KINETIC INHIBITION OF CALCIUM CARBONATE CRYSTAL GROWTH IN THE PRESENCE OF NATURAL AND SYNTHETIC ORGANIC INHIBITORS

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1. ABSTRACT

Addition of carboxylate-containing polymeric materials to a metastable supersaturated calcium carbonate solution greatly reduced calcite crystal growth rates at constant supersaturation and pH = 8.5. Calcite crystallization rates were decreased to half their value in pure solutions by a tannic acid concentration of about 0.3 ppm (parts per million); a fulvic acid concentration of about 0.2 ppm; and a poly(acrylic acid) concentration of about 0.0175 ppm. An equation relating the calcite crystallization rate and the additive concentration follows an expression based on a Langmuir adsorption model. However, the Langmuir isotherm plot has two linear segments suggesting that these polyelectrolyte inhibitors may selectively adsorb initially at the fastest growing crystal faces. This relation between polyelectrolyte concentration and calcite growth rates implies inhibition by carboxylate-containing polymeric materials involves blockage of crystal growth sites on the calcite surface.

2. INTRODUCTION

Formation of mineral scales on heat exchangers and reverse osmosis membranes is a common problem in water treatment processes. Mineral scale forms because of the composi-

tion and hardness of feed water available for industrial applications and because of the presence of scale constituents such as calcium ion and bicarbonate ion. Other industrial processes impacted by mineral scale formation problems include oil and gas production, geothermal power production, sugar refining, pulp and paper fabrication, and laundry applications.

Calcium carbonate formation in natural waters is also a topic of research interest. Natural mineralization processes can be modified by the presence of dissolved organic polyelectrolytes, such as humic and fulvic acids. Dissolved organic carbon (DOC) concentrations are proportional to the concentrations of humic substances in water. DOC concentrations can vary from less than 1 ppm in groundwater to more than 100 ppm in sediment pore water. Often water with high DOC concentrations is supersaturated with calcium carbonate minerals. This persistent supersaturation is attributed to the presence of natural organic polymeric inhibitors. Surface waters precipitate calcium carbonate by physical and chemical processes including: temperature increases, carbon dioxide loss, and photosynthetic utilization of carbon dioxide by algae. Natural organic crystallization inhibitors in water may modify these important biological processes.

Calcite, the thermodynamically stable calcium carbonate polymorph, is the most common scale forming mineral (Polymorphism refers to two or more crystal forms that each has the same chemical composition but different properties and solubility). Calcite coatings form tenacious, hard mineral deposits, and are the most widely studied mineral scale among the sparingly soluble alkaline earth metal salts. Formation of a polymorph other than calcite is facilitated by solution conditions such as pH, temperature, and the presence of crystal growth inhibitors.[1] Spontaneous precipitation studies of calcium carbonate at moderate temperatures often show the calcium carbonate polymorph vaterite to be the first phase to form in solution. Above ambient temperature, the unstable polymorph aragonite has been reported to be the first phase to precipitate.[2]

During the last two decades investigations of additives to prevent or retard calcium carbonate scaling have attracted the attention of academic and industrial scientists. Common inhibitors of carbonate mineral scales include polyphosphates, phosphonates, and synthetic polymeric inhibitors such as poly(acrylic acid), poly(maleic acid), and copolymers containing acrylic or maleic acid. Investigations of these and several other mineral scale inhibitors suggest that inhibitor effectiveness depends on the functional groups in the inhibitor molecule, polymer composition, and molecular weight.[3–7] In addition, during spontaneous precipitation, the scale composition is influenced by the inhibitor.[8,9]

The effectiveness of non-polymeric additives as calcium carbonate inhibitors has been the subject of numerous investigations. For example, phosphate, oxalate, glycerophosphate, and benzene polycarboxylic acids are effective inhibitors at low solution concentration. A Langmuir-type adsorption model describes the inhibition of calcium carbonate crystal growth by these ions.[10–12]

Organophosphonates, an important class of crystallization and scale formation inhibitors, have been successfully used to inhibit calcium carbonate scale formation in a number of applications.[13] However, these compounds may decompose at elevated temperatures, releasing phosphate ion. Elevated phosphate ion concentrations may cause the formation of calcium phosphate scale. Moreover, high concentrations of phosphonates may lead to the deposition of calcium-phosphonate scale on heat exchangers and reverse osmosis membrane surfaces.[14,15]

Low metal ion concentrations (i.e., iron, zinc, copper, etc.), present as impurities in water supplies, have been reported to influence the precipitation of calcium carbonate, calcium sulfate, and calcium phosphates.[16,17] Katz and Parsiegla[18] reported that ferrous, ferric, copper, and zinc ions inhibit the crystal growth of calcium carbonate.

Natural organic compounds (i.e., humic substances) are commonly encountered in surface water and groundwater used for water supply. Humic substances are mixtures of natural products with a complex structure and chemistry. Isolation and characterization of humic substances from surface water and groundwater is an ongoing area of research interest.[19] At present the best-characterized humic material is that isolated from the Suwannee River, Georgia.[20-23]

Nystrom et al.[24] examining membrane filtration of water containing humic substances, reported that humic acid forms a gel-like layer on filters and blocks filter pores. Recently, Freche et al.[25] examined the influence of humic substances on the crystal growth of dicalcium phosphate dihydrate (DCPD) and found that humic substances reduced crystal growth rates of DCPD. A Langmuir-adsorption process at surface growth sites was proposed to explain the inhibitory effect of humic substances.

The constant composition (CC) technique is used in the study reported here to better understand the influence of humic material on calcium carbonate crystallization rates. This technique provides kinetic information at supersaturations that are low and stable, conditions unattainable by conventional seeded growth methods. Figure 1 shows a schematic representation of a typical CC experiment. A detailed discussion of the CC experiment appears elsewhere.[13] Calcium carbonate crystal growth inhibitors tested include Suwannee River fulvic acid (FA), tannic acid (TA), poly(acrylic acid) (PAc), benzene hexacarboxylic acid (BHCA), benzene-1,3,5-tricarboxylic acid (BTCA) and salicylic acid (SA).

3. EXPERIMENTAL

Experiments were carried out in a double-walled, water-jacketed Pyrex glass cell, thermostatically controlled at 30 ± 0.1 °C. Supersaturated solutions were magnetically
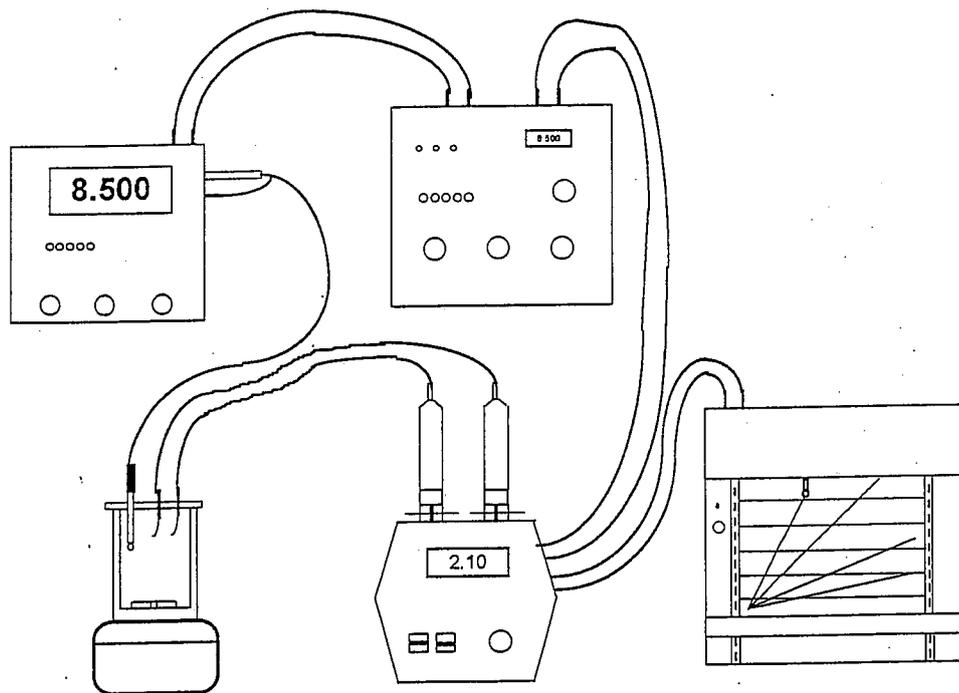

Figure 1. Constant composition experimental apparatus.

stirred by a Teflon coated stirring bar to ensure homogeneity of the solutions and of the seed suspension contained in the cell. Stock solutions of calcium chloride, sodium carbonate, sodium bicarbonate, and sodium chloride were prepared from the respective reagent grade chemicals using distilled, carbon dioxide free water. Calcite seed crystals were prepared and characterized by the method described previously and were stored as dry seed material.[13] Poly(acrylic acid) solutions were prepared from commercial samples (GOOD-RITE K-732, 5100 Dalton, BFGoodrich). Salicylic acid and tannic acids used in the present study were obtained from the Sigma-Aldrich Corporation. Suwannee River fulvic acid used in this investigation was isolated by Leenheer et al.[21] and has been extensively studied.[20–23]

Stable calcium carbonate supersaturated solutions were prepared by placing known volumes of calcium chloride and sodium bicarbonate solutions in the 600-ml cell, the latter addition being made slowly over a period of several minutes. Supersaturated solutions are stable for at least four hours. The mixed solutions were brought to pH=8.5 by the controlled addition of sodium hydroxide. Hydrogen ion measurements were made with a pH combination electrode equilibrated at 30 °C. Supersaturated solution stability was verified by a constant pH reading for at least 45 minutes prior to each experiment. A solution aliquot was taken immediately before the addition of the seed slurry, prepared prior to use by adding a known volume (2 ml) of saturated calcium carbonate to the weighed seed crystals. The suspension was sonicated for 1 minute and then added to the reaction flask. Following the addition of seed crystals, the onset of growth resulted in a solution pH decrease, which was immediately restored to its preset value by the simultaneous addition of two titrant solutions from mechanically coupled 10 ml buret mounted on a modified pH stat (Metrohm, Model 614). The two burettes contained calcium chloride and sodium carbonate at the molar stoichiometry dictated by the precipitating calcite. Calcite growth inhibition experiments were performed by adding inhibitor solution to the bicarbonate solution before the addition of the calcium solution. Titrant solution composition was adjusted to avoid dilution of the working solution. pH control was provided by an amount of sodium hydroxide required for correct pH adjustment of the working solution. More explicitly, the concentration of the titrant in the two burets was calculated as follows:

Buret 1: $CaCl_2 (Cx + 2x)$
Buret 2: $Cx (Na_2CO_3) + 2x (NaHCO_3) + 2y(NaOH)$
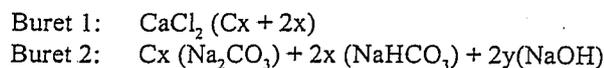
where x is the molar concentration of calcium chloride or sodium carbonate in the working solution and y the amount of sodium hydroxide required for the pH adjustment in the working solution. For maintenance of constant ionic strength, the amount 2C of inert electrolyte (sodium chloride) was added in the working solution where C is a constant (expressing how many times more concentrated the titrants are than the working solution). In the investigation of the crystal growth in the presence of inhibitor, to avoid dilution of the inhibitor in the working solution, the appropriate amount of inhibitor was added to the carbonate containing buret.

During the crystal growth reaction, samples were withdrawn from the cell, filtered through membrane filters and the filtrate analyzed for calcium, to ensure a constant solution composition. The solids on the filters were characterized by infrared spectroscopy, powder x-ray diffraction, and by scanning electron microscopy.

The uptake of titrant solutions with time were traced on a chart recorder and the rates calculated (as mole of $CaCO_3$ precipitated per minute) as described previously.[26] Figure 2 shows the structures of synthetic inhibitors evaluated in this study.
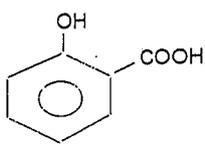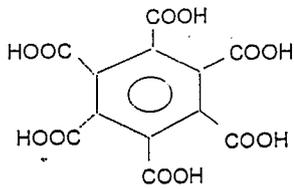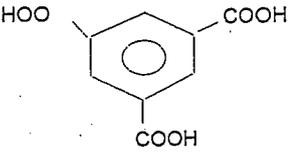
Inhibitor	Acronym	Structure
fulvic acid	FA	-----------------
tannic acid	TA	-----------------
salicylic acid	SA	
benzene hexacarboxylic acid	BHCA	
benzene 1,3,5 tricarboxylic acid	BTCA	
poly (acrylic acid)	PAc	

Figure 2. Inhibitor structures.

4. RESULTS AND DISCUSSION

Solution species concentrations were calculated by using mass balance, proton dissociation, electroneutrality, and equilibrium constants involving calcium ion with inhibitors, by an iterative procedure described previously.[26] Experimental conditions and crystal growth rates for each experiment are given in Table 1. Reproducibility of crystal growth rates among different experiments is satisfactory with a mean of 40.15 ± 1.05 (± 2.6 %) moles of calcium carbonate per (square meter per minute) (mole m^{-2} min^{-1}) (experiments 1 and 2 in Table 1).

The amount of calcium carbonate formed during reaction (Figure 3) is proportional to the volume of titrant added to maintain constant supersaturation. Calcite crystallization rate is calculated as the slope of the amount of calcium carbonate formed versus time plot. Figure 3 illustrates the change in crystallization rate with varying amount of inoculating seed. Growth rates, R, (mole m^{-2} min^{-1}) normalized for the initial surface area of inoculating seed (Table 1, expts 1–5) are constant, confirming that crystallization takes place on added calcite seed crystals.

Calcite growth experiments in the presence of varying concentrations of fulvic acid (FA) demonstrate the concentration-inhibition relationship for FA (Figure 4). Fulvic acid

Table 1. Crystallization of calcite on calcite crystals in
the presence of inhibitors

Experiment	Inhibitor	Conc., ppm	10^6, R, mole m^{-2} min^{-1}
1	none	—	39.1
2	none	—	41.2
3	none	—	38.8[b]
4	none	—	40.4[c]
5	none	—	38.2[d]
6	FA	0.125	27.7
7	FA	0.150	24.5
8	FA	0.20	20.5
9	FA	0.25	17.1
10	FA	0.25	18.2
11	FA	0.35	6.9
12	FA	0.50	2.1
13	FA	1.00	0.3[e]
14	TA	0.15	29.0
15	TA	0.25	24.6
16	TA	0.50	14.5
17	TA	0.75	9.5
18	TA	1.0	2.4
19	TA	1.5	1.5
20	PAc	0.015	25.7
21	PAc	0.0175	21.1
22	PAc	0.020	9.8
23	PAc	0.025	4.2
24	PAc	0.05	0.5[e]
25	SA	1.00	39.5
26	SA	5.00	38.2
27	BHCA	0.25	15.5
28	BTCA	0.50	39.1

$CaCl_2$ = 2 mM, $NaHCO_3$ = 1 mM , NaCl = 10 mM, pH =
8.5, calcite supersaturation = 0.29, 30°C
[a]100 mg seed crystals
[b]131 mg seed crystals
[c]55 mg seed crystals
[d]34 mg seed crystals
[e]Rate calculated based on initial rate

concentration as low as 0.125 ppm reduces the crystallization rate by ~ 30% (Figure 4 curve B); at 0.35 ppm, a rate reduction of ~ 80% is observed. As illustrated in Figure 4 (curves B,C,D,E, F, and G), increasing the concentration from 0.125 to 0.50 ppm resulted in rate reduction of 30 to >90% and, at 1.0 ppm, the precipitation is almost completely inhibited for at least 100 minutes.

Calcite crystal growth reduction by tannic acid (TA) (Table 1 and Figure 5) indicates that TA is an effective calcite growth inhibitor at relatively low solution concentrations. For example, the calcite crystallization rates in the presence of 0.15, 0.50, 1.0, and 1.5 ppm are 29.0, 14.5, 2.4, and 1.5 × 10^{-6} mole m^{-2} min^{-1} respectively, compared to 39.1 × 10^{-6} mole m^{-2} min^{-1} obtained in the absence of TA (Table 1).

Constant composition experimental results demonstrate the effectiveness of synthetic polymeric inhibitor materials, such as poly(acrylic acid) (PAc), as calcite growth inhibitor (Table 1 and Figure 6). Poly(acrylic acid) at very low concentration (i.e., 0.015
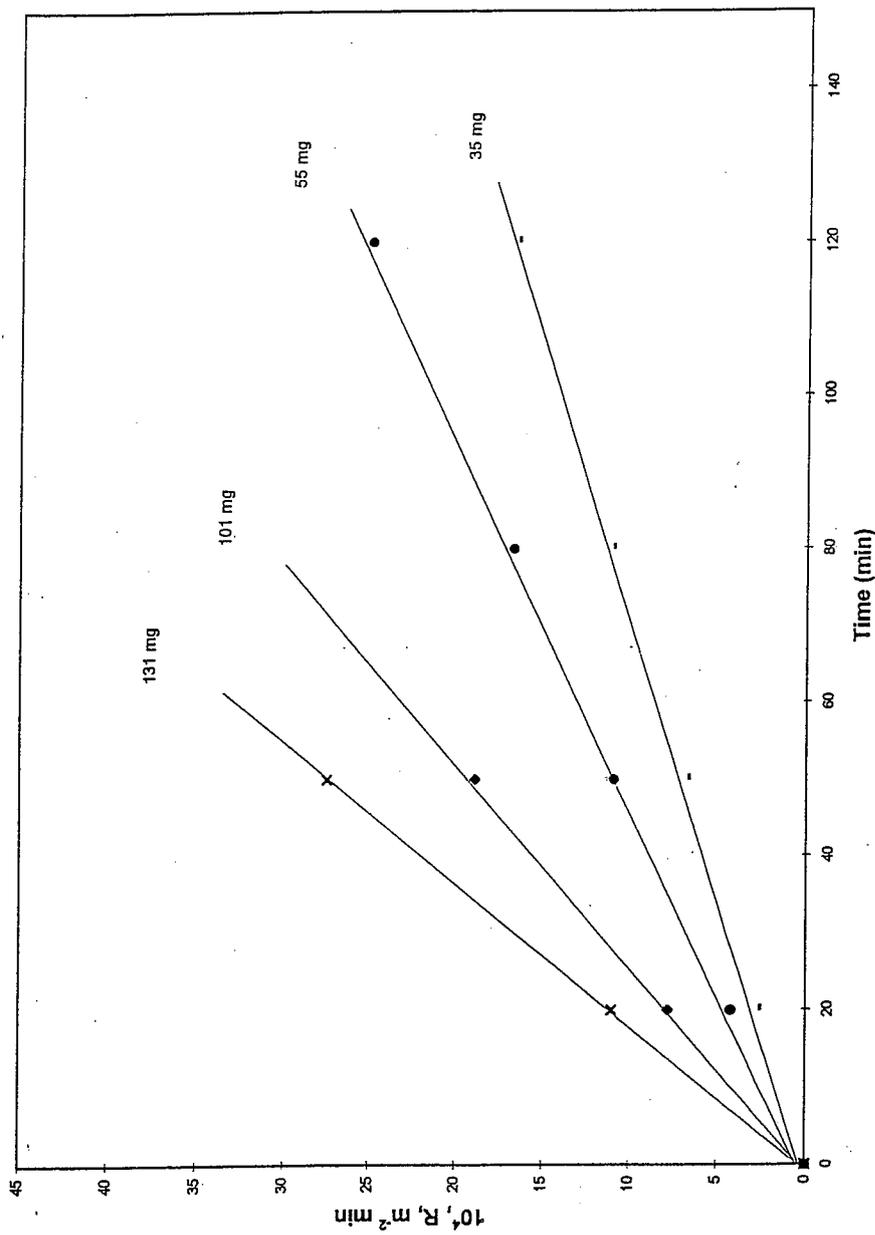
Figure 3. Effect of seed concentration on calcite crystal growth. Plots of calcite growth as a function of time.
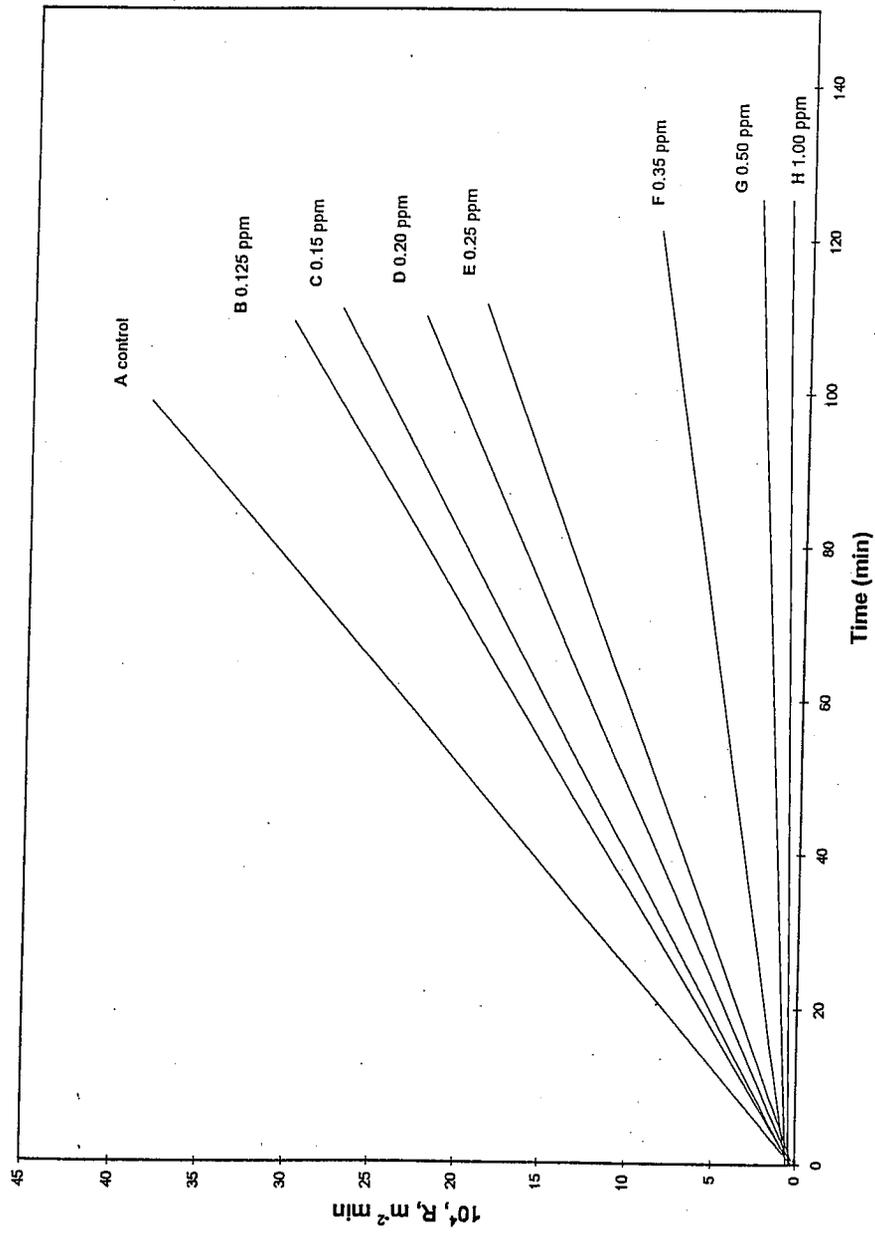
Figure 4. Crystal growth of calcite at constant supersaturation. Amount of calcite growth as a function of time in the presence of fulvic acid.
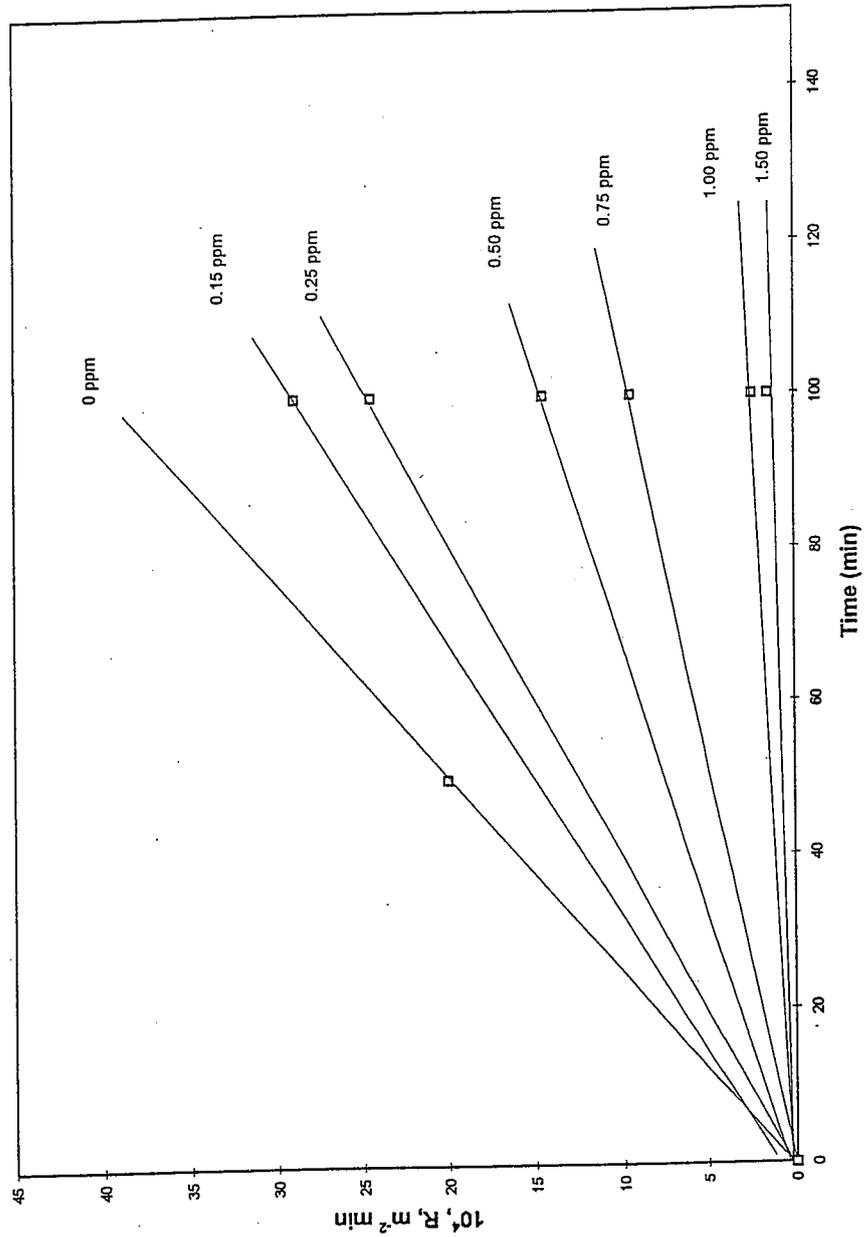
Figure 5. Crystal growth of calcite at constant supersaturation in the presence of varying concentrations of tannic acid.
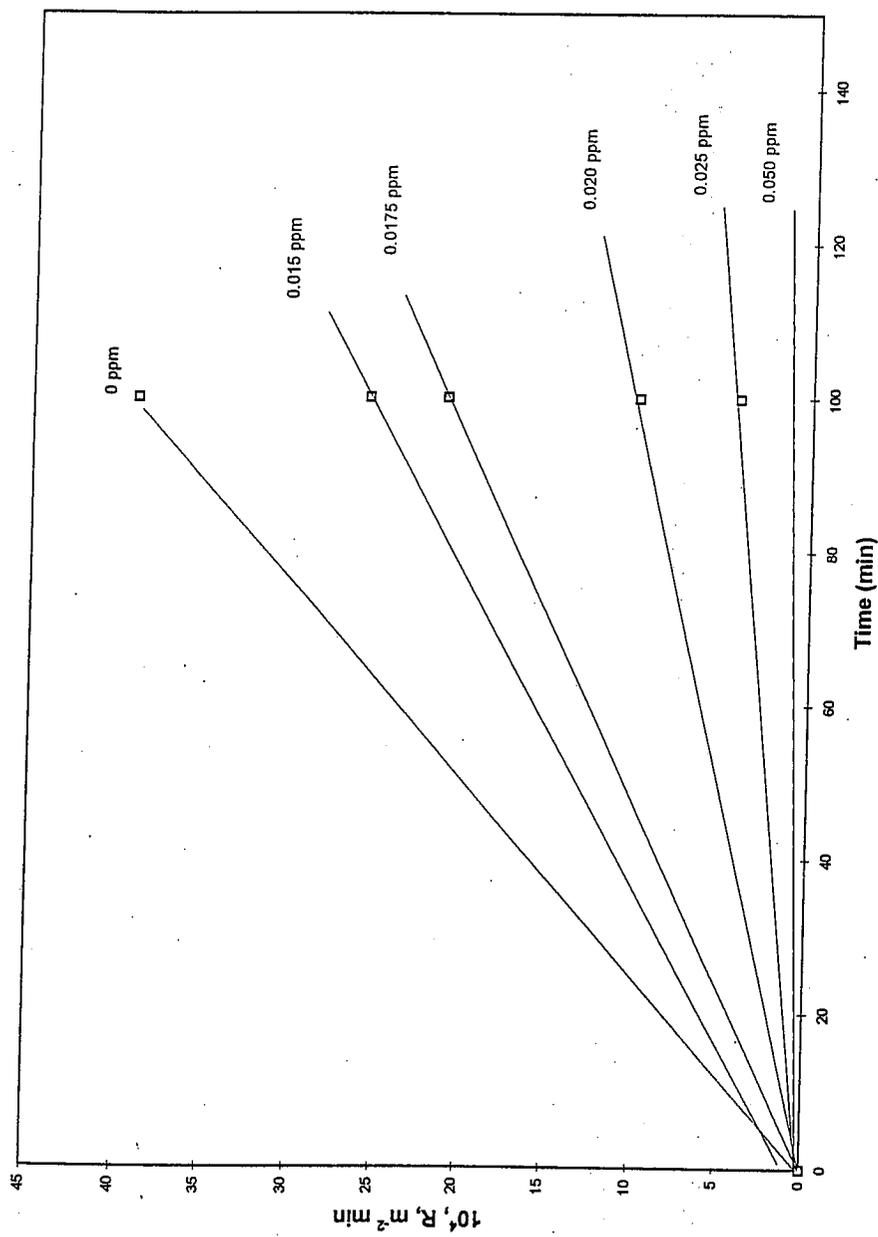
Figure 6. Crystal growth of calcite at constant supersaturation in the presence of poly (acrylic) acid at varying concentrations.

ppm) has a marked inhibitory effect on calcite growth. Calcite growth rates in the presence of 0.015, 0.020, and 0.05 ppm of PAc are 25.7, 9.8, and 0.5 × 10^{-6} moles $CaCO_3$ m^{-2} min^{-1} respectively, compared to 39.5 × 10^{-6} mole m^{-2} min^{-1} obtained in the absence of inhibitor (Table 1).

To study the influence of hydroxyl and carboxyl functional groups present in the same molecule, crystal growth experiments were conducted at varying concentrations of demsalicylic acid (SA). The kinetic data on the inhibition effectiveness of SA (Table 1) demonstrate that SA at concentrations as high as 5.00 ppm does not significantly reduce the growth rate. The inhibition effectiveness of several synthetic compounds containing carboxyl, and both hydroxyl and carboxyl groups (i.e., BHCA, BTCA, and SA) under similar growth conditions is illustrated in Figure 7.

For experiments with solution inhibitor concentration of 0.25 ppm, BHCA exhibits much stronger inhibitor activity than higher concentrations of BTCA (0.5 ppm) and SA (5 ppm). The greater inhibitory effect of BHCA compared to BTCA and SA indicates that inhibitor ionic charge and total number of ionizable groups determines inhibitor effectiveness. The importance of inhibitor charge has been reported in studies involving the crystal growth rate reduction for growth reaction of other sparingly soluble salts. Growth rates (10^{-6} $mole^{-1}$ m^{-2} min^{-1}) obtained at fixed inhibitor concentration (0.25 ppm) in the presence of BHCA are 15.5 compared to 17.1 and 24.6 obtained for FA and TA, respectively. At low concentrations the FA is nearly as effective as BHCA in reducing calcite crystallization rates.

Results of the CC experiments illustrate the effectiveness of natural and synthetic compounds as crystal growth inhibitors (Table 1 and Figure 8). Inhibition effectiveness of FA, TA, SA, BHCA, and PAc at 0.25 ppm concentration of each inhibitor present initially in supersaturated solutions illustrates that the synthetic materials are more effective than the natural polyelectrolytes. Tannic acid (Figure 8) is a less effective growth inhibitor than BHCA and PAc (Figure 8). Inhibitor effectiveness (from most effective inhibitor to least effective inhibitor) for compounds containing hydroxyl and/or carboxyl groups is : PAc >> BHCA ~ FA > TA >> BTCA ~ SA ~ control (no inhibitor).

For many sparingly soluble salts, the mechanism of crystal growth rate inhibition can be described as an adsorption process at crystal growth sites on the mineral surface. Chelating anions may be adsorbed at cationic sites on the crystal surface and inhibit the growth when present at very low concentrations. In addition, inhibitors having large binding constants may also form ion pairs with calcium ions present in the calcium carbonate supersaturated solution, decreasing supersaturation. However, under the experimental conditions employed in the present investigation the decrease in the rate of crystallization must be attributed to the surface adsorption rather than simple calcium-inhibitor complex formation. Inhibitor concentration is much lower than that of calcium ion. The percent of calcium ion complexed to fulvic acid at the highest FA concentration is less than 5%. (M. M. Reddy, unpublished results, 1997).

The adsorption process and its influence on the crystal growth rate can often be interpreted in terms of a Langmuir-type isotherm[7,15,20,23] represented by the following equation:

$$R_0/(R_0 - R) = 1 + (K_a C)^{-1} \tag{1}$$

where R and R_0 are the rates of crystal growth in the presence and absence of inhibitors respectively, K_a is the adsorption affinity constant of the substrate for the inhibitor ion, and C is the inhibitor concentration. Langmuir function plots for FA and TA according to equation 1 (Figure 9) illustrate that inhibitor adsorption on calcite crystals deviates from
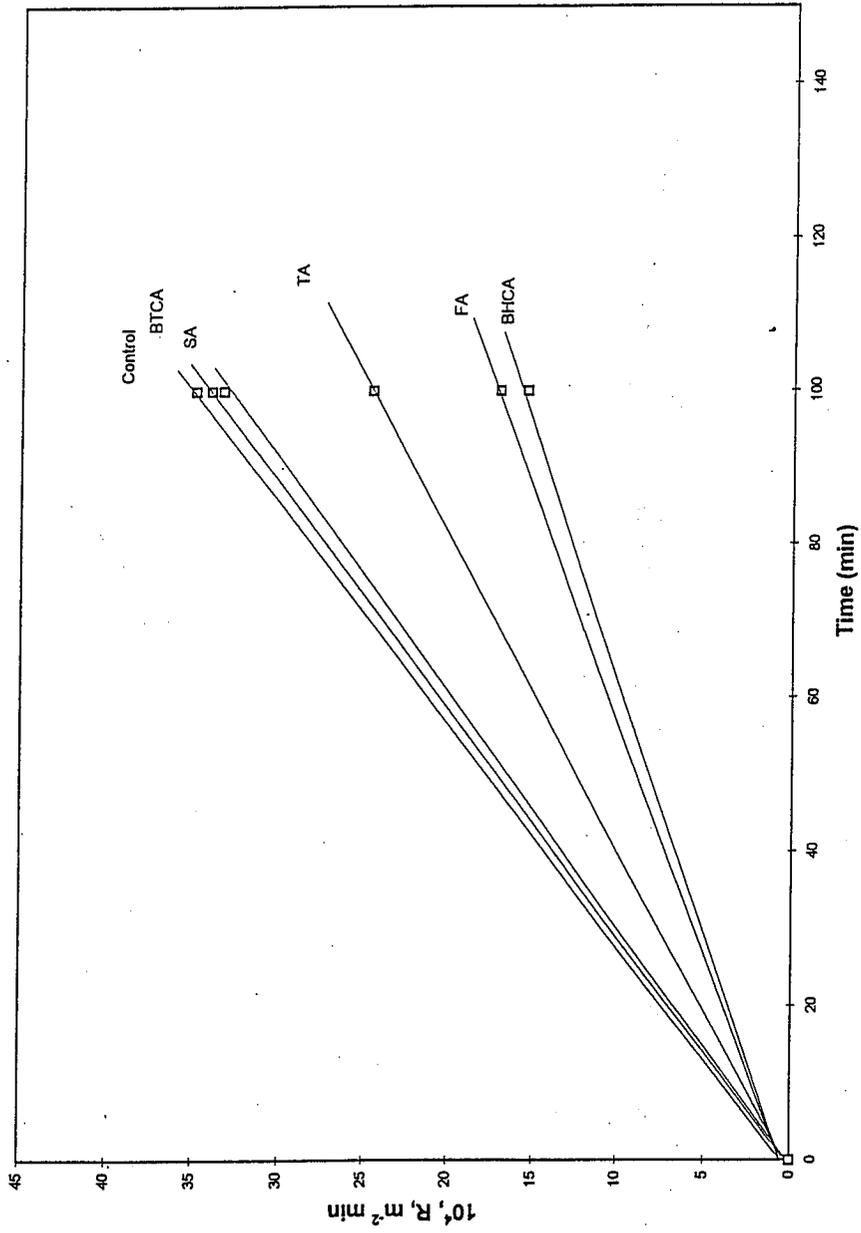
Figure 7. Calcite crystal growth in the presence of various additives at constant supersaturation.

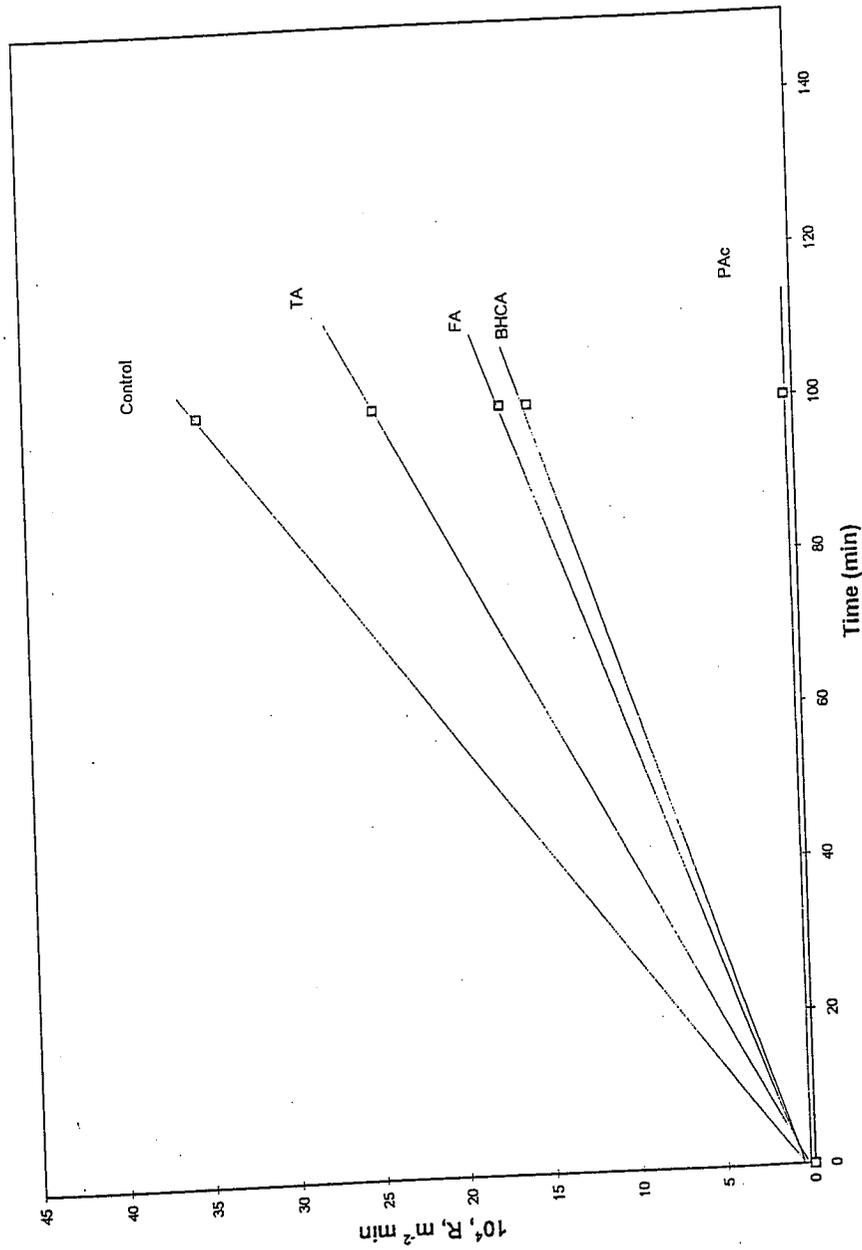Kinetic Inhibition of Calcium Carbonate Crystal Growth

Figure 8. Calcite crystal growth in the presence of various additives and poly (acrylic acid) at constant supersaturation.
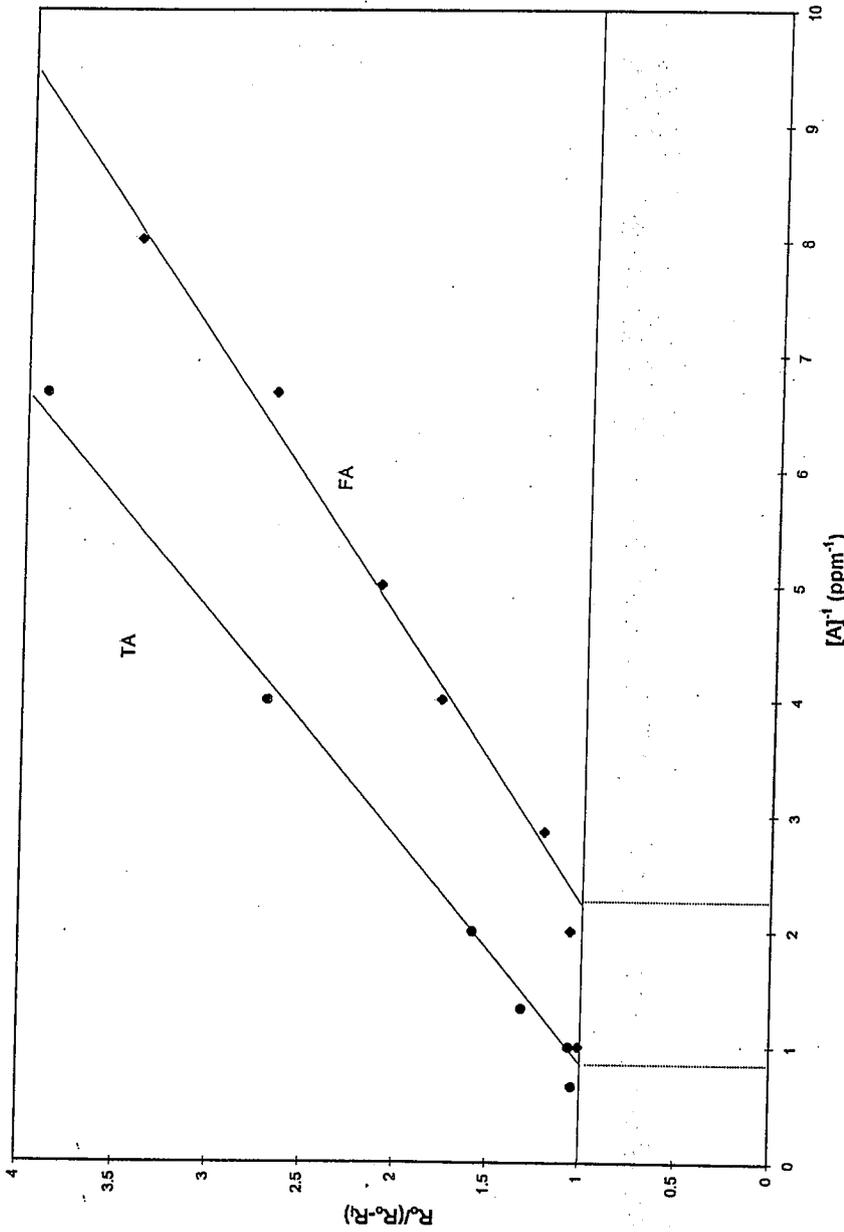
Figure 9. Plots of the rate of calcite formation as a function of the reciprocal of the tannic or fulvic acid concentration.
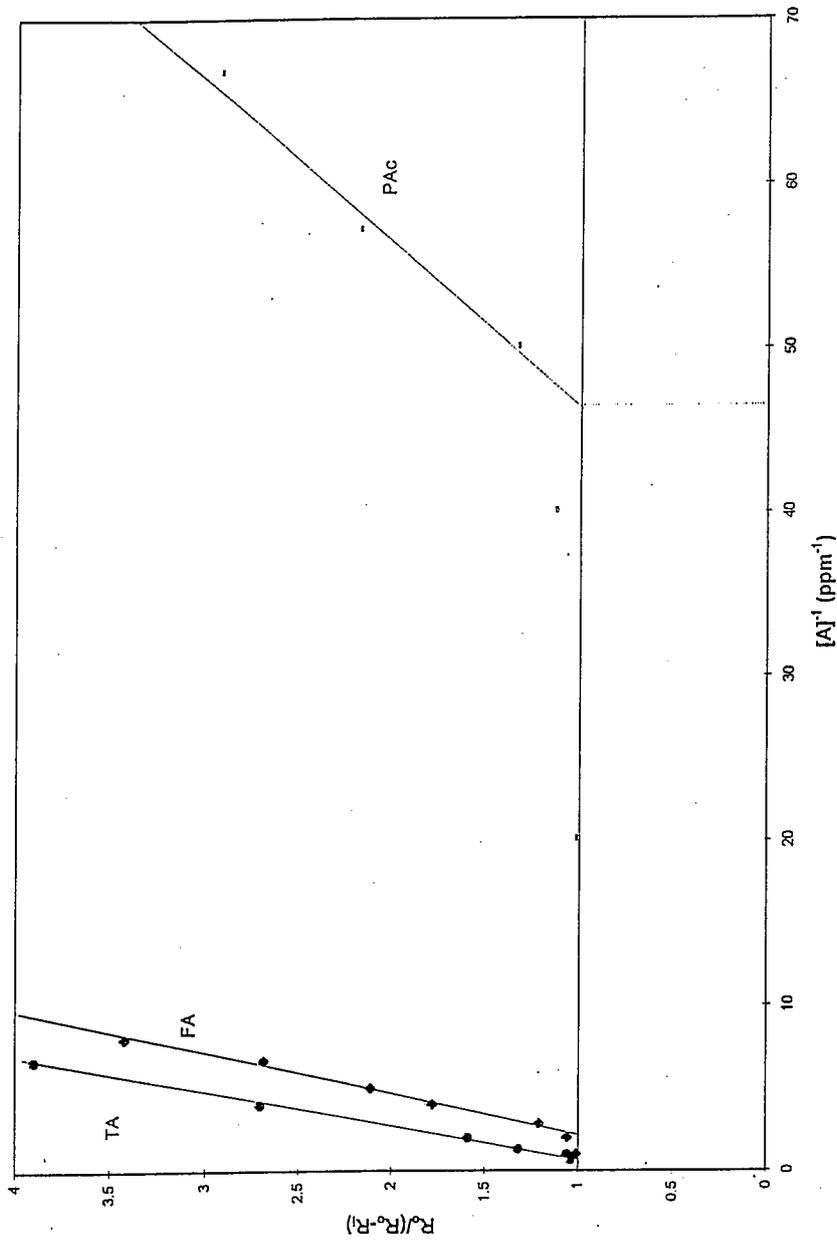
Figure 10. Plots of the rate of calcite formation as a function of the reciprocal of the inhibitor concentration for poly(acrylic acid) as well as TA and FA.

the simple adsorption model—there are two linear segments instead of one predicted by equation 1.

The line corresponding to growth inhibition at low additive concentration (high reciprocal additive concentrations) does not extrapolate to the value of unity at high additive concentrations (Figure 9) expected from equation 1. The appearance of two linear portions in this plot could be due to the failure of the Langmuir-adsorption model assumptions: 1) uniform adsorption sites and 2) absence of interactions between adsorbent molecules. Calcite growth is almost completely inhibited i.e., $R_0/(R_0-R) \sim 1$, at 0.45 ppm for FA, and 1.15 ppm TA (Figure 9). Polyacrylic acid exhibits a more pronounced segmented Langmuir function plot than FA or TA (Figure 10).

A detailed discussion of calcite growth inhibition mechanisms by simple ionic substances has been presented elsewhere.[26] Simple ionic inhibitors, which follow a Langmuir model, generally adsorb upon all growing crystal faces equally. This adsorption and blockage of growth sites reduces the crystal growth rate to zero at a characteristic minimum inhibitor concentration. These inhibitors follow a Langmuir function that is linear with an intercept of unity. Moreover, the smallest measurable rate has a Langmuir function value close to unity.

This regular Langmuir function behavior is also observed for simple polyvalent ions such as HCBA.[27] However, complex or polymeric inhibitor ions preferentially adsorb on more rapidly growing crystal faces. This adsorption behavior may lead to marked changes in crystal habit and morphology at inhibitor concentrations less than those needed to prevent growth. If polyelectrolyte inhibitor adsorption is greatest on those calcite crystal faces with the highest kink density, then growth for those faces will decrease to a value very close to zero. Other more slowly growing faces will continue to grow until their growth sites are blocked by inhibitor ions. This two-stage inhibition process leads to two linear segments in the Langmuir function plot as observed for the polyelectrolyte inhibitors examined here.

5. SUMMARY

Several natural and synthetic carboxylate-containing polymeric compounds have been shown to greatly reduce the calcite crystal growth rate at a fixed calcite supersaturation and pH=8.5. These synthetic and natural inhibitors seem well suited for use as scale inhibitors in a range of commercial applications. Further work characterizing the crystal growth inhibition process of natural and synthetic carboxylate-containing polymeric compounds under actual industrial conditions seems appropriate.

ACKNOWLEDGMENTS

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