EFFICACY OF HYDROXYAPATITE DISPERSANTS IN THE PRESENCE OF SURFACANTS

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The dispersion of hydroxyapatite, Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}OH, HAP, in aqueous systems in the presence of variety of polymers of different composition and ionic charge has been investigated. The dispersion data show that polymer effectiveness as HAP dispersant strongly depends upon polymer architecture. It has been found that anionic, non-ionic, amphoteric, and cationic surfactants are ineffective as HAP dispersants. Additionally, it has also been observed that cationic surfactant and cationic polymer exhibit antagonistic effect on the performance of anionic polymeric dispersants.

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INTRODUCTION

Water used in many industrial processes contains a variety of soluble and insoluble species such as dissolved minerals, natural organic matter, suspended matter, domestic, and industrial wastes.\textsuperscript{1} If the water containing these impurities is used without any treatment, in many cases it leads to the deposition of unwanted deposits on equipment surfaces. The deposits commonly encountered fall into four categories: a) mineral salts, b) corrosion products, c) suspended matter i.e., clay, silt, calcium carbonate, calcium phosphate, and d) microbiological mass.

The natural organic matter normally encountered includes fulvic acid, tannic acid, polysaccharides, etc. These organic acids not only complex with other chemical species present in water but also exhibit marked influence on the stability and removal of inorganic particles. It has been reported that the presence of trace levels of fulvic acid and tannic acid inhibit the precipitation of sparingly salts such as calcium phosphate\textsuperscript{1}, calcium carbonate\textsuperscript{2,3}, and calcium sulfate\textsuperscript{3}. Additionally, in the case of calcium carbonate these organic acids are also known to change the crystal morphology\textsuperscript{2}.

The suspended matter typically present in feed water includes clay, minerals, metal oxides, metal carbonates, algae, bacteria, and viruses. The solid concentration usually ranges from <5 mg/L to >300 mg/L, and in some cases, especially during floods, may go up to >500,000 mg/L\textsuperscript{2}. The metal oxides, phosphate, and carbonates present in water may include corrosion products (i.e., Fe\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{3}O\textsubscript{4}, SiO\textsubscript{2}, ZnO, Al\textsubscript{2}O\textsubscript{3}, MgO, calcium phosphate, and calcium carbonate. If not properly treated, deposition of suspended matter on equipment surfaces leads to decreased heat transfer, increased operational costs, and in some cases premature replacement of expensive equipment.

In industrial water systems calcium phosphate scale results from the presence of orthophosphate in the circulating water. The main source for phosphate in the circulating water is its use as a chemical treatment to prevent corrosion on low carbon steel water pipes and heat exchanger equipment. To prevent calcium phosphate scale formation, the use of calcium phosphate inhibitor is required when using this type of corrosion control.\textsuperscript{1} It has been reported that initially formed phase in circulating water is amorphous calcium phosphate, ACP. It has been suggested that if ACP is allowed to remain in contact with the solution, it transforms to the thermodynamically stable hydroxyapatite, HAP, Ca\textsubscript{5}(PO\textsubscript{4})\textsubscript{3}OH. In high temperature application such as boiler HAP is formed on the boiler surface. HAP is also the major inorganic component of teeth. In addition, calcium phosphates are widely produced in industry, in such forms as, ceramics, nutrient supplements, medicine, dentrifices, and stabilizers for plastic. They are utilized in solid state chemistry as fluorescent lamp phosphors and play a role in waste water treatment processes. Dental tartar is a calcareous deposit on teeth consisting primarily of calcium phosphates and other calcium magnesium salts.
During the last three decades suspension of calcium phosphates, clays, metal oxides, calcium carbonate, pigments, ceramic materials, and other insoluble inorganic particulate solids in aqueous systems through the use of small quantities of synthetic polymeric and non-polymeric additives has become an increasingly important area of study with high technological relevance. The effectiveness of polymers as dispersants for clay, calcium phosphate, silica, magnesium silicate, and iron oxide has been investigated by several researchers. Results of these studies reveal that polymers containing different functional groups i.e., carboxyl, sulfonic, amide, ester, etc., exhibit good to excellent dispersancy activity. 

Dubin in his study on the evaluation of polyphosphates, phosphonates, and homopolymers of acrylic acid, maleic acid, and acrylic/maleic acid-based copolymers as dispersants for iron oxide showed that copolymers performed better than polyphosphates and phosphonates. Patel in his investigation on the evaluation of polymers as dispersants for calcium phosphate reported that sulfonated polymers exhibit better performance than maleic acid based terpolymers. Amjad reported that acrylic acid based terpolymers performed better than poly(acrylic acids) as hydroxyapatite dispersants.

Surfactants are generally classified into four groups: a) anionic, b) non-ionic, c) amphoteric, and d) cationic. In laundry detergents, surfactants are used to aid in the removal of oily soil and in the suspension of solids in a washing liquid. In hard water (water containing multivalent cations), anionic surfactants tend to form insoluble salts with metal ions, and then they are no longer available to participate in the cleaning process. Cationic surfactants are generally used in textile as a fabric softener. The interactions of cationic surfactants with anionic surfactants have been investigated. Results of this study show that anionic surfactants such as sodium dodecyl sulfate and sodium octylbenzene sulfonate form insoluble salts with calcium ions in aqueous solutions. In another study on the compatibility of anionic surfactants with cationic surfactants, it was shown that using the phase diagram it is possible to formulate homogeneous and stable compositions. In a recent contribution from our laboratories we presented results on the impact of surfactants in preventing the precipitation of calcium phosphate by anionic polymers. In the present paper, we report on the results of investigations conducted to gain information about the impact of various surfactants and a cationic polymeric flocculant on the performance of polymers used as iron oxide dispersants in industrial water systems. In addition, optical microscopy was used for particle size characterization.

In our recent contribution we presented results on the performance of various polymers as iron oxide dispersants in the presence of surfactants. The present study is concerned with the impact of surfactants on the performance of polymers used as dispersants in various industrial applications. The dispersants we have selected include homo- and copolymers of varying compositions to disperse HAP in aqueous systems. Additionally, performance of surfactants containing different functional groups as dispersants for HAP and in combination with polymers has also been investigated.

**EXPERIMENTAL**

Grade A glassware, reagent grade chemicals and carbon dioxide free distilled water were used. Hydroxyapatite (HAP) used in the present study was obtained from Aldrich, USA. The molar ratio of calcium to phosphate was found to be 1.67 ±0.01 and the specific surface of HAP as determined by B.E.T. method was 30±0.5 m²/g with particle size between 50 – 250 µm. HAP was characterized by XRD ((Model Rigaku Geigerflex) and displayed the characteristic powder x-ray diffraction pattern. The polymeric materials and surfactants used as dispersants were selected from commercial and experimental materials. All dispersant solutions were prepared on a dry weight basis. The desired concentrations were obtained by dilution. TABLE 1 lists the polymers and surfactants tested in the present study.

**Dispersancy:** The synthetic water used in the present study was prepared by mixing known volumes of stock solutions of calcium chloride (0.375 M), magnesium chloride (0.184 M), sodium chloride (1.300 M), sodium sulfate (0.300 M), sodium bicarbonate (0.0600 M), surfactant, and polymer solution (100 ppm) to known volume of distilled water in 250 mL beaker. The synthetic water (100 mL) in the beaker was transferred to 100 mL graduated cylinder. The synthetic water has the following composition: 125 mg/L Ca, 38 mg/L Mg, 246 mg/L Na, 561 mg/L Cl, 144 mg/L sulfate, 71 mg/L bicarbonate, and varying concentration of surfactants and polymers. The dispersancy experiments were run at room temperature (~23 °C). The HAP dispersion test was conducted by adding 0.300 g of HAP to known volume of synthetic water containing varying amount of dispersant (surfactants
and/or polymers). After the addition of HAP, cylinders were covered with Parafilm and manually mixed with a motion similar to repeatedly turning over an hourglass for 1 minute and left to stand. The pH of the synthetic water was 7.6-7.8 and under these conditions HAP particles are negatively charged.

**TABLE 1. List of polymers and surfactant tested.**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Ionic charge</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(acrylic acid)*</td>
<td>negative</td>
<td>H1</td>
</tr>
<tr>
<td>Poly(methacrylic acid)*</td>
<td>negative</td>
<td>H2</td>
</tr>
<tr>
<td>Poly(maleic acid)*</td>
<td>negative</td>
<td>H3</td>
</tr>
<tr>
<td>Poly(2-ethyloxazoline)*</td>
<td>neutral</td>
<td>H4</td>
</tr>
<tr>
<td>Poly(diallyldimethyl ammonium chloride)*</td>
<td>positive</td>
<td>H5</td>
</tr>
<tr>
<td>Poly(acrylic acid:dimethyl itaconate)*</td>
<td>negative</td>
<td>H6</td>
</tr>
<tr>
<td>Poly(maleic acid:sulfonated styrene)*</td>
<td>negative</td>
<td>H7</td>
</tr>
<tr>
<td>Sodium lauryl sulfate*</td>
<td>negative</td>
<td>SLS</td>
</tr>
<tr>
<td>Sodium xylene sulfonate*</td>
<td>negative</td>
<td>SXS</td>
</tr>
<tr>
<td>Cocoamidopropyl betaine*</td>
<td>negative/positive</td>
<td>CAPB</td>
</tr>
<tr>
<td>Octyl phenol ethoxylate</td>
<td>neutral</td>
<td>OCP</td>
</tr>
<tr>
<td>Cetyltrimethylammonium chloride</td>
<td>positive</td>
<td>CTAC</td>
</tr>
</tbody>
</table>

*A commercial; *experimental

A standard experiment consisted of eight tests running simultaneously in eight cylinders. At hourly intervals transmittance (%T) readings were taken using a Brinkmann® Probe Colorimeter equipped with a 420 nm filter. Results from these experiments have shown good reproducibility within ± 6%. Dispersion (%D) was calculated from %T readings as a function of HAP dispersed compared to control (80% T, no dispersant). Therefore, greater dispersion was indicated by greater %D. The %D was calculated using the following equation:

\[ %\text{Dispersion (}\%\text{D)} = [100 – (%\text{T} \times (1/80) \times 100)] \]

**RESULTS AND DISCUSSION**

**A. Dispersant Concentration:** In FIGURE 1 profile of %D versus poly(acrylic acid), H1, concentration is illustrated. The data clearly indicate that dispersant concentration strongly affects the ability of H1 (or dispersant) to disperse HAP. For example, at a 1.0 ppm concentration, H1 shows poor dispersancy (< 7%). However, as the dispersant concentration is increased from 1.0 ppm to 5.0 ppm (five folds) concentration, dispersant performance significantly improved (from 6% D to 45%). It is interesting to note that increasing H1 concentration by a factor of two (i.e., from 5.0 ppm to 10.0 ppm) results in ~22% increase in %D values. As noted in FIGURE 1 further increase in H1 concentration results in an incrementally increase in %D values (from 55% to 58%).

![FIGURE1. HAP dispersed in the presence of varying concentration of poly(acrylic acid), H1.](image)

**B. Polymer Architecture**

Effect of Homo-Polymers: The influence of homo-polymers containing different functional groups i.e., anionic (-COOH), non-ionic (-CONH2), and cationic (quaternized ammonium chloride) on HAP dispersion was studied by conducting a series of experiments in the presence of 5.0 ppm polymers. The data presented in FIGURE 2 for a number of carboxyl containing polymers such as poly(acrylic acid), H1; poly(methacrylic acid), P-MAA, H2; and poly(maleic acid), P-MA, H3 clearly show that H1 is good dispersant for HAP. The poor performance shown by H2 and H3 may be attributed to poor adsorption onto HAP particles. FIGURE 2 also presents dispersion data for non-ionic polymers (i.e., poly(2-ethyloxazoline), H4) and cationic charged polymer (i.e., poly(diallyldimethylammonium chloride), H5. It is evident that compared to anionic polymers, non-ionic and cationic charged polymers exhibit poor performance (<5% D) suggesting that –COOH group plays an important role in dispersing HAP. It is interesting to note that whereas H4 which shows poor performance as HAP dispersant has been reported to exhibit excellent performance as silica polymerization inhibitor. Thus, polymer ionic charge plays an important role as a dispersants and as scale inhibitor.
Effect of Copolymers: The influence of substituting the carboxyl group with other groups of varying chain length and ionic charge (i.e., dimethylitaconate, DMI; sulfonated styrene, SS) was investigated for their ability to disperse HAP. Results presented in FIGURE 3 clearly show that polymers containing ester and sulfonate (i.e., acrylic acid:dimethylitaconate, AA:DMI, H6) maleic acid:sulfonated styrene, MA:SS, H7; compared to homo-polymers, exhibit good to excellent dispersion power for HAP. The results presented in FIGURE 3 suggest that presence of ionic charged and bulkier groups increases the performance of copolymers by providing steric stabilization of HAP particles. It is worth noting that the polymer performance trend observed in the present study i.e., copolymers>homopolymers, is consistent with previous studies on the precipitation of calcium phosphate\cite{15} and calcium phosphonates.\cite{16}

C. Surfactant performance

Recently, El-Shall et al.\cite{17} have examined the effect of a commercial non-ionic surfactant on the filterability of gypsum crystals. It was reported that the presence of a small amount of soluble impurities alters the growth rate and habit of formed crystals. Mahmoud et al.\cite{18} in their study on the evaluation of surfactants reported that whereas cetyltrimethylammonium bromide (CTAB) decreased the induction time and increased the growth efficiency, while addition of sodium dodecyl sulfate (SDS) increased the induction time and decreased the growth efficiency compared with the baseline (without additives).

To examine and compare the performance of surfactants i.e., sodium lauryl sulfate (SLS), sodium xylene sulfonate (SXS), octylphenol ethoxylate (OPE), cocamidopropyl betaine (CAPB) and cetyltrimethyl ammonium chloride (CTAC), a series of dispersion experiments were carried out under similar experimental conditions. Results presented in FIGURE 4 clearly show that all surfactants (i.e., cationic, anionic, amphoteric, and non-ionic) compared to poly(acrylic acid), H1, are ineffective HAP dispersants. For example, %D values obtained in the presence of 5.0 ppm are <5% compared to 55% obtained in the presence of H1 respectively. As illustrated in FIGURE 4 increasing the surfactants concentration by two fold i.e., from 5.00 to 10 ppm, does not show any significant improvement in surfactant performance. It is worth noting that whereas polymers containing –COOH and SO$_3$H groups show excellent performance, the presence of these groups in surfactants does not show any efficacy as HAP dispersants. The observed difference in performance between polymers and surfactants may be attributed to poor adsorption and/or molecular weights. It is interesting to note similar performance trend was also observed in dispersion of iron oxide by surfactants and polymers.\cite{14}

D. Effect of surfactants on polymers performance

In view of above results (FIGURE 1) that anionic polymers exhibit marked dispersing property, a series of experiments were carried out to study the impact of surfactants on the performance of copolymer of MA:SS. Results presented in Figure 5
show that under similar experimental conditions, addition of 5.0 ppm of ionic, non-ionic, and amphoteric surfactants i.e., SLS, SXS, OPE, CAPB does not exhibit any significant influence on the performance of H7. However, as noted in FIGURE 5 addition of 5.0 ppm of CTAC exhibits antagonistic effect on the performance of H7. For example, %D values obtained in the presence of 10 ppm of H7 are 81% compared to 58% obtained in the presence of 10.0 ppm of H7 and 5.0 ppm CTAC. The negative influence shown by CTAC on H7 may be attributed to poor compatibility of cationic surfactant with anionic polymer, H7. As noted in Figure 5 similar antagonistic effect by CTAC was also observed for homopolymers (H1, H2).

In order to check the effect of CTAC concentrations on the performance of H7, a copolymer of maleic acid and sulfonated styrene, a number of dispersancy experiments were carried out in the presence of 10.0 ppm of H7 and varying concentrations of CTAC. Results are illustrated in FIGURE 6. It can be seen that addition of low levels i.e., 2.5 ppm of CTAC exhibits ~5% decrease in H7 performance. As shown in Figure 6 increasing the concentration by a factor of two i.e., from 2.5 to 5.0 ppm, results in ~25% decrease in H7 performance and ~35% decrease in H7 performance is observed in the presence of 10.0 ppm of CTAC. The data presented in Figure 6 clearly show that addition of low concentrations of CTAC exhibits marked antagonistic effect on the performance of H7.

E. Effect of cationic polymer on polymers performance

Cationic polymers are extremely important materials used to clarify the wastewaters via processes known as coagulation and flocculation. Wastewaters requiring treatment come from a wide range of sources including food processing, industrial manufacturing, and wastewater generated from during the extraction and refining of petroleum. Cationic polymers commonly used to treat wastewater include homopolymer of polyethylenediaimine, diallyldimethylammonium chloride, and copolymers of acrylic acid:acrylamide. These polymers neutralize the charge of the colloidal particles in the water to form large particles. In most cases these large particles (flocks) are removed via settling in a clarifier and are recollected as sludge. Occasionally, clarifier upsets cause the residual polymer to carryover. It has been reported that low levels of cationic polymer, if present in the recirculating water, can interact with the highly anionic charged polymers commonly used as scale control agents and dispersant in water treatment formulations.

The results of HAP dispersancy experiments carried out in the presence of varying concentration of cationic polymer, diallyldimethyl ammonium chloride, DAC, and 10.0 ppm of copolymer containing –COOH and SO3H, H7, are presented in FIGURE 6. It can be seen that addition of small concentration i.e., 2.5 ppm of DAC exhibits antagonistic effect on the performance of H7. For example, %D values obtained in the presence of 10.0 ppm of H7 and 2.5 ppm of DAC are 65% compared to 81% obtained in the presence of 10.0 ppm of H7 and 0 ppm of DAC, a reduction of ~20% in %D values. As illustrated in FIGURE 6 increasing the DAC concentration by four fold i.e., from 2.5 ppm to 10.0 ppm, results in further decrease in %D value (i.e., from 65% to 23%).
FIGURE 6 presents the comparative data on the influence of cationic surfactant (CTAC) and cationic polymeric flocculant (DAC) on the performance of H7. The data clearly show that under similar experimental conditions DAC compared to CATC exhibits stronger antagonistic effect on the performance of H7. The observed negative influence shown by DAC may be attributed to higher cationic charge present in poly(diallyldimethyl ammonium chloride) compared to cetyltrimethyl ammonium chloride, thus resulting in precipitation of anionic polymers. It is worth noting that similar antagonistic influence shown by cationic surfactants and cationic polymers on anionic polymers has been reported in our earlier investigations on the inhibition of calcium phosphate precipitation, calcium phosphonate precipitation, and iron oxide dispersion by various polymeric additives.13,14,16

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