



Inhibition of homogenous formation of calcium carbonate by poly (acrylic acid). The effect of molar mass and end-group functionality



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HIGHLIGHTS

- End-groups strongly affect the effectiveness of polymeric scale inhibitors of CaCO₃.
- Poly(acrylic acids) with end-groups of moderate hydrophobicity are most effective.
- This is true for temperatures between 25 °C and 100 °C.
- Effective scale inhibitors also stabilize less stable polymorphs of CaCO₃.

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ABSTRACT

The ability of poly(acrylic acid) (PAA) with different end groups and molar masses prepared by Atom Transfer Radical Polymerization (ATRP) to inhibit the formation of calcium carbonate scale at low and elevated temperatures was investigated. Inhibition of CaCO₃ deposition was affected by the hydrophobicity of the end groups of PAA, with the greatest inhibition seen for PAA with hydrophobic end groups of moderate size (6–10 carbons). The morphologies of CaCO₃ crystals were significantly distorted in the presence of these PAAs. The smallest morphological change was in the presence of PAA with long hydrophobic end groups (16 carbons) and the relative inhibition observed for all species were in the same order at 30 °C and 100 °C. As well as distorting morphologies, the scale inhibitors appeared to stabilize the less thermodynamically favorable polymorph, vaterite, to a degree proportional to their ability to inhibit precipitation.

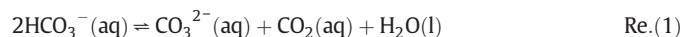
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1. Introduction

Calcium carbonate is one of the most common scales found in both thermal (e.g., multi-stage flash, MSF) and membrane (e.g., reverse osmosis) desalination processes. At lower temperatures, it is the main component of alkaline scale, while at higher temperatures it is found mixed with magnesium hydroxide in desalination plant scales [1]. The exact temperature at which Mg(OH)₂ deposition becomes competitive with CaCO₃ deposition will depend on the extent to which carbon dioxide is degassed from the brine [2].

In MSF desalination, CaCO₃ generally appears above 45 °C as a result of the thermal decomposition of the bicarbonate ion (Re. (1)); increasing

temperature pushes bicarbonate to carbonate by the entropically-favored reaction.



The precipitation of CaCO₃ occurs when the ion product exceeds the K_{sp} (Re. (2)). The concentration of Ca²⁺ and HCO₃⁻ ions in standard seawater (Salinity = 35 g/kg) are 10.3 and 1.8 mM respectively, but the concentration of CO₃²⁻ will be much lower and sensitively dependent on conditions [3].



Calcium carbonate can be found as an amorphous solid and in three different crystalline forms, calcite (K_{sp} at 25 °C = 3.3×10^{-9}), aragonite (K_{sp} at 25 °C = 4.6×10^{-9}) and vaterite (K_{sp} at 25 °C = 1.2×10^{-8}) [4,5] listed in order of increasing solubility and decreasing thermodynamic

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stability. The crystal shape and morphology of calcium carbonate precipitation is affected by factors such as temperature, pH, supersaturation, the ratio of $[Ca^{2+}]/[CO_3^{2-}]$ and the presence or absence of additive [6]. At high temperatures ($T > 70^\circ C$), aragonite is favored, while calcite is favored at low temperature ($T < 30^\circ C$). At any temperature all polymorphs eventually recrystallize to the thermodynamically-favored calcite [7]. Rhombohedral calcite is favored at a 1:1 $[Ca^{2+}]/[CO_3^{2-}]$ ratio, while scalenohedral calcite is favored when the $[Ca^{2+}]/[CO_3^{2-}]$ ratio is ≥ 1.2 [7].

To control scaling in desalination plants, several methods of control have been adopted. The most important methods are acid treatment, mechanical cleaning and the use of polymeric scale inhibitors. The primary method used historically to control scale formation in MSF desalination plants has been acid treatment. In this treatment, the pH of seawater is maintained around 4.5 using acid, most often sulfuric acid due to its low cost. Controlling the pH of treated seawater is crucial for both inhibition of scale and prevention of corrosion. Acid reacts with the CO_3^{2-} and HCO_3^- ions present in seawater yielding H_2O and CO_2 and preventing formation of $CaCO_3$ and $Mg(OH)_2$ [8].

Scale inhibitors are chemical additives used to control the formation and/or deposition of scale. There are three common groups of polymeric scale inhibitors: polymers containing carboxylic acids such as poly(acrylic acid) and poly(maleic acid); polymers containing phosphate groups, such as polyphosphates and polyphosphate esters; and polymers containing sulfonate groups [9]. The attractive features of these chemical additives include ease of handling, relatively low cost, low dose rate, and ability to inhibit hard calcium sulfate scale formation [10,11].

It has been suggested that scale inhibitors may operate by three distinct mechanisms; by sequestration, dispersion, or adsorption [9]. As solubility is defined as the maximum concentration of dissolved ions in equilibrium with solid phase at a fixed temperature and background ionic composition, that maximum concentration of dissolved ions can be reduced prior to nucleation by sequestration with scale inhibitors.

Scale forms primarily heterogeneously, on interfaces (of bubbles, plant surfaces, and particles of suspended matter), but this heterogeneous nucleation is still primarily in the bulk phase. If scale particles formed in solution can be prevented from aggregating onto surfaces and remain suspended in the final brine, they will not contribute to scaling. By adsorbing to the surface of these particles and providing additional electrostatic and/or steric stabilization, scale inhibitors can retard aggregation of these particles, effectively dispersing them in suspension until they are ejected in the waste brine.

Differences in crystal form can arise from selective adsorption of scale inhibitors on the points of crystal growth, causing differential reduction in the growth rate of different crystal planes. For example, in the case of calcium carbonate, scale inhibitors can stabilize the vaterite and prevent its transformation into calcite or aragonite [12]. The new crystal morphologies may grow more slowly overall, may not aggregate as effectively as the native crystal morphologies, or may form a deposit that is more porous and more easily removed [13].

We have previously found in investigations of inhibition of the related calcium oxalate (CaC_2O_4) scaling system (prevalent in sugar manufacture) that the effectiveness of poly(acrylic acid) (PAA) scale inhibitors is sensitively dependent not only on dose and molar mass, but also on the end-groups attached to the polymer [14–16]. Reversible-termination radical polymerization methods, such as Reversible Addition–Fragmentation chain Transfer polymerization (RAFT) [17] and Atom Transfer Radical Polymerization (ATRP) [18] provide a way in which the molar mass and end-group functionality of PAA can be controlled to a high degree of precision, enabling such structure–property relations to be conclusively established. For CaC_2O_4 scaling, we found that most effective scale inhibition by PAA was obtained not for hydrophilic end groups, or hydrophobic end-groups large enough to generate significant surface activity, but moderately hydrophobic

end-groups [14]. These polymers had the greatest impact on crystal speciation and morphology [15].

The main aim of this paper is to determine if similar trends occur in $CaCO_3$ scaling as have been observed previously for CaC_2O_4 . The efficiency of PAA of controlled molar mass with different end-groups as inhibitors of $CaCO_3$ crystallization in the bulk solution was determined at ambient and elevated temperatures, using conductivity and turbidity measurements. We have also previously observed differing impacts of this same set of PAAs on the decomposition of the HCO_3^- ion which suggests that they should have different effects on $CaCO_3$ scaling [19].

2. Experimental

2.1. Synthesis and characterization of poly(acrylic acid)

Poly(acrylic acid) with different end-groups (Table 2) and molar masses were synthesized by Atom Transfer Radical Polymerization (ATRP) of *t*-butyl acrylate and subsequent hydrolysis with trifluoroacetic acid, as described previously [15]. Molar masses of PAA were estimated by 1H and NMR spectroscopy (Bruker-300) and Gel Permeation Chromatography (GPC Waters 1525 HPLC, Waters auto-sampler 712 WISP and Waters 2414 RI detector).

The following PAAs were tested: carboxymethyl-1,1-dimethyl-PAA (CMM-PAA, $M_n = 1500, 7600, 11,800$); ethyl-isobutyrate-PAA (EIB-PAA $M_n = 1700, 5100, 7200$); cyclohexyl-isobutyrate-PAA (CIB-PAA, $M_n = 1700, 1900, 3500, 5100, 8400, 11,000, 13,200$); *n*-hexyl-isobutyrate-PAA (HIB-PAA, $M_n = 1400, 2000, 3600, 4200, 6700, 8900, 13,100$); *n*-decyl-isobutyrate-PAA (DIB-PAA, $M_n = 2400, 4500, 6200$); and *n*-hexadecyl-isobutyrate-PAA (HDIB-PAA, $M_n = 1700, 4100, 9400, 7200$) (see Supplementary material, Fig. S1).

2.2. Crystallization test conditions

Two stock solutions, 0.167 M CO_3^{2-} as Na_2CO_3 (10,000 ppm) and 0.413 M Ca^{2+} as $CaCl_2$ (16,500 ppm), were prepared. These solutions were filtered and degassed using a 0.45 μm Millipore solvent filter. PAA solutions were prepared by dissolving 0.015 g of PAA in 20 mL water (750 ppm) and were used after three days to ensure complete dissolution of the polymer.

Tests were conducted at a pH of 9.2 under four sets of conditions of varying temperatures and supersaturation levels ($SL = Q_{sp}/K_{sp}$, where Q_{sp} is the solubility quotient), as outlined in Table 1. It should be noted that the Ca^{2+} concentrations are much less than those expected under typical thermal desalination conditions, and at a correspondingly lower $[Ca^{2+}]/[CO_3^{2-}]$ ratio: thus while the supersaturation values are comparable to thermal desalination conditions, they correspond to distinctly different environments for crystal growth [20].

Time-resolved measurements of crystal formation, and microscopic examination of the crystals formed in these experiments was carried

Table 1
Crystallization test conditions with PAA.

Condition set	1	2	3	4
pH	9.2			
T °C	25	60	100	100
$[Ca^{2+}]$ ppm	66	66	36	66
$[CO_3^{2-}]$ ppm	100	100	30	100
$[Ca^{2+}]/[CO_3^{2-}]$	1:1	1:1	1.8:1	1:1
[PAA] ppm	1.50	1.50	0.50	6.70
$K_{sp} \times 10^{-9}$	4.95	2.80	1.69	1.69
SL	556	983	277	1629

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