsorbed polymer layer	
	pH 7	pti 9
AA/10	0.60	0.58
MA/10	0.74	0.71
AA/20	0.70	

polymer with a higher molar ratio of catecholic groups on the chain (EGMEDB 20%), also shows conformational characteristics similar to those of BE-48. Thus, the methacrylic acid copolymer and the acrylic acid copolymer with an increased number of catecholic groups on the chain produce hydrophobic microdomains under the experimental conditions of sedimentation tests.

 I_3/I_1 values obtained for pyrene in the adsorbed layers of copolymers at the smithsonite/water interface at pH 7 and 9 are presented in Table III. BE-39 and BE-48 show high I_3/I_1 values, indicating the presence of hydrophobic domains in the adsorbed layers. In the case of BE-44, the values are very close to those of pyrene in pure water. Moreover, the observed monomer emission intensities were very weak, suggesting very low pyrene concentration in the adsorbed layers.

The results show two different conformational states for BE-44 and BE-48 at the smithsonite/water interface. BE-44 is adsorbed at the interface in an extended chain conformation while BE-48 retains its hypercoiled conformational state at the interface. The hydrophobic microdomains at the interface are proposed to enhance interparticular interactions which result in smithsonite flocculation.

CONCLUSIONS

Properties of colloidal suspensions of fine smithsonite in the presence of synthetic copolymers are examined. Sedimentation tests confirmed the presence of selective inter-

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actions of ethylene glycol methacrylate ethylene dioxybenzoate (EGMEDB) groups with smithsonite mineral. Importantly, the methacrylic acid copolymer acted as a flocculant while the acrylic acid copolymer of the same copolymer composition was a dispersant. When the catecholic group (EGMEDB) content in the acrylic acid copolymer was increased it also behaved as a flocculant. The flocculation/dispersion behavior of smithsonite suspensions in the presence of these copolymers cannot be explained on the basis of electrokinetic properties alone. Fluorescence probing showed the presence of hydrophobic microdomains at the interface when the copolymers behaved as flocculants. The interparticular association through the hydrophobic microdomains of the adsorbed polymer layers is suggested to be the reason for the flocculation of smithsonite suspensions.

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