



Evaluation of maleic acid based polymers as scale inhibitors and dispersants for industrial water applications



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HIGHLIGHTS

- Prevention of scale formation and particles dispersion important for fouling minimization.
- Polymers and copolymers of maleic acid are excellent compounds for these purposes.
- Polymer molecular weight and functional groups control fouling and dispersion.

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ABSTRACT

The formation of inorganic scale deposits of the alkaline earth metals is a persistent problem. Dispersion of solid particles separating out from the fluids is also very important for fouling due to deposition. Scale formation and stabilization of suspensions are often overcome through the use of water soluble polymers. In the present work, a series of polymeric compounds were tested as inhibitors of calcium carbonate and calcium sulfate dihydrate (gypsum) precipitation and as dispersion agents of hematite (Fe_2O_3) suspensions in electrolyte solutions. Acrylic acid (AA) and maleic acid (MA) polymers were found to inhibit the precipitation of calcium carbonate and gypsum from supersaturated solutions to extents exceeding 90% at concentrations as low as 2 ppm. The molecular weight (MW) was an important parameter in determining the activity of the tested inhibitors. Lower MW polymers (ca. 2000) proved to be more efficient than higher MW polymers. A similar trend was exhibited for the dispersion ability of the hematite particles. AA and MA copolymers in which functional groups were introduced (pyrrole, sulfono and amide groups) were efficient precipitation inhibitors and dispersion agents, but the efficiency depended strongly on the co-polymer architecture. Copolymers containing sulfono groups improved inhibitory activity and dispersion ability and showed higher calcium ion tolerance.

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1. Introduction

The formation of sparingly soluble salts in steam generators, boilers, cooling towers, pipes, tubing and other equipment commonly employed in water intensive processes is a serious problem, often impairing significantly the overall process and in all cases increasing the cost of production due to the concomitant maintenance cost. Carbonate and sulfate scaling of alkaline earth metal ions is of particular concern because these salts, as a rule show inverse solubility, i.e. their solubility decreases with increasing temperature. Moreover, in the case of calcium carbonate polymorphism is a complicating factor [1]. Scale deposits, according to their mode of formation, may be distinguished in two categories: Salts depositing more or less selectively onto the surfaces of the equipment in contact with the aqueous fluids (usually at elevated temperature) and precipitates accumulating because of sedimentation or transport

by fluid flow. As a rule, in this latter case the deposits are formed in the bulk spontaneously due to the increase of the solution supersaturation, or they form as corrosion by-products which at a second stage sediment out. Among the various strategies adopted to retard or prevent scaling is the use of chemical additives [2,3] which, depending on their chemistry and the nature of the solids forming, inhibit nucleation (threshold inhibitors [4]), crystal growth or both [5]. Scale deposits are in most cases crystalline, with a surface charge directly or indirectly pH dependent. The chemical additives through the ionization of their functional groups, cause changes in the distribution of electrical charges on the surface of the suspended particles, thus determining the stability of the respective suspensions.

Polymaleic acid polymers have been shown to inhibit the formation of scale at very low concentrations [6]. A problem which may be limiting the efficiency of the water soluble polymers as scale retardants is the formation of salts with alkaline earth metal ions or the formation of micelles if the respective concentration in solution exceeds the critical micellization concentration.

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In the present work, the effects of various polymers and copolymers containing different functional groups (carboxyl, sulfono, and amide) were tested with respect to their ability to inhibit calcium carbonate (pH dependent formation [7–9]) and calcium sulfate (pH independent precipitation in the range of 3–10 [10–12]). Since it is established that for the most part inhibitors interfere with the nucleation and crystal growth processes through adsorption on the crystals forming from supersaturated solutions, it is anticipated that their presence in the aqueous solutions shall cause changes in the distribution of the surface charge of the particles thus affecting secondary processes such as aggregation. Experiments were therefore conducted to evaluate the effect of the presence of polymers in solution on the stability of hematite dispersions. The surface of hematite has a pH dependent charge and the pH dependent adsorption of water soluble macromolecules is expected to affect the stability of the respective suspensions.

2. Experimental methods

2.1. Materials

Grade A glassware and analytical grade chemicals were used. Stock solutions of calcium chloride, sodium sulfate, sodium bicarbonate and sodium carbonate were prepared from the respective crystalline solids (Merck) using distilled water, filtered through a 0.22 μm filter paper and standardized as described previously [13]. Iron oxide (Fe_2O_3)

used in this investigation was obtained from Fisher Scientific Co. Powder X-ray diffraction showed that it consisted exclusively of $\alpha\text{-Fe}_2\text{O}_3$ (hematite). The polymers tested were laboratory preparations and commercial materials. Polymer stock solutions were prepared on a dry weight basis. The desired concentrations of the polymers were obtained by dilution. Table 1 lists the polymers tested.

2.2. Inhibitor evaluation protocols

2.2.1. Calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, gypsum) nucleation and crystal growth

Supersaturated solutions of calcium sulfate for precipitation experiments were prepared by adding a known volume of stock solutions of sodium sulfate and inhibitor solutions to glass bottles containing known volume of distilled water maintained at 66 $^\circ\text{C}$. Following temperature equilibration, a known volume of calcium chloride stock solution was added in such amount that the final CaSO_4 solution concentration was 45.0 mM. The total volume of the supersaturated solutions containing varying concentrations of the test inhibitors was 100 mL. Precipitation in these solutions was monitored by analyzing aliquots of the filtered (0.22 μm filter paper) solution for calcium by EDTA titrations. The pH value of the calcium sulfate supersaturated solution was adjusted to 7.00 ± 0.05 by the addition of standard HCl and/or NaOH solutions as needed. At this pH value the additives tested were fully ionized.

Table 1

Polymers investigated as scale inhibitors in calcium sulfate and calcium carbonate supersaturated solutions and as dispersion agents for Fe_2O_3 in water.

Polymer	Repeat unit	MW	Abbreviation
poly(maleic acid)	$-(\text{CH}(\text{COOH})-\text{CH}(\text{COOH}))_n-$	<1 k	HP1
poly(vinyl pyrrolidone)	$-(\text{CH}_2-\text{CH}(\text{N}(\text{C})\text{O}))_n-$	15 k	HP2
poly(acrylamide)	$-(\text{CH}_2-\text{CH}(\text{CONH}_2))_n-$	~6 k	HP3
poly(acrylic acid)	$-(\text{CH}_2-\text{CH}(\text{COOH}))_n-$	~6 k	HP4
poly(acrylic acid)	$-(\text{CH}_2-\text{CH}(\text{COOH}))_n-$	~2 k	HP5
poly(methacrylic acid)	$-(\text{CH}_2-\text{CH}(\text{COOH})(\text{CH}_3))_n-$	~6 k	HP6
poly(methacrylic acid)	$-(\text{CH}_2-\text{CH}(\text{COOH})(\text{CH}_3))_n-$	30 k	HP7
poly(2-acrylamido 2-methylpropane sulfonic acid)	$-(\text{CH}_2-\text{CH}(\text{COOH})(\text{CO}(\text{NH}_2)\text{C}(\text{CH}_3)_2\text{SO}_3\text{H}))_n-$	~10 k	HP8
Sodium salt of maleic acid alt-N vinylpyrrolidone copolymer (AP 28.2)	$-(\text{CH}(\text{COO}^-\text{Na}^+)-\text{CH}_2-\text{CH}_2-\text{CH}(\text{N}(\text{C})\text{O}))_n-$	15 k	CP1
Na/Zn salt of maleic acid-alt-N-vinylpyrrolidone copolymer (AP 28.52.1)	$-(\text{CH}(\text{COO}^-)-\text{CH}_2-\text{CH}_2-\text{CH}(\text{N}(\text{C})\text{O}))_n-$ (Na^+ , Zn^{2+})	60 k	CP2
Sodium salt of maleic acid-N-vinylpyrrolidone-alt-vinyl acetate ternary copolymer (ATP 6.2)	$-(\text{CH}(\text{COO}^-\text{Na}^+)-\text{CH}_2-\text{CH}_2-\text{CH}(\text{N}(\text{C})\text{O}))_m-(\text{CH}_2-\text{CH}(\text{COOCH}_3))_n-$ Ratio $\text{Na}^+/\text{Zn}^{2+} = 9:1$	15 k	CP3
poly(maleic acid:sulfonated styrene)	$-(\text{CH}(\text{COOH})-\text{CH}(\text{COOH}))_m-(\text{CH}_2-\text{CH}(\text{SO}_3\text{H}))_n-$ Where $m:n:p=1.0:0.83:0.19$	<10 k	CP4
poly(acrylic acid:2-acrylamido-2-methylpropane sulfonic acid)	$-(\text{CH}_2-\text{CH}(\text{COOH}))_m-(\text{CH}_2-\text{CH}(\text{CO}(\text{NH}_2)\text{C}(\text{CH}_3)_2\text{SO}_3\text{H}))_n-$	<15 k	CP5
poly(acrylic acid:acrylamide)	$-(\text{CH}_2-\text{CH}(\text{COOH}))_m-(\text{CH}_2-\text{CH}(\text{CONH}_2))_n-$	~10 k	CP6

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