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The Influence of Cationic Polymers on the Performance of Anionic Polymers as Precipitation Inhibitors for Calcium Phosphonates

Zahid Amjad and Robert W. Zuhl
9911 Brecksville Road, Cleveland, Ohio 44141

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ABSTRACT

The precipitation of calcium phosphonates in the presence of a variety of anionic polymers has been investigated. The inhibition data show that polymer effectiveness as calcium phosphonate inhibitor strongly depends upon polymer architecture. The results also indicate that performance of polymers is strongly influenced by low concentrations of cationic additives such as polymeric floccualants, coagulants, and biocides.

INTRODUCTION

Organophosphorus compounds form a broad family of chemicals which find applications in a variety of industrial processes including crude oil production, electroplating, industrial water treatment, paper and pulp slurries, scale removal, and pigment dispersion. These organophosphonates differ structurally from polyphosphates in that they have a P-C bond. The structural differences account for their superior ability under extremes of pH and temperature. In water treatment processes, phosphonates are used for a variety of reasons. Most important, they inhibit the formation of scale forming salts and control corrosion. Phosphonates are also used to sequester metal ions such as iron, copper, manganese, and zinc. Additionally, phosphonates exhibit some dispersancy activity towards suspending matter such as clay, silt, calcium carbonate, etc. In biological systems, phosphonates have been shown to decrease tartar build-up on tooth enamel and assist in preventing kidney stones. For their *in vivo* application, phosphonates are best known for their ability to block bone resorption, treating afflictions such Paget's disease, hypercalcemia of tumor origin and in other bone resorptive process disorders such as osteoporosis.

Although there are many phosphonates available, three of the most commonly used phosphonates are aminotris(methylene phosphonic acid), AMP; hydroxyethylidine, 1,1-diphosphonic acid, HEDP; and 2-phosphonobutane 1,2,4-tricarboxylic acid, PBTC. However, under certain pH, concentration, and temperature conditions, HEDP has been shown to precipitate in the presence of calcium ions. The precipitation of Ca-HEDP salt not only creates fouling of reverse osmosis membrane and heat exchanger surfaces, it also decreases the solution concentration of HEDP to such extent that calcium phosphate, calcium carbonate, and calcium sulfate scaling can occur.

Inhibition of calcium phosphonate precipitation by polymeric inhibitors has recently been the subject of numerous studies. Boffardi and Schweitzer[1] recognized that the relative poor calcium tolerance of phosphonates can be overcome by the addition of acrylic acid-based copolymer. Smyk and Hoot[2] in their investigation on the performance of various polymers as Ca-HEDP inhibitors showed that acrylic acid-based terpolymer perform better than homopolymers of acrylic acid. Amjad[3] in another study on the inhibition of Ca-HEDP precipitation reported that various factors such as calcium hardness, pH, temperature, and type and concentration of impurities exhibit marked influence on the inhibitory activity of polymeric additives. In the present work, we investigated the precipitation of Ca-HEDP salt in the presence of various polymers such as shown in Table 1. This study also reports the impact of cationic polymeric impurities (i.e., flocculant, coagulant, biocide, etc.) on the performance of Ca-HEDP inhibitors.

Table 1. Polymers Evaluated

Polymer	Acronym
Polyacrylic acid	HP-1
Polymethacrylic acid	HP-2
Polyacrylamide	HP-3
Poly-acrylic acid:2-acrylamido-2-methyl propane sulfonic acid	CP-1
Poly-acrylic acid:acrylate ester	CP-2
Poly-acrylic acid:2-acrylamido-2-methylpropane sufonic acid:sulfonated styrene	TP-1
Poly- acrylic acid:2-acrylamidomethylpropane sulfonic acid:substituted acrylamide	TP-2

EXPERIMENTAL

The polymers, flocculant, coagulant, and biocides used were selected from commercial and experimental materials and were tested on a dry weight basis. Grade A glassware and reagent grade chemicals were used. Subsaturated solutions of Ca-HEDP were prepared by adding a known volume of HEDP stock solution to a glass bottle thermostated at 50 ^{O}C, containing a known volume of water and sodium bicarbonate solution. Following temperature equilibration, the calcium stock solution was added in such a manner that the final concentration would be 150 mg/L. Polymer solutions were added after the addition of HEDP, but before the additionof calcium chloride, as dilute solution in water. The pH of Ca-HEDP solutions were adjusted to 8.50 using dilute solution of NaOH and/or HCl. Precipitation in Ca-HEDP supersaturated solutions was monitored by analyzing aliquots of filtered (0.22 micron) solution for HEDP concentration as described previously.[3] Polymer efficacy as Ca-HEDP inhibitor was calculated using the following equation:

$$\text{Inhibition}(\%) = (\text{HEDP})_s - (\text{HEDP})_c \;/\; (\text{HEDP})_I - (\text{HEDP})_c \times 100$$

Where:

$(\text{HEDP})_s$ = HEDP concentration in the filtrate in the presence of polymer at 20 hr.
$(\text{HEDP})_c$ = HEDP concentration in the filtrate in the absence of polymer at 20 hr.
$(\text{HEDP})_I$ = HEDP concentration at the beginning of the experiment.

Unless noted otherwise, all precipitation experiments were carried out under similar experimental conditions (i.e., 150 mg/L Ca, 15 mg/L HEDP, 10 mg/L polymer, and 1 mg/L flocculant/coagulant/biocide).

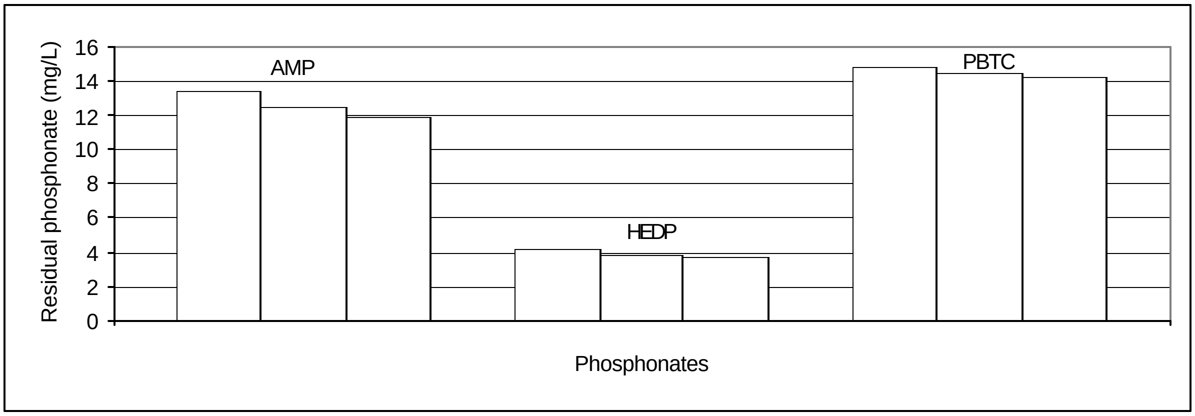
RESULTS AND DISCUSSION

Polymer Performance: In the past two decades many water soluble polymers with different compositions and molecular weights have been developed and investigated as precipitation inhibitors for a variety of alkaline earth metal salts of carbonate, sulfate, phosphate, fluoride, etc. These polymers are mainly homo-, co-, or ter-polymers having acrylic, maleic, or methacrylic acid as the initial monomer in conjunction with other monomers containing acrylamide, ester, phosphono, phosphino, hydroxyl, and sulfonic acid groups. In addition to acting as precipitation inhibitors some of the polymers act as a dispersant for particles suspended in solution and also as metal ion stabilizer for iron, aluminum, zinc, and manganese. The ability of these polymers to act as dispersant, precipitation inhibitor and/or metal ion stabilizer depends on the polymer composition, ionic charge, and the molecular weight.

Screening tests for Ca-AMP, Ca-HEDP, and Ca-PBTC precipitation were carried out under standard test conditions. Figure 1 shows the plots of residual phosphonate concentration as a function of time. As illustrated in Figure 1 within 1 hr >90% HEDP precipitated out as Ca-HEDP salt compared to ~15% AMP and <5% PBTC. It is interesting to note that further increase in reaction time from 1 to 5 and 20 hrs does not significantly affect the residual phosphonate concentration in the calcium phosphonate supersaturated solutions. Based on the data presented in Figure 1, the ranking of phosphonate in terms of calcium phosphonate salt precipitation follows:

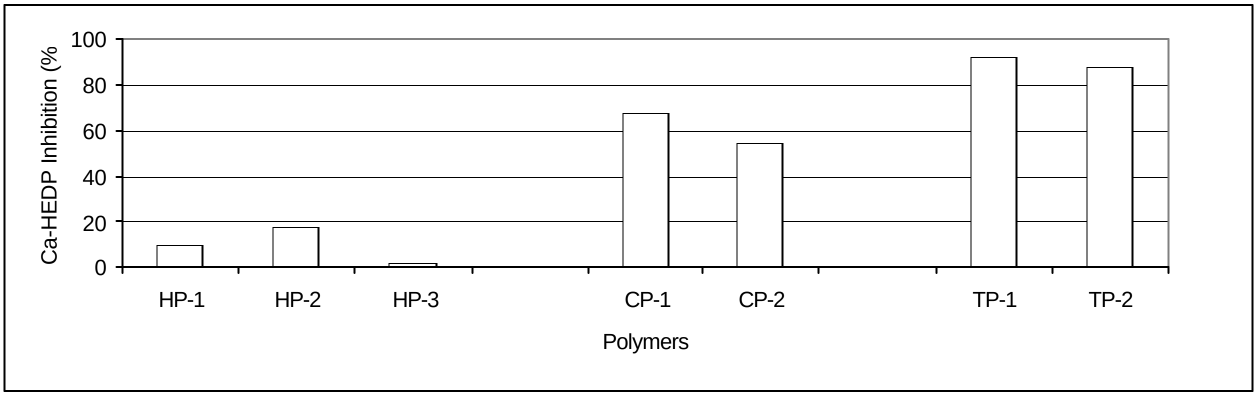
HEDP < AMP < PBTC

Figure 1. Residual Phosphonate Concentration in the Absence of Inhibitor as a Function of Time (1, 5, 20 hr).



In order to evaluate the performance of various commercial and experimental polymers as inhibitors for Ca-HEDP, a series of experiments were carried out under similar experimental conditions. Results are presented in Figure 2. It can be seen that polymers containing only carboxyl group (i.e., HP-1 and HP-2) show poor performance (i.e., < 15% inhibition). It is worth noting that under similar experimental conditions non-ionic polymer, HP-3, does not show any inhibitory activity. Figure 2 also shows performance data on copolymers (CP-1 and CP-2) containing two monomers of different functional groups (i.e., $S0_3$, COOR, COOH, etc.). It can be seen that CP-1 and CP-2 compared to homopolymers (HP-1 and HP-2) exhibit better performance. For example, % inhibition values obtained with CP-1 and CP-2 are 65 and 55 respectively, compared to 8 and 18 obtained with HP-1 and HP-2. Performance data on terpolymers (i.e., TP-1 and TP-2) as presented in Figure 2 clearly indicate that terpolymers outperform both co- and homopolymers suggesting that polymer composition play an important role in inhibiting the precipitation of Ca-HEDP salt from aqueous solution. It is interesting to note that similar trend in polymer performance has been reported for calcium phosphate system.

Figure 2. Performance of Various Polymers as Ca-HEDP Inhibitors

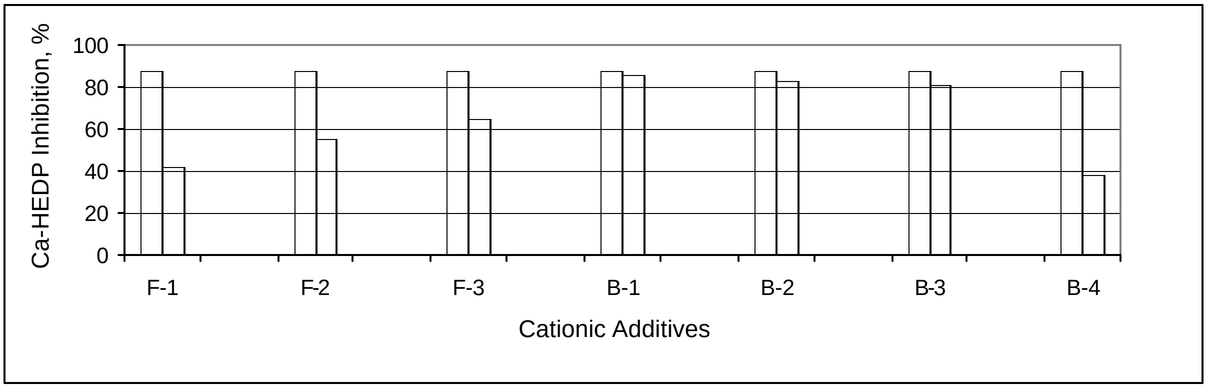


Influence of Organic Coagulants/Flocculants: Organic polymers are used in the water treatment industry to clarify water containing suspended matter. These polymers are of two major types, namely coagulants and flocculants. Coagulants are typically cationic and have molecular weight of <100,000 Daltons. Examples of cationic coagulants include polyimine, polyquaternium compounds and quaternium based cationic copolymers. Flocculants are typically much larger cationic molecules (i.e., Mol. Wt. >1,000,000 Daltons) that provide long bridges between small flocs to enhance particle growth. Commonly used flocculants include copolymers of acrylamide and diallyldimethyl ammonium chloride.

The coagulant/flocculant is typically added to the raw water in an amount suitable to coagulate/flocculate suspended matter. In most cases large particles (flocs) are removed via settling in a clarifier and are recollected as sludge. Occasionally, clarifier upsets cause cationic polymer "carryover". In such instances, cationic polymers may interfere with the performance of anionic polymers used as precipitation inhibitors and dispersant in the water treatment formulation. Commonly used polymeric cationic flocculants/coagulants include poly diallyldimethyl ammonium chloride (F-1), poly-acrylamide:diallyldimethyl ammonium chloride (F-2), and poly(acrylamide:2-acryloxy(ethyltrimethyl ammonium chloride (F-3).

The effect of F-1, F-2, and F-3 on the performance of Ca-HEDP inhibiting polymer (TP-1) was studied under standard test conditions. It is evident from Figure 3 that the presence of low concentration of cationic polymer has a marked antagonistic effect on the performance of Ca-HEDP inhibiting polymer. The data presented in Figure 3 also reveal that under similar precipitation conditions a loss in inhibitory activity due to the presence of cationic polymer was more (i.e., ~60%) for homopolymer (F-1) compared to 45 and 35% obtained for copolymers (F-2 and F-3). The observed tolerance of TP-1 to the presence of cationic copolymers (F-2 and F-3) may be attributed to the lower cationic charge present in F-2 and F-3.

Figure 3. Effect of Cationic Flocculants, and Biocides on the Performance of TP-1.



Effect of Biocides: To prevent the formation of biofilm and to achieve optimum system efficiency, microbiological growth within the water system must be controlled. Biofilm formation is generally controlled by the addition of biocides, biostats, and biodispersants to the water system. Currently available biocides vary considerably in terms of their characteristics such as chemistry, biodegradability, compatibility with other additives, activity and selectivity. Both oxidizing and non-oxidizing biocides find application in water treatment market. Some commonly used bioicides include chlorine, ozone, chlorine dioxide, quaternary ammonium chloride, gluteraldehyde, etc.

The effect of several non-oxidizing biocides on the performance of Ca-HEDP inhibiting polymer, TP-1, was investigated by conducting series of experiments under standard test conditions. The biocides tested include gluteraldehyde, B-1, n-alkyldimethyl benzyl ammonium chloride, B-2, trishydroxymethylnitromethane, B-3, and polyquat (B-4). The results presented in Figure 3 show that B-1, B-2, and B-3 do not show any antagonistic effect on the performance of TP-1. However, the results are markedly different for the quaternary ammonium compound (B-4) tested.

REFERENCES

1. B. P. Boffardi and G. W. Schweitzer, CORROSION/85, Paper 132, National Association of Corrosion Engineers, TX (1985).
2. E. E. Smyk, H. E. Hoots, K. F. Fivizzani, and K. E. Fulks, CORROSION/88, Paper No. 14, National Association of Corrosion Engineers, Houston, TX, (1988).
3. Z. Amjad, Tenside Surfactants Detergents, 34, 102, 1997.

Noveon, Inc.
9911 Brecksville Road
Cleveland, OH 44141-3247, U.S.A.

Phone: 1-800-380-5397 or 216-447-5000
FAX: 216-447-6315 (USA Customer Service)
216-447-6144 (International Customer Service)
216-447-5770 (Marketing & Technical Service)

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