ADSORPTION OF CHARGED AND UNCHARGED POLYACRYLAMIDES ON HEMATITE

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Abstract. Adsorption of acrylamide based homo and copolymers on hematite was investigated as a function of the nature of the polymer charge and functionality of the polymer. Effect of addition of sodium dodecylsulfonate and dodecylamine hydrochloride was also studied and was determined to result in an increase or decrease in the amount of polymer adsorbed depending on, the charge characteristics of the surfactant and the polymer, pH of the suspension, concentration of the various species and the order in which these species were added to the system. The surfactant adsorption under given conditions on the other hand, was found not to be affected by the presence of the polymer molecules. The data is analyzed to elucidate the mechanism of adsorption of polyacrylamide type polymers on hematite both with and without the surfactant species being present in the system.

Introduction

Beneficiation of mineral fines using floc flotation technique is dependent on the adsorption of the polymeric flocculant only on the desired mineral component. One of the methods to achieve selective adsorption of polymers is by controlling the interactions between the polymer and the surfactants used as collectors. These interactions not only could modify the adsorption behavior of various molecular species on the mineral particle but can also lead to precipitation resulting in higher consumption of the reagents. Precipitation can also adversely affect separation efficiency of the process. At present effective separation of clays from sylivite at Cominco in Canada, is achieved commercially through controlled interaction between the polymeric and collector species. It would, however, be necessary to understand the mechanism of such interactions before this phenomena could be successfully applied to beneficiate other complex ores. In order to study the principles which govern the effect of such interactions in mineral processing, a systematic investigation of adsorption of polyacrylamide type polymers on hematite was undertaken.

Materials

Hematite - synthetic hematite 99.2-99.5% Fe was obtained from Pfizer, Inc. and its particle size was reported to be 9% less than 5 microns. Surface area of the sample was determined, using Quanetasorb, to be 8.7 m²/g.

Polymers - C¹⁴ tagged nonionic and ionic polyacrylamides were synthesized using radiation induced heterogenous polymerization technique. A description of the synthesis and characterization techniques has been given elsewhere. (17) Anionic copolymers (PAMS) were synthesized using 2-acrylamido-2-methylpropanesulfonic acid (AMPS) a product of Lubrizol Corp. as the comonomer.

Cationic polyacrylamides (PAM) were synthesized using dimethylaminoethyl methacrylamide (DHPAA) as the comonomer. This reagent was received in the stabilized form from the Jefferson Chemical Company. The hydroquinone inhibitor was removed by passing a 50:50 aqueous solution of this reagent through an activated carbon column. The aqueous solution obtained was used immediately after the inhibitor removal stage.

Viscosity average molecular weight of the polymers was estimated to be 2.5 million for PAM (nonionic polyacrylamide) 2.1 million for PAMS (anionic polyacrylamide) and 1.9 million for PAH (cationic polyacrylamide). Surfactants - sodium dodecylsulfonate was purchased from the Aldrich Chemical Co. and was reported to be 99.9% pure. It was used without any further purification.

Dodecylamine hydrochloride was a product of Eastman Kodak Co. and was used as received.

Inorganic reagents - Fisher certified NaOH and HCl were used for pH modification. ACS reagent grade NaCl, a product of Amend Drug and Chemical Company was used for adjusting the ionic strength.

Water - Triple distilled water (TDW) of specific conductivity of 10⁻⁶ cmoh was used in this investigation.

Techniques

Adsorption tests - 0.4 g of material was equilibrated with 8 cm³ of triple distilled water or 3 x 10⁻² kmol/n NaCl solution in a screw cap glass vial for 4 hours by shaking at the desired temperature in a wrist action shaker. After 4 hours of equilibration, pH was adjusted using NaOH or HCl and the suspension was further equilibrated for 2 hours. Required amount of polymer solution was then added and the suspension was agitated for an additional 12 hours before adding the surfactant solution. After adding the surfactant, 2 hours of further agitation was required to reach the equilibrium. At each step the teflon tape covering the vial was replaced with a new piece. After equilibration, pH of the suspension was measured using a thin glass electrode attached to a digital Corning pH meter (Model 125). The contents of the vial were transferred to a centrifuge tube and were centrifuged in an IEC Model B20-A centrifuge at 15,000rpm for 10 minutes. Residual amount of the polymer and the surfactant were determined in the supernatant and adsorption densities were calculated using the respective calibration curves.

Analytical - the amount of C¹⁴ labelled polymers was determined using a Beckman Model LS 100C spectrophotometer.

Surfactant analysis was conducted using a two phase titration method (20). It was confirmed that the polymers employed in this investigation did not interfere with the surfactant analysis and vice versa.

Results and Discussion

Preliminary studies were conducted to evaluate the effect of parameters such as agitation intensity and time which formulate the equilibrium adsorption test procedures. Also, the reversibility of adsorption of the polyacrylamide type polymers on hematite was investigated since the knowledge of the extent and of the rate of desorption are helpful in understanding the mechanism of the polymer adsorption process.
Effect of Agitation on Polymer Adsorption Properties

To determine if shaking of the polymer solution during equilibrium adsorption test modifies its adsorption behavior in any way, non-equilibrium adsorption tests involving one hour of agitation were conducted. One of the polymer solutions used in the adsorption test was shaken in a wrist action shaker for twelve hours (duration of the equilibrium adsorption tests) and the other was kept on a bench top. Adsorption results obtained after one hour of agitation are presented in Table 1. Also, to determine if the two agitation conditions had resulted in any substantial changes in the molecular weight distribution of the polymers, intrinsic viscosity of the supernatants after adsorption was measured using a capillary viscometer. The estimated molecular weights are also presented in the above Table. Within the experimental error the two results are similar indicating that shaking of the polymers did not cause changes in the structure of the polymer molecules to affect their adsorption behavior on hematite.

Chromatographic Separation of Polymer during Adsorption

It has been reported in the literature that displacement of initially adsorbed low molecular weight fraction by higher molecular weight fraction could occur under certain conditions, (1,12). To determine if there was any preferential adsorption of higher molecular weight fractions during the present investigation, molecular weight of the polymer before and after the equilibrium adsorption test was determined. From the results given in Table 2 it can be observed that molecular weight estimates of the polymer before and after completion of an adsorption test did not differ from each other significantly. This indicated that either the molecular weight distribution of the polyacrylamide used was not broad enough to result in any measurable chromatographic separation during the adsorption process or, that the present system was not capable of causing any such separation.

Desorption-Reversibility of Polymer Adsorption

It is possible to obtain some knowledge of the strength of the bond formed between the polymer and the adsorbent by determining the extent of desorption or reversibility of the polymer adsorption process. Among other factors, the type of solvent has been known to affect the rate of adsorption, although the effect of desorption or the reversibility of the polymer adsorption process, however, any fit of the results obtained is broad (1,12). To determine if there was any preferential adsorption of higher molecular weight fractions during the present investigation, molecular weight of the polymer before and after the equilibrium adsorption test was determined. From the results given in Table 2 it can be observed that molecular weight estimates of the polymer before and after completion of an adsorption test did not differ from each other significantly. This indicated that either the molecular weight distribution of the polyacrylamide used was not broad enough to result in any measurable chromatographic separation during the adsorption process or, that the present system was not capable of causing any such separation.

Adsorption of Polyacrylamide Type Polymers on Hematite

In the present investigation an attempt was made to desorb the polymer from the hematite surface by decreasing the bulk concentration (by replacing part of the solution solids with pure salt solution or DIW) and shaking the suspension in a wrist action shaker for additional 12 hours. It was expected that desorption of the adsorbed polymer molecule would increase the "new" residual polymer concentration. A decrease in the residual concentration on the other hand would indicate continued adsorption. From the results presented in Table 3 it is clear that desorption of the polymers, irrespective of their ionic nature, did not occur under the present experimental conditions. Adsorption of polyacrylamide type polymers on hematite was therefore, considered to be irreversible under all these conditions.

Adsorption of Polymers on Hematite

Adsorption of acrylamide based homo - and copolymers on hematite under different pH conditions, is presented in Figs. 1 to 3. Most of the adsorption isotherms are characterized by a steep slope at low concentrations followed by a slower uptake of the polymer at higher concentrations. A plateau however, is not reached within the polymer concentration range tested. Also, it was determined that up to a certain initial polymer concentration almost all the polymer got adsorbed on the solid, and it was only at higher concentrations that a partitioning of the polymer between the surface and the bulk solution was detected. This type of adsorption behavior is characteristic of monolayer type of adsorption for non-polymeric material and can be described by the Langmuir equation. In the case of polymer adsorption, however, any fit of the data to the Langmuir equation is probably fortuitous since, polymer molecules can assume different conformations and exhibit varying degree of attachment to the surface as adsorption progresses. Moreover, polymer adsorption is generally an irreversible process and lateral interactions between adsorbed polymer molecules cannot be ruled out thus, violating two of the basic assumptions involved in the derivation of the Langmuir equation.

A number of investigators (2-3,8,10-11,21) have reported polymer adsorption results that have been interpreted on the basis of their apparent agreement with the Langmuir equation. In some cases this has been used to estimate the saturation adsorption and to calculate adsorption rate constants which in turn have been used to develop polymer adsorption mechanisms (10).

According to the above discussion any information obtained on the basis of Langmuir equation should not be considered as anymore meaningful than from the use of an empirical equation and should be of limited use only.

Adsorption isotherms generated in the present study were similar in shape to the Langmuir isotherm but they did not satisfy the criterion of

of a linear C/A versus C relation. In fact on the basis of large initial slope these isotherms may be classified as "high affinity" type, meaning that the affinity of the solute for the substrate is high even at very low concentrations (4–6). The region corresponding to the initial rise where interactions between adsorbed chains and segments within a chain are expected to be minimal is the most informative region. This region, however, is often inaccessible because of almost a vertical rise in the isotherms in the lower concentration range and due to the difficulties encountered in getting reliable measurements of the polymer amount in very dilute solutions.

**Effect of pH:** Modifications in variables such as pH and ionic strength can result in (i) alterations in surface charge characteristics of hematite since $H^+$ and $OH^-$ are potential determining ions and (ii) changes in polymer structure due to hydrolysis especially under basic pH conditions.

Hydrolysis of polyacrylamide-type polymers containing amide (~CONH$_2$) groups has been reported to occur under both acidic and basic pH conditions (9, 16, 19, 22). Since hydrolysis of amide groups by acids has been reported to be significant only at temperatures higher than 100°C, it can be assumed that under present experimental conditions of 25°C polymer structure did not change in the acidic pH range. Kinetics of hydrolysis of polyacrylamides under basic pH conditions are fast enough to result in a conversion of significant number of ~CONH$_2$ groups to ~COOH groups in the following manner (13).

$$\text{RCONH}_2 + \text{OH}^- \rightarrow \text{RCOOH} + \text{NH}_3$$

Depending on the pH which governs the dissociation of ~COOH groups, a nonionic polymer such as polyacrylamide can behave as an anionic polymer. It is obvious that conformation of the polymer molecule will vary with the pH. Polymer conformation will also be influenced by the changes in the ionic strength (18). This type of behavior in general, is typical of all polyacrylamide-type polymers. The degree of hydrolysis and overall charge characteristics, however, will also depend on the nature of the charge and the amount of functional groups present on a particular copolymer and can have a major influence on the adsorption process.

One common feature of the adsorption of polyacrylamide type polymers on hematite is that at higher concentrations of polymer, adsorption is lower under basic pH conditions than at acidic or natural pH (see Figs. 1–3). This may be attributed to the polymer hydrolysis resulting in the formation of carboxylic acid functional groups in all three types of polymers. For example, in the present case under the basic pH conditions, hematite is negatively charged and introduction of any negative charges on the polymer backbone will result in an increase in the electrostatic repulsion thus, reducing the polymer adsorption.

Adsorption at higher concentrations under natural and acidic pH conditions, was found to be very similar for PAM and PAH but for PAH it was higher at acidic pH than that at natural pH. It has been reported that the principal mechanism for the adsorption of polyacrylamide type polymers on oxide minerals is through hydrogen bonding, the hydrogen bonding between surface oxygen atoms and oxygen or nitrogen of the polymer (14). In addition, for polyacrylamides with charged functional groups, electrostatic interaction also needs to be considered. For the polymers studied here, the degree of sulfonate and amine group substitution in the polyacrylamide backbone was only about 0.1 mol percent and it is possible that the small effect to a large extent, was masked by the large number of hydrogen bond forming ~CONH$_2$ groups. Based on charge considerations it is expected that at acidic pH values, where hematite is significantly positively charged, adsorption of the anionic polymer should be more than in the basic or natural pH and should be lowest for cationic polyacrylamide (PAM). The data obtained for PAMS adsorption followed the expected trend whereas for PAH the adsorption was similar both at acidic and at natural pH. The similarity in the adsorption behavior of PAM under above pH conditions may be attributed to the masking of electrostatic interactions by hydrogen bonding. Under the basic pH conditions when the solid and the polymer are oppositely charged, the adsorption is expected to be higher than under acidic or natural pH conditions; hydrolysis of the polymer however, could have caused negative charges on the backbone which along with formation of neutral amine molecules can result in lower adsorption values. Besides changes in the adsorption due to modifications in charge characteristics of hematite and polymers; conformation of the polymers which determines the surface coverage at a given concentration can also play a major role in the adsorption process.

For example, as a result of hydrolysis under basic pH conditions polyacrylamide acquires negative charges which can cause swelling of the polymer coil and therefore, an increase in the area per molecule. This increase in the surface coverage per molecule can lead to decreased adsorption density as has been observed for all the three polymers under basic pH conditions.

**Effect of Ionic Strength:** Ionic strength changes can affect polymer adsorption through (i) modification in the solvent power of the medium and (ii) increased competition between counter ions and polymer segments for adsorption at the solid/liquid interface. If polymer is more soluble at higher ionic strength a decrease in adsorption would be expected. The increased competition between added ionic species and polymer molecules would also lead to reduced adsorption. A third factor which needs to be considered in the case of polyelectrolytes is the possible modifications in polymer conformation as a result of the added indifferent electrolyte. Electrostatic repulsion between charged functional groups will be minimal in the presence of salt permitting increased coiling of the polymer chain. This should lead to a reduction in area per molecule and thereby, in increased adsorption.

Adsorption of PAM (nonionic polyacrylamide) on hematite as a function of the residual polymer amount at different concentrations of NaCl is plotted in Fig. 4. It is clear from the data presented that there is no significant effect of varying the salt concentration from 0 to 5.1 kmol/m$^3$ NaCl on the adsorption of PAM on
hematite. Adsorption of PAMS (anionic polyacrylamide—a polyelectrolyte) on hematite was determined to be higher at higher salt concentration (5 x 10−2 kmol/l NaCl) (see Fig. 5). This indicates that under the present experimental conditions changes in conformation of polyelectrolytes influence the adsorption of the polymers more than the other factors mentioned earlier.

Effect of Temperature: Variations in temperature can affect polymer adsorption through changes in (i) solvent power of the medium, and (ii) adsorption of the solvent molecules competing with the polymer. Both factors have similar roles in nonfunctional solute adsorption except that in the case of polymers entropic effects due to (ii) can be of considerable magnitude.

Adsorption of nonionic polyacrylamide on hematite at 25°, 45° and 75°C is plotted in Fig. 6. Similar adsorption behavior was observed at 25° C and 45°C however, at 75°C a trend towards higher adsorption was indicated. This type of adsorption behavior suggests significant influence of entropic effects in the adsorption of polyacrylamide on hematite.

Effect of Functional Groups: Effect of sulfonate or amine functional groups in the polyacrylamide chain on adsorption is illustrated in Fig. 7. It should be noted that the anionic (PAMS) and cationic (PAM) polymers contain 3 mol percent of the respective functional groups. It was determined that adsorption of PAMS on hematite at pH 7 was higher than that of the nonionic PAM or the cationic PAM polymer. This probably can be attributed to the opposite nature of the charges on PAMS and the hematite surface under the given experimental conditions.

Effect of Addition of Surfactant on the Adsorption of Anionic Polyacrylamide (PAMS) on Hematite:

Sodium Dodecylsulfonate—PAMS—Hematite:
Effect of addition of sodium dodecylsulfonate on the adsorption of PAMS on hematite under natural pH conditions, as a function of order of reagent addition is illustrated in Fig. 8.

When sulfonate was added first (S+P) or together with the polymer (FPS) adsorption of the polymer was found to be reduced to the same degree from that of the polymer alone. In the former case, the surface was contacted with the sulfonate first, leaving lesser uncovered area available for polymer adsorption and therefore, causing a reduction in the adsorption. In the latter case even though both sulfonate and polymer were added simultaneously it is possible that because of bulky nature of the polymer molecules their mobility and therefore, diffusion to the solid/liquid interfacial region was slower than that of the sulfonate molecules and as a result, polymer adsorption essentially took place on a surface which had sulfonate molecules adsorbed on it. This is comparable to the situation discussed above (S+P) and the observed reduction in polymer adsorption therefore, is not unexpected.

Addition of polymer followed by that of sulfonate (P+5) also resulted in reduced polymer adsorption as compared to that when no sulfonate was present in the system. The decrease was more significant in higher polymer concentration range. This interesting effect can be explained as follows:

Adsorption of the polyacrylamide type polymers, as discussed earlier, can be considered to be irreversible. By irreversibility of polymer adsorption it is implied that even though the polymer molecule as a whole is adsorbed irreversibly the individual segments in contact with the surface may be in a reversible equilibrium state. And since the number of segments in contact with the surface is normally very large, the reversible nature of particular segment may not lead to polymer desorption. The presence of surfactant can, however, affect this situation under conditions where the surfactant adsorption on the surface and the kinetics of it are high, i.e., the kinetics of sulfonate adsorption is faster than the polymer segmental adsorption/desorption kinetics. Surfactant molecules under such conditions can replace polymer segments consequentively leading to the desorption of the polymer molecule. This effect can be even more pronounced at high polymer adsorption density since, under these conditions the number of segments per polymer molecule in contact with the surface can be expected to be lower than those at low adsorption density. This clearly shows why desorption of the PAMS was higher when larger amount of polymer was present in the system as opposed to that at low polymer concentrations.

Dodecylamine Hydrochloride—PAMS—Hematite: An increase in polymer (PAMS) adsorption as shown in Fig. 9, was obtained in the presence of dodecylamine hydrochloride under natural pH conditions. Since precipitation-redissolution phenomena was observed in this system, the increase in polymer adsorption could also have occurred due to the precipitation in addition to that caused by interaction between the oppositely charged species. These results have been discussed elsewhere [17,23].

Effect of Polymer Addition on Sulfonate Adsorption on Hematite

Sulfonate adsorption on hematite under natural pH conditions was not affected significantly irrespective of concentration or the order of polymer addition (see Fig. 10). This indicated that the addition of the polymer to a solution containing particles with sulfonate already adsorbed on them did not cause desorption of the sulfonate. These results also showed that due to the nature of the conformation of adsorbed polymer molecules enough surface area was accessible to the sulfonate adsorption as illustrated in Fig. 11.

In summary, the above discussion clearly shows that if the polymer and surfactant species are similarly charged then, depending on the order of the reagent addition, a significant reduction in polymer adsorption could occur. The adsorption of the surfactant however, remains unaffected possibly as a result of access to the uncovered sites due to the structure of the adsorbed polymer molecules.

Conclusions

Based on the above discussion, the following conclusions regarding adsorption of
polyacrylamide type polymers or hematite can be reached. The adsorption of the ionic and nonionic polyacrylamides on hematite is governed primarily by hydrogen bonding between the surface oxygen and the oxygen or nitrogen on the polymer. Electrostatic interaction between the polymer functional groups and the hematite surface play only a secondary role in the present system because of relatively low degree of functionality of the copolymers.

The relatively small effect of salt addition on the adsorption of PAMS - an anionic polyacrylamide on hematite and almost negligible effect of ionic strength on the adsorption of PAM on hematite indicates that either the changes in parameters such as solvent power of the medium and conformation of the polymer are not significant or their effects are mutually cancelled out.

The effect of temperature on the adsorption of polyacrylamide on hematite was not found to be very significant leading to the conclusion that entropic rather than enthalpic changes play a major role in the adsorption process.

Desorption tests indicated that, irrespective of the polymer charge, its adsorption on hematite can be considered to be irreversible under the present experimental conditions.

Polymer adsorption was determined to be affected significantly depending on the nature of the surfactant charge, amount of the surfactant added and the order in which the polymer and the surfactant were added to the system. The reduction in polymer adsorption in the presence of surfactant is attributed to the unavailability of uncovered area for the polymer adsorption. The increase in the polymer adsorption on the other hand, in the presence of oppositely charged surfactant, is probably due to electrostatic charge attraction between the polymer and the surfactant molecules.

The surfactant adsorption, irrespective of the polymer addition, was not affected significantly. This is attributed to the factor that enough surface area was accessible for surfactant adsorption even after the surface was covered with the polymer molecules.

It can be expected that in the presence of polymer molecules, the surface wettability, irrespective of the order of reagent addition will be controlled by the hydrophilic nature of the polymer. One can, for example, expect that the presence of any of the polymers studied, will depress the flocculation of hematite using sulfonate as the collector in the acidic pH range. The influence of PAMS-sulfonate interaction on the flocculation behavior of hematite on the other hand, is difficult to analyze because of possible opposite effects of the changes in the polymer conformation and the polymer adsorption in the presence of the sulfonate molecules. Hydrophobic interaction between the polymer and the surfactant molecules will result in a tendency towards coiling of the polymer which should enhance the flocculation by bridging (7), but at the same time polymer adsorption could be reduced either as a result of reduction in the uncovered surface area available for polymer adsorption or by desorption of the adsorbed polymer molecules as discussed earlier. In the present case the second factor may control the overall behavior since due to the low degree of copolymerization (3 mol percent of the functional groups) the change occurring in the conformation of the polymer molecules would be of lesser degree than what maybe required to be of significant in affecting the flocculation process.

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References


TABLE 1
Effect of mechanical agitation on adsorption of Nonionic Polyacrylamide (PAM) on Hematite under natural pH conditions.

<table>
<thead>
<tr>
<th>Initial Polymer Conc.</th>
<th>Agitation</th>
<th>Adsorption Density</th>
<th>M. Wt. of Polymer in Supernatant</th>
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<td>2000 mg/g</td>
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<td>17.4 mg/g</td>
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<td>2000 mg/g</td>
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<td>250 mg/g</td>
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TABLE 2
Chromatographic Separation of Nonionic Polyacrylamide (PAM) During Adsorption on Hematite.

PAM/Hematite
NaCl Conc. = 3 x 10^-2 kmol/m^3
pH = 3.5

Molecular Wt. before adsorption = 2.36 x 10^6
Molecular Wt. after adsorption = 2.22 x 10^6

TABLE 3
Desorption of Polymers
Polymer/Hematita
NaCl Conc. = 3 x 10^-2 kmol/m^3
Room Temperature = 25°C
Adsorption Time = 12 Hrs.
'Desorption Time' = 12 Hrs.
Initial Polymer Conc. = 1000 mg/kg

<table>
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<tr>
<th>Polymer</th>
<th>pH</th>
<th>Residual Polymer Conc. after 12 Hrs. of Adsorption mg/kg</th>
<th>Residual Polymer Conc. after 12 Hrs. of 'Desorption,' mg/kg Estimated</th>
<th>Experimental</th>
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<td>8.78</td>
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Figure 1. Equilibrium Adsorption Isotherm of Nonionic Polyacrylamide (PAM) on Hematite at Three Different pH Values.

Figure 2. Equilibrium Adsorption Isotherm of Anionic Polyacrylamide (PAMS) on Hematite at Three Different pH Values.
Figure 3. Equilibrium Adsorption Isotherm of Cationic Polyacrylamide (PAM) on Hematite at Three Different pH Values.

Figure 4. Effect of Salt Addition on Nonionic Polyacrylamide (PAM) Adsorption on Hematite Under Natural pH Conditions.
Figure 5. Effect of Salt Addition on Anionic Polyacrylamide (PAMS) Adsorption on Hematite Under Natural pH Conditions.

Figure 6. Effect of Temperature on Adsorption of Nonionic Polyacrylamide (PAM) on Hematite.
Figure 7. Effect of Various Functional Groups on Polyacrylamide-Adsorption on Hematite.

Figure 8. Effect of Order of Addition of Sodium Dodecylsulfonate on Adsorption of Anionic Polyacrylamide (PAMS) on Hematite Under Natural pH Conditions.
Figure 9. Effect of Addition of Dodecylamine Hydrochloride (Added First) on Adsorption of Anionic Polyacrylamide (PAMS) on Hematite Under Natural pH Conditions.

Figure 10. Effect of Order of Addition of Anionic Polyacrylamide (PAMS) on the Adsorption of Sodium Dodecylsulfonate on Hematite Under Natural pH Conditions.

Figure 11. Adsorption of Sodium Dodecylsulfonate Molecules on a Surface already Coated with the Nonionic Polyacrylamide (PAM).