A STUDY OF POLYMER/SURFACTANT INTERACTION AT THE MINERAL/SOLUTION INTERFACE

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ABSTRACT

Interaction between a cationic polymer (acrylamide,methacrylamido propyltrimethylammonium chloride copolymer) and cationic and anionic surfactants (dodecylammonium chloride and dodecylsulfonate) on quartz is studied using adsorption, electrokinetic and flotation techniques. At pH 6.5, the polymer depresses amine flotation of quartz but without depressing amine adsorption on it. Electrokinetic experiments yielded zeta-potential values characteristic of the polymer as long as polymer is adsorbed irrespective of both amine adsorption and original potential of quartz.

Around pH 10 where amine is most surface active, polymer adsorption from a solution containing both the polymer and amine is negligible. Furthermore, at this pH any preadsorbed polymer is displaced from the surface upon subsequent addition of amine.

A molecular model is proposed for the polymer—surfactant layer on the quartz particle with the massive polymer species masking the adsorbed amine, to account for the hydrophilic characteristics of the particle. In accord with this model, quartz is activated by the adsorbed cationic polymer for flotation by the anionic sulfonate.

INTRODUCTION

In many industrial processes, such as flotation and enhanced oil recovery, polymers are now used along with surfactants. Flocculation followed by flotation of iron ore is a recent example of such a process [1, 2]. In addition, nowadays polymers very often are added either to aid filtration, to clean effluents or as grinding aids. These reagents can markedly affect other downstream processes such as flotation [3–10]. In such operations, selectivity can be affected through interactions between polymer and surfactant in the bulk or at the solid/liquid or liquid/gas interface. At the solid/liquid interface, not only the amount of each reagent adsorbed but also the manner (orientation) of adsorption has an important effect on the process. However, to the authors' knowledge, no precise information on these factors exists in the literature, although there have been a few reports on interactions in bulk solutions [11–24]. Recent work [11] on such solution properties as relative viscosity, conductivity, and surface tension with various nonionic, anionic and cationic polyacrylamides and sodium dodecylsulfonate or dodecylamine
hydrochloride showed measurable interaction effects but only in the case of the oppositely charged polymer and surfactant systems. Also depending on the ionic natures of the polymer and surfactant they can precipitate, and in some cases the precipitate thus formed can dissolve upon increasing the surfactant concentration. This redissolution was considered to occur through complexation. It was noted that the observed effects can affect the adsorption behavior of different species at the solid/liquid interface and thereby influence processes such as flocculation, flotation and micellar flooding.

In this work, interactions of a cationic polymer, and anionic and cationic surfactants at the quartz/aqueous solution interface are examined using adsorption and electrokinetic techniques together with flotation. Clearly seen is the power of the use of the electrokinetic technique in conjunction with other techniques in deriving information on the possible arrangement of adsorbed species at the interface.

EXPERIMENTAL

Materials

High purity crystalline quartz (Arkansas) purchased from Ward’s Natural Sciences Establishment was crushed and ground in a stainless-steel ball mill; the $-20\mu m$ fraction was cleaned by boiling in HCl solution and repeated rinsing with water, freeze-dried and stored till use. The average particle size as measured using a Fisher subsieve sizer was $6\mu m$. For flotation experiments, $-590$ to $+210\mu m$ fraction of quartz was used after cleaning with a magnetic separator and leaching with warm nitric acid.

The cationic copolymer PAMA used in this study was prepared from $^{14}C$-labeled acrylamide and methacrylamidopropytrimethylammonium chloride by irradiating them in acetone-water solution using $^{60}Co$ source at 6 krad s$^{-1}$ for 18 h. Unreacted monomer was removed by repeated washing with acetone and the sample was freeze-dried and stored till use. The molecular weight was estimated from intrinsic-viscosity data to be $0.8 \times 10^6$.

Dodecylammonium chloride and sodium dodecylsulfonate purchased from Eastman Kodak Co. and Aldrich Chemical Co., respectively, were used as collectors without further purification.

Procedure

For adsorption tests, $2 g$ of the $-20\mu m$ quartz were conditioned first for two hours on a wrist-action shaker in $10 ml$ of NaCl solution adjusted to the desired pH, and then for another six hours after adding $10 ml$ of the polymer solution. (Equilibrium was attained within this interval at all pH levels, Fig. 1). The pH was then measured, the sample was centrifuged and the residual polymer concentration was determined using a liquid scintillation counter. Adsorption of amine was determined by titration against a known concentra-
tion of sodium dodecylsulfonate using a two-phase technique [25]. To determine the extent of polymer desorption, after centrifugation 10 ml of the supernatant were replaced with 10 ml of NaCl solution, and the sample agitated for another six hours.

For zeta-potential measurements, 0.02 g of quartz was conditioned in 40 ml of total solution in the same manner as in the adsorption experiments. Polymer-adsorption data in these cases was simultaneously determined by centrifuging the samples after zeta-potential measurements and analyzing the supernatant for residual polymer concentrations.

For flotation, 1 g of the −590 to +210-μm quartz was conditioned with the necessary reagents on a tumbler at 16 rpm for 10 min and then floated in a modified Hallimond tube for 15 s using nitrogen at a gas flow rate of 36 cm³/min⁻¹ [3].

RESULTS AND DISCUSSION

PAMA adsorption

The extent of adsorption on PAMA on quartz was first determined under natural pH conditions (pH 6.3 ± 0.6). Figure 2 shows measurable adsorption at concentrations as low as 1 mg per kg. Adsorption appears to reach a plateau at about 500 mg per kg. The results of dilution tests show that adsorption of PAMA is essentially irreversible by dilution under the conditions used here. Furthermore, it is seen that, while equilibrium was possibly attained within the six hours of conditioning below 100 mg per kg, above this concentration adsorption continues to take place even after dilution.
Fig. 2. Adsorption isotherm of PAMA on quartz under natural pH conditions.

Quartz flotation in amine and PAMA solutions

The effect of polymer addition on quartz flotation using amine was tested at two different amine levels. Results given in Fig. 3 show that complete depression of flotation is achieved at 1 mg per kg polymer. In order to determine whether or not this depression of hydrophobicity is due to reduced adsorption of amine (the traditional explanation), adsorption of amine on quartz was determined in the presence and absence of the polymer. The results are tabulated inside Fig. 3. Most interestingly, the presence of the polymer resulted in decreased flotation without any significant effect on the surfactant adsorption. We have made similar observations for the calcite-oleate system using starch as depressant [26].

Fig. 3. Depression of flotation of quartz using dodecylamine by the cationic polymer PAMA at natural pH. Adsorption of amine in the presence and absence of the polymer is shown in the inset.
Zeta potential in amine solutions

To obtain additional information about the nature of the mineral surface under these conditions, the zeta potential of the −20-μm quartz particles was determined together with polymer adsorption, at different polymer and amine concentrations, as a function of pH. Ionic strength was maintained at $3 \times 10^{-2}$ kmol m$^{-3}$ using NaCl for all tests. Figure 4 shows the pH dependence of quartz zeta potential in $3 \times 10^{-2}$ kmol m$^{-3}$ NaCl and $5 \times 10^{-4}$ kmol m$^{-3}$ amine plus $3 \times 10^{-2}$ kmol m$^{-3}$ NaCl solutions. An isoelectric point of about pH 3.0 is obtained for quartz, in agreement with literature values which vary from 1 to 3.7 [27]. The presence of amine is found to have a significant effect on zeta potential with charge reversal in a narrow pH region around 10. Notably, this is also the pH region in which the highest quartz flotation is usually obtained [28]. This phenomenon has been explained by taking into account the formation of the highly surface-active amine—aminium complex in this pH range (see Fig. 5). At higher pH values most of the amine is in the neutral form which does not lend itself to adsorption [29].

Fig. 4. Zeta potential of quartz in water and in dodecylamine solution as a function of pH, both under constant ionic-strength conditions.
Zeta potential in polymer solutions and polymer adsorption

Zeta potential of quartz particles at 0.1, 0.4, 0.8, and 2.5 mg per kg polymer addition is given in Figs. 6–9 as a function of pH together with adsorption at the three higher dosages. Even at only 0.1 mg per kg polymer addition, the zeta potential is altered markedly at all pH values above 2, and at
0.4 mg per kg, it reaches a value of about +12 mV which shows very little variation with pH and further addition of polymer. On the other hand, polymer adsorption increases with both pH and polymer dosage. The increase of adsorption with pH suggests that electrostatic forces play a significant but not exclusive role in the adsorption of this polymer on the quartz surface. Electrostatic force is not considered to be the exclusive controlling parameter because, even at the isoelectric point of quartz, there is a measurable effect of polymer adsorption on zeta potential even though the adsorption

Fig. 7. Zeta potential of quartz and polymer adsorption on it as a function of pH at 0.4 mg per kg PAMA dosage under constant ionic-strength conditions.

Fig. 8. Zeta potential of quartz and polymer adsorption on it as a function of pH at 0.8 mg per kg PAMA dosage under constant ionic-strength conditions.
is minimal. This drastic effect on zeta potential could be due to both charge neutralization and shift in the shear plane. It is suggested that, at 0.4 mg per kg and higher additions, polymer has coated the quartz surface sufficiently for the results to represent solely the zeta potential of the adsorbed polymer layer (essentially independent of the charge of the quartz substrate).

\[ I = 3 \times 10^{-2} \text{kmol/m}^3 \text{NaCl} \]
\[ T = 25 + 1^\circ \text{C} \]
\[ \text{S/L} = 0.005\% \]
\[ \text{CONC. POLYMER} = 2.5 \text{mg/kg} \]

Fig. 9. Zeta potential of quartz and polymer adsorption on it as a function of pH at 2.5 mg per kg PAMA dosage under constant ionic-strength conditions.

**Zeta potential and polymer adsorption in polymer—amine solutions**

Figure 10 gives the zeta potential of quartz particles in solutions containing both the polymer and the amine, together with polymer adsorption, as a function of pH. In this series of experiments, a premixed solution of polymer and amine adjusted to the desired pH was added to a preconditioned sample of quartz suspension. Experiments were done to determine also the effect of order of addition of polymer and amine; the results from these tests are given in Table 1.

It is noted from Fig. 10 that in the neutral and acidic pH regions, polymer adsorption is significant, but in the alkaline pH region the adsorption of PAMA is prevented by the amine, which is most surface active in this pH range. Most interestingly, the zeta-potential value obtained in the pH region where polymer adsorbs is similar to the values obtained in solutions containing polymer alone. It is to be noted that amine also adsorbs under the neutral pH condition (see the table in Fig. 3). Thus, even though amine also does adsorb, the zeta potential measured is that of the polymer. Noting that flotation of quartz was totally depressed under these conditions, these results clearly suggest that the quartz particles with amine adsorbed on them are coated by the polymer. The massive polymer species can be considered to mask the amine on the particles, generating a hydrophilic surface. The suggested model is shown schematically in Fig. 11a.
Fig. 10. Zeta potential of quartz and polymer adsorption as a function of pH in solutions containing both the polymer (2.5 mg per kg) and dodecylamine (5 × 10⁻⁴ kmol m⁻¹).

TABLE 1
Comparison of zeta potential and adsorption in quartz/amine, quartz/PAMA, and quartz/amine/PAMA systems

<table>
<thead>
<tr>
<th>pH</th>
<th>Zeta</th>
<th>( r_{PAMA} )</th>
<th>( r_{Amine} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz/amine</td>
<td>6</td>
<td>-6.5</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>+16.5</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>+26.8</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>+26</td>
<td>—</td>
</tr>
<tr>
<td>Quartz/PAMA</td>
<td>6</td>
<td>+10</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>+9.5</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>+10</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>+10</td>
<td>1.95</td>
</tr>
<tr>
<td>Quartz/amine/PAMA (amine and PAMA added simultaneously)</td>
<td>6</td>
<td>+9</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>+25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>+27</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>+23</td>
<td>0</td>
</tr>
<tr>
<td>Quartz/amine/PAMA (polymer added first)</td>
<td>6</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>9.6</td>
<td>+17.5</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10.2</td>
<td>—</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>10.4</td>
<td>+21.5</td>
<td>0</td>
</tr>
</tbody>
</table>
Noting that the polymer PAMA did adsorb on quartz in alkaline solutions but did not when amine was present, tests were conducted to determine whether the amine can possibly cause desorption of the polymer around pH 10 where amine is most surface active. These experiments entailed conditioning of the mineral first with the polymer and then with amine. If polymer adsorption is irreversible, when amine is added after the polymer has already adsorbed, the zeta potential should be about +10 mV, the value obtained in the absence of amine. However, the zeta potential results at pH 9.6 and 10.4 are +17.5 and +21.5 mV, respectively (Table 1). Also, the polymer adsorption in both tests is zero. These zeta-potential values are similar to the values obtained with amine alone (some difference results from the extreme sensitivity of the zeta potential of quartz in amine solutions around pH 10). Since

Fig. 11. (a) Schematic representation of the cationic polymer PAMA and dodecylamine co-adsorption on quartz particles resulting in their flotation depression. (b) Schematic representation of quartz/dodecylsulfonate system. (c) Schematic representation of the cationic polymer PAMA and dodecylsulfonate co-adsorption on quartz particles resulting in their flotation activation.
Electrokinetic experiments conducted together with adsorption proved to be a powerful method of studying the nature of polymer—surfactant interactions that are responsible for the observed effects on particle wettability of these reagents. While the presence of amine alone produced increasing changes in the zeta potential with increasing pH, with maximum effect around pH 10, polymer addition alone even at a dosage as low as 0.4 mg per kg yielded a constant value of about +10 mV (possibly characteristic of the quartz surface masked by polymer) in the complete pH range. Even when the polymer and the surfactant were present together in the system, a zeta potential near +10 mV was obtained in the acidic and neutral pH regions where polymer adsorption had occurred. Noting that the amine adsorption under these conditions did not make the quartz particles hydrophobic and that it did not influence the zeta potential, a model is proposed where the massive polymer species adsorb on the amine-coated particles masking the adsorbed amine. This model is supported by the activation by PAMA observed for sulfonate adsorption on quartz particles and their flotation.

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these “polymer first — amine second” tests yielded a value for zeta potential close to that obtained when both reagents were added simultaneously, it is possible that in this case the polymer molecule was displaced by the competing amine—aminium complex. This suggests that polymer desorption can be induced by appropriate competing species. Similar desorption of hydrolyzed polyacrylamide from clay has been achieved recently using phosphates [30]. Whereas desorption was not induced by mere dilution (Fig. 1), in this case desorption is possible since sites vacated by individual segments can now be occupied by the competing species resulting eventually in the desorption of the entire polymer molecule.

On the basis of the model proposed here, it should be possible to float quartz using an anionic surfactant even though normally quartz will not respond to an anionic surfactant (Fig. 11b,c). Flotation experiments conducted with dodecylsulfonate (together with PAMA) showed that quartz can indeed be floated completely with this reagent combination (Fig. 12) [4]. Adsorption experiments showed quartz to extract the sulfonate from the solution but only in the presence of PAMA (see table in Fig. 12). In addition to interactions of the polymer and the surfactant on the particle surface, interactions in the bulk liquid [11] also can contribute to the activation of quartz by PAMA for flotation using the anionic surfactant, but they are not considered to be primarily responsible for the observed flotation.

![Graph](image)

**Fig. 12.** Activation of flotation of quartz using dodecylsulfonate by the cationic polymer PAMA at natural pH. Adsorption of sulfonate in the presence and absence of the polymer is shown in the inset.

**Concluding remarks**

Flotation of quartz by amine is depressed by the cationic polymer PAMA, while the amine adsorption itself is not affected.
Electrokinetic experiments conducted together with adsorption proved to be a powerful method of studying the nature of polymer—surfactant interactions that are responsible for the observed effects on particle wettability of these reagents. While the presence of amine alone produced increasing changes in the zeta potential with increasing pH, with maximum effect around pH 10, polymer addition alone even at a dosage as low as 0.4 mg per kg yielded a constant value of about +10 mV (possibly characteristic of the quartz surface masked by polymer) in the complete pH range. Even when the polymer and the surfactant were present together in the system, a zeta potential near +10 mV was obtained in the acidic and neutral pH regions where polymer adsorption had occurred. Noting that the amine adsorption under these conditions did not make the quartz particles hydrophobic and that it did not influence the zeta potential, a model is proposed where the massive polymer species adsorb on the amine-coated particles masking the adsorbed amine. This model is supported by the activation by PAMA observed for sulfonate adsorption on quartz particles and their flotation.

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