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Calcite Crystal Growth Rate Inhibition by Polycarboxylic Acids

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Calcite crystal growth rates measured in the presence of several polycarboxyclic acids show that tetrahydrofurantetracarboxylic acid (THFTCA) and cyclopentanetetracarboxylic acid (CPTCA) are effective growth rate inhibitors at low solution concentrations (0.01 to 1 mg/L). In contrast, linear polycarbocylic acids (citric acid and tricarballylic acid) had no inhibiting effect on calcite growth rates at concentrations up to 10 mg/L. Calcite crystal growth rate inhibition by cyclic polycarboxyclic acids appears to involve blockage of crystal growth sites on the mineral surface by several carboxylate groups. Growth morphology varied for growth in the absence and in the presence of both THFTCA and CPTCA. More effective growth rate reduction by CPTCA relative to THFTCA suggests that inhibitor carboxylate stereochemical orientation controls calcite surface interaction with carboxylate inhibitors.

Key Words: **calcite; inhibitor; polycarboxylic acid; kinetics.**

INTRODUCTION

Calcium carbonate scale formation is a significant problem in large commercial water treatment processes including cooling water technology and desalination. Carbonate scale formation is often alleviated by the use of chemical water treatment additives. Chemical additives, known as "threshold inhibitors," reduce or eliminate scale by inhibiting calcium carbonate formation. However, threshold inhibitors in use today often contain nitrogen or phosphorus which present a water quality problem by contributing to nutrient loading in lakes and rivers (1). Polyelectrolyte threshold inhibitors without P or N, employed to reduce or eliminate mineral scale formation while minimizing nutrient loading, may have physical or chemical properties that make it unsuitable for use as a commercial scale inhibitor.

Natural organic polyelectrolyte acids (humic and fulvic acids) are effective crystal growth inhibitors (2, 3), but have variable structure. For example, fulvic acids from different sources within the Florida Everglades have dissimilar calcite growth rate inhibition properties (4). Factors regulating calcite growth rate inhibition by aquatic fulvic acids include structure, molecular weight, functional group character, and functional group ionization. It seems likely that the factors in fulvic acids that enhance their effectiveness as calcite growth inhibitors may suggest compounds or arrangements of carboxylate groups that are useful as threshold inhibitors.

Kinetic inhibitors have different effects on calcite growth depending on how these compounds interact with specific growth sites on calcite surfaces (5). Compounds binding strongly to calcite growth sites (dislocations on the calcite surface, termed "kinks") are often efficient growth inhibitors; effective compounds are usually also good sequestering agents for lattice cations (6). However, not all good sequestering ligands are good threshold inhibitors. Adsorption, affinity, and potential as a growth rate inhibitor are enhanced by low solubility of salts involving the lattice ions and the inhibiting anion.

In this report we examined growth rate inhibition by four polycarboxylic acids. Two pairs of polycarboxylic acids, cyclic and linear, were chosen for study because of structural characteristics analogous to structural components of humic and fulvic acids (7, 8).

MATERIALS AND METHODS

Analytical reagent grade chemicals (except where noted), distilled water, and grade A glassware are used in all experiments. Tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) and 1,2,3,4-cyclopentanetetracarboxylic acid (CPTCA) were purchased from TCI America, 9211 N. Harborgate St., Portland, OR 97303 (Fig. 1 and Table 1) (the use of trade names is for identification purposes only and does not constitute endorsement by the United States Geological Survey). Table 1 demonstrates that both cyclic polycarboxylic acids contain only trace amounts of impurities that may enhance calcite growth rate inhibition. Citric acid monohydrate was purchased from J. T. Baker Chemical Co. Tricarballylic acid was purchased from Aldrich Chemical Co.

Stereochemical configurations of THFTCA and CPTCA were determined by comparing the infrared spectra of cyclic anhydrides of these compounds with standards of known stereochemical configuration. The cyclic anhydrides were synthesized by dissolving these compounds in acetic anhydride followed by evaporation to dryness. Infrared spectra were determined in KBr pellets on a Perkin Elmer System 2000 FT-IR. The THFTCA was in the 2*c*,3*t*,4*t*,5*c*-configuration, and the CPTCA was in the cis,cis,cis,cis-configuration (Fig. 1).

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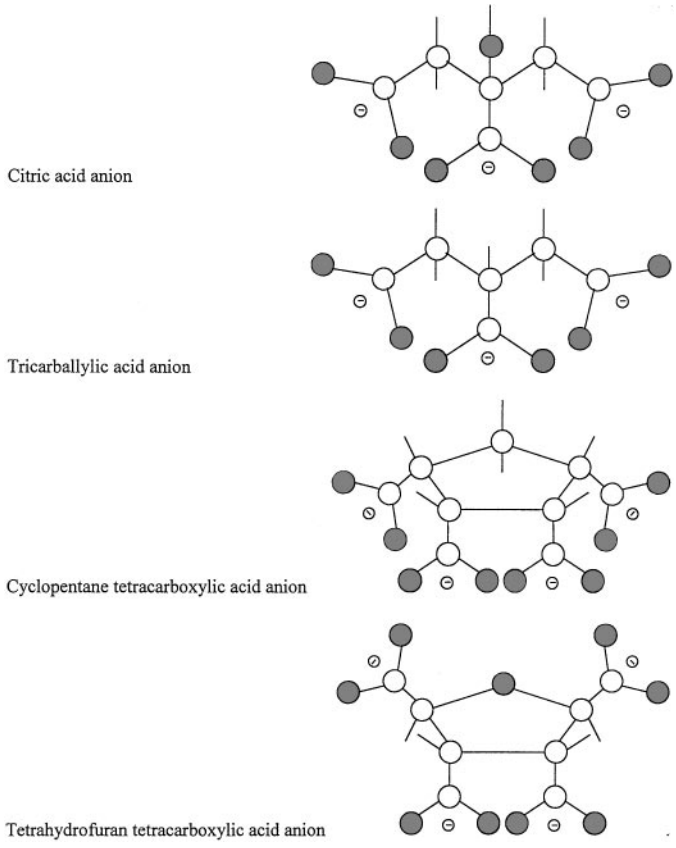

FIG. 1. Schematic diagram of polycarboxylic acid anions used in this study.

Calcite crystal growth experiments were carried out with inhibitor concentrations varying by intervals of an order of magnitude (i.e., 1.0, 0.1, and 0.01 mg/L). Tricarballylic acid and citric acid, which were less effective growth inhibitors, were used in experiments at concentrations up to 10 mg/L.

Calcite growth rates are determined using a constant composition experimental system (9). Constant solution chemical composition during each experiment maintained constant calcite supersaturation (Table 2) by potentiometrically controlled addition of lattice ions (as calcium ion and carbonate ion), enabling accurate determination of growth rates in the absence and in the presence of added substances.

TABLE 1
Chemical Analysis of Model Compounds

	1,2,3,4-Cyclopentane-tetracarboxylic acid	Tetrahydrofuran-2,3,4,5-tetracarboxylic acid
Formula	$C_5H_6(COOH)_4$	$C_4H_4O(COOH)_4$
Molecular weight	248.14	246.17
Carbon (%)[a]	43.97	38.85
Hydrogen (%)	4.07	3.24
Oxygen (%)	51.82	56.45
Nitrogen (%)	<0.01	0.02
Ash (%)	0.1	<0.05
Total	100.07	99.08
Dry-loss (%)[b]	0.11	0.49

[a] Percentages are weight percent of dried sample.
[b] Samples were dried in air at 105°C overnight before further analysis.

TABLE 2
Summary of Experiments and Results[a]

Compound	Inhibitor concn (mg/L)	Rate (mol m^{-2} min^{-1})	r^2
Cyclic Polycarboxylic Acids			
Control	0.00	6.56×10^{-5}	0.9979
Control	0.00	7.55×10^{-5}	0.9984
Cyclopentanetetracarboxylic acid	1.00	0	n/a
Cyclopentanetetracarboxylic acid	1.00	0	n/a
Cyclopentanetetracarboxylic acid	0.10	0	n/a
Cyclopentanetetracarboxylic acid	0.10	0	n/a
Cyclopentanetetracarboxylic acid	0.01	1.67×10^{-5}	0.9967
Cyclopentanetetracarboxylic acid	0.01	1.31×10^{-5}	0.9879
Tetrahydrofurantetracarboxylic acid	1.00	0	n/a
Tetrahydrofurantetracarboxylic acid	1.00	0	n/a
Tetrahydrofurantetracarboxylic acid	0.10	2.91×10^{-5}	0.9983
Tetrahydrofurantetracarboxylic acid	0.10	2.45×10^{-5}	0.9977
Linear Polycarboxylic Acids			
Control	0.00	9.97×10^{-5}	0.9990
Control	0.00	9.78×10^{-5}	0.9993
Tricarballylic acid	1.00	1.07×10^{-4}	0.9993
Tricarballylic acid	1.00	1.12×10^{-4}	0.9990
Tricarballylic acid	10.00	7.76×10^{-5}	0.9985
Tricarballylic acid	10.00	1.04×10^{-4}	0.9989
Citric acid	1.00	7.57×10^{-5}	0.9986
Citric acid	1.00	6.70×10^{-5}	0.9991
Citric acid	10.00	6.58×10^{-5}	0.9979
Citric acid	10.00	6.35×10^{-5}	0.9992

[a] Experimental conditions: $T = 25°C$; pH 8.55 ± 0.02; Ω (ion activity product/K_{sp}) = 4.5; $[Ca]_{TOTAL} = [CO_3]_{TOTAL} = 0.0019$ M; $P_{CO_2} = 10^{-3.55}$ atm.

The calcite growth reaction at pH ~8.5 can be written as

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_{3\ solid} + H^+. \quad [1]$$

During calcite seeded crystallization, decreasing pH causes the double burette (Fig. 2) system to add calcium chloride and sodium carbonate titrant solutions (at 5× reactor solution concentration). Titrant solutions contained potassium nitrate to maintain constant ionic strength. Measurement of total dissolved calcium ion concentration and alkalinity before and after all experiments verified constant composition. Experiments were run for 100 min.

Metastable working solutions (IAP (the ion activity product of calcium ion and carbonate ion)/K_{sp} (the thermodynamic solubility product of calcite) ~4.5), prepared prior to the start of each experiment by dropwise addition of calcium solutions to carbonate solution in the reaction cell, are stable for at least 24 h. Ionic strength was maintained at 0.1 M. Seed material (Baker Analyzed Reagent calcium carbonate, J. T. Baker Chemical, Lot No. 26832) used was analyzed by X-ray

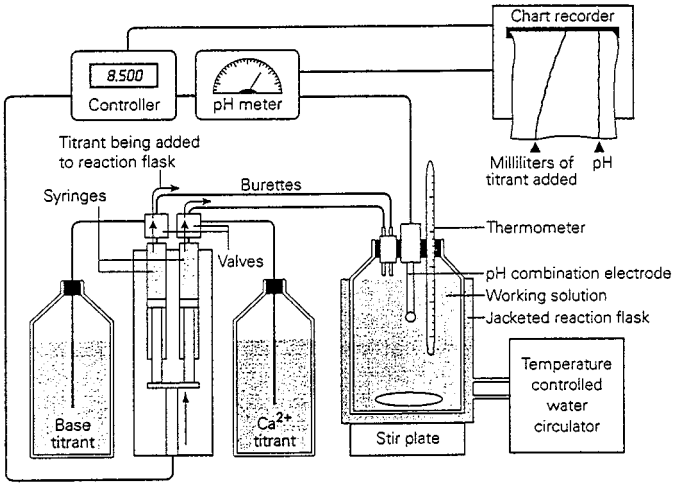

FIG. 2. Schematic diagram of the constant composition experimental system.

diffractometry and was free of any mineral phases other than calcite. The specific surface area (SA) (0.256 ± 0.008 m^2/g) was determined by a three-point nitrogen adsorption technique (10). Organic acid solutions (filtered through 0.1-μm Whatman cellulose nitrate filters and used within 36 h) were prepared in sodium bicarbonate working solutions.

Experiments were initiated by rapid addition of dry seed material to the solutions. A computer and strip-chart recorder monitored titrant addition in response to calcite growth. The slope of the line representing the added titrant versus time is a direct measure of calcite growth and is converted to crystal growth rates by the following equation:

$$\text{rate (mol m}^{-2}\text{ min}^{-1}) = \text{slope (L/min)} m_{\text{titrant}}\text{(mol/L)}/(\text{mass}_{\text{seed}}\text{SA}_{\text{seed}}(\text{m}^2). \quad [2]$$

Experiments yielded linear plots for titrant addition over time ($r^2 > 0.995$).

Growth inhibition by organic acids is expressed as reduced rates, R/R_o, for each experiment:

$$R/R_o = \text{rate in the presence of inhibitor/rate in the absence of inhibitor.} \quad [3]$$

Thus, a smaller reduced rate indicates greater growth inhibition.

Upon completion of experiments, solutions were rapidly filtered through 0.45-μm Whatman cellulose nitrate membrane filters. The filters with the crystals were air-dried for 15 min at 50°C. Selected crystal samples were viewed in secondary electron mode on a JEOL scanning electron microscope at the Denver Federal Center in Lakewood, CO, under a 20-kV, 64-μA beam.

RESULTS AND DISCUSSION

Calcite crystal growth begins immediately upon addition of seed and plots of added reagent versus time are linear (Fig. 3). Calcite growth rates are calculated from the slope of titrant added versus time (Fig. 3) using Eq. [2]. Reagent addition plots have a zero intercept and good linearity for calcite growth both in the absence and in the presence of polycarboxylic acids. Some plots in Fig. 3 are slightly nonlinear at the start of crystal growth. This reflects time necessary for the inhibition molecules to reach an adsorbent steady-state distribution on the crystal surface. Calcite growth rate inhibition effectiveness can be illustrated by plotting the reduced rate (Eq. [3]) versus inhibitor concentration. In the absence of added polycarboxylic acid, the reduced rate is one (Fig. 4).

Calcite growth in the presence of CPTCA is completely prevented at the 1.0 and 0.1 mg/L concentrations (the reduced rate is zero) (Fig. 4). Growth rate is decreased with respect to that of control experiments by about 80% at a CPTCA concentration of 0.01 mg/L (Fig. 4, Table 2). This low concentration for an effective inhibiting compound indicates that CPTCA is about as efficient a calcite growth rate inhibitor as commercial phosphonate inhibitors (11).

THFTCA is a somewhat less efficient calcite growth rate inhibitor than CPTCA: calcite growth was prevented at 1.0 mg/L concentration and was reduced by about 60% at a concentration of 0.1 mg/L (Fig. 4). By weight, THFTCA exhibits inhibitory effectiveness similar to that of hydrophobic humic substances (mostly fulvic acid) from the Florida Everglades. For these aquatic fulvic acids, a few tenths of a milligram per liter causes significant calcite growth rate reduction (4). Unlike

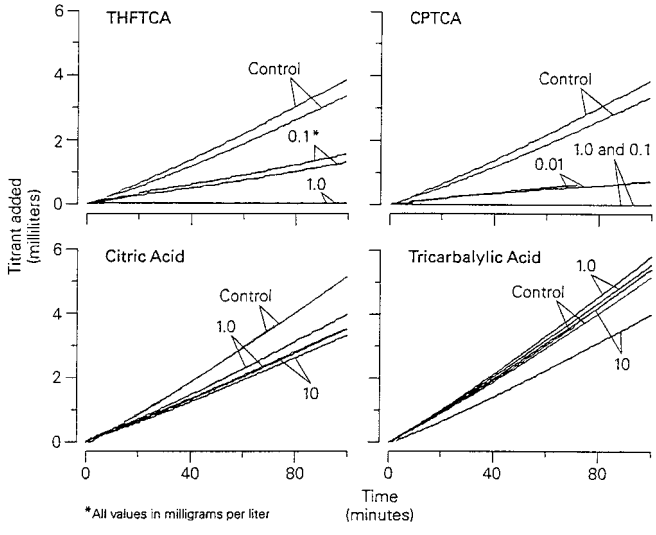

FIG. 3. Crystal growth of calcium carbonate onto calcite seed crystals at constant supersaturation expressed as the amount of calcite growth (proportional to titrant added) versus time in the absence and in the presence of polycarboxylates. Calcite seeded crystal growth rates are calculated from the slopes of the best-fit curves that vary with polycarboxylate concentration. The legend indicates the carboxylate concentration in milligrams per liter.

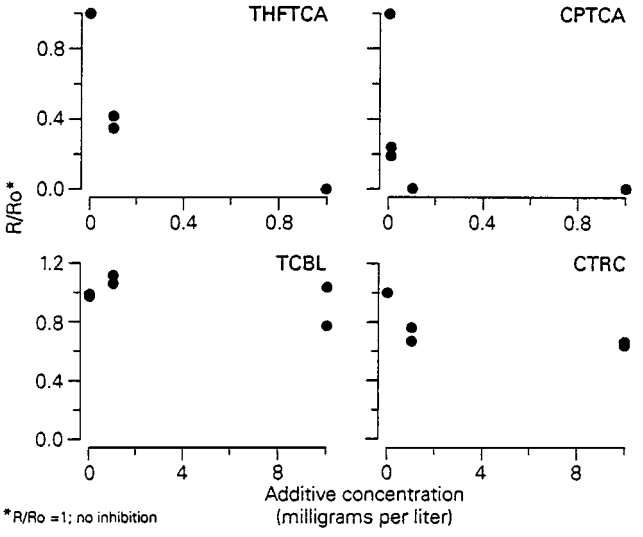

FIG. 4. Calcite crystal growth rates expressed as reduced rates (R/R_o) for experiments at various concentrations of polycarboxylic acids plotted versus the polycarboxylate acid concentration. Each point represents one experiment. $R/R_o = 1$ indicates no crystal growth inhibition.

natural humic acid substances or the rigid, cyclic, polycarboxylic acids discussed above, citric acid and tricarballylic acids are poor calcite growth inhibitors. Citric acid exhibited only moderate calcite crystal growth rate reduction at concentrations as high as 10 mg/L (Table 2, Fig. 4), while the growth rate in the presence of tricarballylic acid was higher than that in the control experiments at 1 mg/L and yielded mixed results at 10 mg/L. The similarity in calcite growth rate inhibition of THFTCA and aquatic humic acids suggests that calcite crystal growth rate inhibition efficiency may be a diagnostic tool in structural studies of humic and fulvic acids. High calcite growth rate inhibition efficiency of humic and fulvic acids is consistent with multiple ionized carboxylate groups attached directly to a five-membered ring. Other carboxylate configurations in fulvic acids may also play a part in calcite growth rate reduction.

Citric acid, tricarballylic acid, CPTCA, and THFTCA have similar degrees of ionization at pH 8.55 and under the experimental conditions employed in this study, the decrease in crystallization rates in the presence of THFTCA or CPTCA is not caused by calcium–inhibitor complex formation. The percent calcium complexed even at the highest inhibitor concentrations is less than 5% of total calcium.

Reacted and unreacted calcite seed crystals were examined by scanning electron microscopy to characterize morphological changes that occurred during growth with and without the presence of cyclic polycarboxylic acids (Fig. 5). The crystal size and morphology of calcite seed crystals prior to crystal growth are shown in Fig. 5A. The calcite crystal size and growth morphology following calcite crystal growth in the absence of an inhibitor are shown in Fig. 5B. Unreacted calcite seed crystals

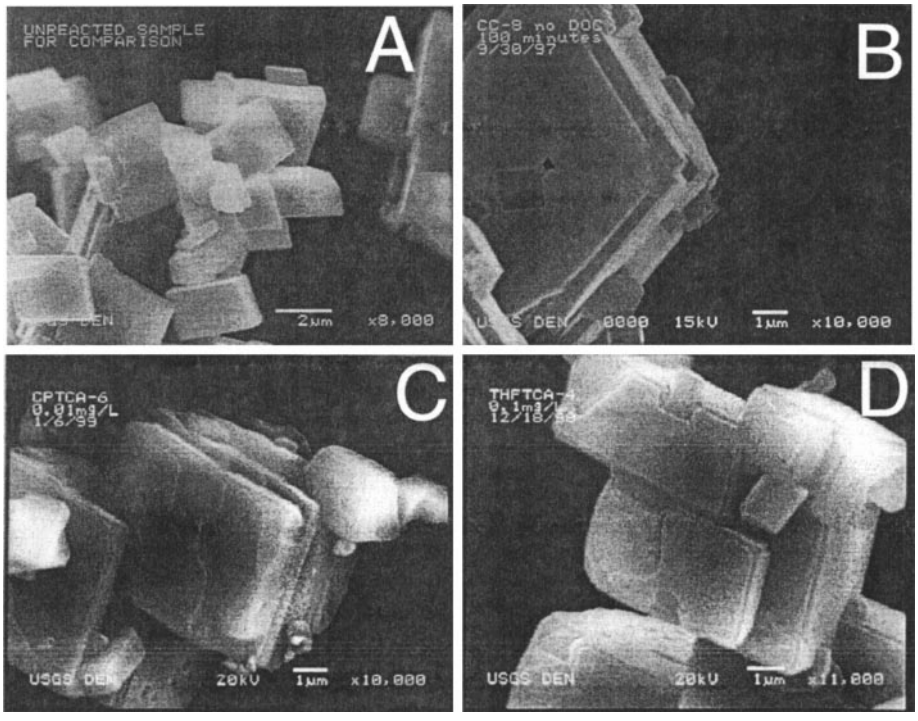

FIG. 5. SEM photomicrographs of calcite seed crystals before and after crystal growth experiments in the absence and in the presence of cyclic polycarboxylic acids. (A) Unreacted seed crystals. (B) Calcite crystals grown for 100 min with no added organic acids. Note the laterally continuous planes of growth. (C) Calcite seed after growing for 100 min in a solution containing 0.01 mg/L CPTCA and (D) in a solution containing 0.1 mg/L THFTCA. Note the laterally discontinuous planes of growth in photomicrographs C and D.

are well-formed, sharp-edged rhombs. Seed crystals that grew for 100 min in the absence of organic acids increased their mass by about 25% and exhibited uniform growth planes with step features on the face perimeters.

Calcite seed crystal morphology associated with growth in the presence of cyclic polycarboxylic acids differs from seed crystal growth morphology observed in control experiments. Calcite growth in solutions containing 0.01 mg/L CPTCA exhibited a growth rate about 20% of the control experiment (Table 2). Crystal mass increased by less than 10% and crystal growth planes are not uniform (Fig. 5C). Growth surfaces and growth edges appear broken and discontinuous. Seed crystals grown in solutions containing higher CPTCA concentrations exhibited no growth at all. Growth in solutions containing 0.1 mg/L THFTCA (the growth rate was reduced to about 40% of the control experiment (Table 2)) also had somewhat discontinuous growth planes (Fig. 5D). Changes in growth morphology in comparison with the control experiment are less pronounced for growth in the presence of THFTCA than in the presence of CPTCA.

Calcite seeded crystal growth at moderate supersaturation is initiated by multiple surface nucleation events followed by spiral growth (12). In the absence of growth rate inhibitors, small growth spirals merge to form straight steps. Calcite seeded growth in the presence of solutes exhibits adsorption of these solutes. The adsorption process reduces the growth rate by blocking the propagation of the uniform growth steps. This adsorption–blockage process produces the jagged, discontinuous growth surface appearance shown in Figs. 5C and 5D.

Crystal growth inhibition occurs in several ways, but all mechanisms appear to require adsorption of inhibiting molecules on the crystal surface. The growth rate inhibition effectiveness of CPTCA at low concentrations implies that low surface coverage mediates the rate-determining step. This observation is consistent with preferential adsorption of CPTCA at growth sites on the crystal surface. Determination of calcite surface coverage by adsorption of CPTCA from solution may assist in elaborating the mechanism of inhibition. However, it is difficult to quantify the total area occupied by CPTCA on a calcite surface because the interfacial properties and adsorption cross section are unknown. Moreover, these properties may vary with changing solution composition. CPTCA adsorption by calcite was a small fraction of the total solution concentration. Changes in CPTCA concentration due to adsorption were near the analytical detection limit.

Inhibitor molecular structure differences may modify the crystal growth process. Didymus *et al.* (13) examined the influence of low-molecular-weight and macromolecular organic additives on the morphology of calcium carbonate. They found that the efficiency of monofunctional additives to influence morphology increased with overall charge. For the same charge, the morphological changes were reduced with decreasing partial charge on the ligand oxygen atoms. Additional inhibitor effectiveness factors for multifunctional molecules include distance between ligands and ligand conformation. In the case of CPTCA and THFTCA, the distance between carboxylate groups and their orientation is fixed by stereochemical requirements (Fig. 1). Cyclopentane rings are slightly puckered. Intramolecular hydrogen bonding between adjacent carboxyl groups stabilizes the ring into a more ridged structure for partially ionized acids. Ionized acids are stabilized by charge repulsion. Ring configuration can change to favor certain metal complexes or cyclic anhydride structures. For all polycarboxylates studied here, the distances between ionized carboxyl groups are similar: each carboxyl group is separated from an adjacent carboxyl group by two carbon atoms.

Acrylic polyelectrolyte (polycarboxylate) structure is related to the effectiveness of these molecules as inhibitors of calcium oxalate crystallization (14). Growth rate inhibition by acrylate polyelectrolytes increased with increasing polymer acid functional group content. This observation is consistent with our observation that compounds with four carboxyl groups (CPTCA AND THFTCA) are more effective inhibitors than those with three carboxyl groups (citric acid and tricarballylic acid). Crystal growth inhibition by polyacrylates appears to be due to polymer adsorption on the growing crystal surface. Polyacrylates are more effective in inhibiting calcium oxalate growth than polymethylacryates although they are similar in calcium ion binding. More efficient growth inhibition by polyacrylates than polymethylacrylates is due to closed chain packing on the crystal surface of the polyacrylates—subtle differences in inhibitor stereochemistry lead to distinct differences in crystal growth rate.

Carboxylate groups of THFTCA have a different stereochemical orientation (two carboxylates are above the plane of the ring and two are below the plane of the ring) than the carboxyl groups of CPTCA (all carboxyl groups are on the same side of the plane of the ring) (Fig. 1). With all four carboxyl groups of the CPTCA in a cis,cis,cis,cis-configuration, CPTCA has more available binding sites adjacent to the plane of the calcite surface and therefore is a better growth inhibitor than THFTCA.

Carboxylate additives' ability to retard crystallization is related to the match of the distance between carboxyl groups and the calcium ions in the calcite lattice—rigid molecular structures tend to be more specific in inhibition properties than more flexible molecules (6). In our experiments, both rigid cyclic tetracarboxylic acids are effective calcite growth rate inhibitors; flexible polycarboxylic acids (i.e., citric and tricarballylic acids) are not. A possible reason for this difference between rigid and flexible polycarboxylic acids is that it is energetically more difficult to detach larger, rigid inhibitors because two or more bonds must be broken simultaneously (15), in contrast to the flexible aliphatic polycarboxylic acids that are more free to detach bond by bond.

SUMMARY

Calcite crystal growth rates are reduced in the presence of low concentrations of cyclic, rigid, polycarboxylic acids.

Tetrahydrofurantetracarboxylic acid and cyclopentanetetracarboxylic acid reduced calcite crystal growth rates at concentrations from 0.01 to 0.1 mg/L. Under the same conditions, the linear polycarboxylic acids cause no growth rate reduction. Growth morphology differed during crystallization in the presence and in the absence of inhibitors, indicating a surface inhibition process. Rate reduction was influenced by carboxylate group stereochemical orientation for the cyclic polycarboxyclic acids. Greater growth rate reduction by CPTCA relative to THFTCA suggests that carboxylate functional group orientation has a predominate role in calcite surface interaction with carboxylate inhibitors. Polycarboxylic acid structural rigidity and stereochemical orientation appears to satisfy a steric requirement for calcite growth inhibition effectiveness. Cyclic polycarboxylic acids and/or their polymeric analogs and derivatives may be useful in preventing calcium carbonate scale formation in a range of industrial and water processing applications.

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