Carboxymethyl Inulin: A New Inhibitor for Calcium Carbonate Precipitation

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ABSTRACT: A new polysaccharide-based polycarboxylate, carboxymethyl inulin (CMI), was synthesized recently. The influence of small amounts (0.1–200 ppm) of this material on the crystallization of calcium carbonate, an important scale-forming salt, is studied. The effects of CMI are compared to those of a commercial inhibitor (a copolymer of acrylate and maleate) and of other carboxymethylated saccharides. It is shown that CMI is a good calcium carbonate precipitation inhibitor. CMI influences the spontaneous precipitation of calcium carbonate, the morphology of the formed crystals (vaterite and calcite), and the growth rate of calcium carbonate seed crystals. The effect is related to the carboxylate content, the chainlength, and the concentration of the additive. For the application of CMI as crystallization inhibitor, products with a high degree of substitution (degree of substitution > 1) and a high degree of polymerization (average degree of polymerization = 30) are the most effective. Also, other carboxymethylated polysaccharides (dextrins, cellulose) show good crystallization-inhibition properties, although the performance of the copolymer of acrylate and maleate is not met. A great advantage of CMI, as compared to carboxymethyl cellulose (CMC), is that aqueous solutions of CMI display, contrary to those of CMC, a very low viscosity. A carboxymethylated disaccharide (carboxymethyl sucrose) has no influence on the calcium carbonate crystallization, which shows that the long-chain character is essential for a polycarboxylate inhibitor. *JAOCS 73,* 55–62 (1996).

KEY WORDS: Carboxymethyl cellulose, carboxymethyl dextrin, carboxymethyl sucrose, crystallization inhibition, detergents, polyelectrolyte, polyfructoside, polysaccharide.

The inhibition of precipitation of sparingly soluble salts, such as calcium carbonate, is important in many fields. Because of the lower solubility of calcium carbonate at higher temperatures, calcium carbonate scale formation occurs whenever hard water is heated, for example, in boilers and heat exchangers, during cleaning processes, and during the washing of laundry (also referred to as incrustation) (1–3). Also, during seawater desalination, the precipitation of calcium carbonate is a major operating problem (4). Due to relatively high concentrations of Ca ions and dissolved CO_2 in subsurface waters, calcium carbonate is an important scale-forming mineral during gas and oil production (5).

It is well established that certain compounds such as organic phosphonates (2,4–6), inorganic polyphosphates (6–8), polyelectrolytes (3,4,6,8–11), and surfactants (12), as well as certain metal ions, such as Mg (5,13), reduce the growth of calcium carbonate. The most frequently used inhibitors for calcium carbonate deposition are polyelectrolytes such as polyacrylate, polymethacrylate, and copolymers of acrylate and maleate. Possible mechanisms for the effect of inhibitors are adsorption on growing crystal surfaces leading to growth inhibition, sequestration of Ca (II) ions, and a dispersing action for calcium carbonate (3,10,11).

Because of the inefficient biodegradability of currently used inhibitors, there is a need for new inhibitors that are more environmentally acceptable. Polysaccharides are particularly attractive as raw materials for modification into polyelectrolytes, which can be applied as crystallization inhibitors. The parent polysaccharides and the carboxylated derivatives are expected to be biodegradable, provided that the molecular weight is not too high and that part of the monosaccharide units is still present.

A new polysaccharide-derived polycarboxylate has been synthesized starting from inulin. Inulin is a natural β-(2→1)-polyfructoside with a glucose unit at the reducing end, which recently became commercially available. Carboxylate groups were introduced into the polysaccharide by carboxymethylation with monochloroacetate as the reagent (14). This paper presents the potential application of the product, carboxymethyl inulin (CMI), as inhibitor for calcium carbonate precipitation. Spontaneous precipitation as well as seeded crystal growth experiments were performed. Effects of the addition of CMI were compared to those of a commercial inhibitor (a copolymer of acrylate and maleate) and of other carboxymethylated saccharides [carboxymethyl sucrose (CMS), carboxymethyl dextrins (CMD), and carboxymethyl cellulose (CMC)].

EXPERIMENTAL PROCEDURES

Inhibitors used for the crystallization experiments. CMI was obtained by reaction of inulin with monochloroacetate

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(MCA) in an aqueous alkaline medium (14). As a starting material, inulin with an average degree of polymerization (DP = 30) (E. Merck, Darmstadt, Germany; Inulin für biochemische Zwecke, type I inulin) as well as inulin with an average DP = 10 (isolated from chicory root, donated by Suiker Unie, Roosendaal, The Netherlands) (type II inulin) were used. CMI samples with a degree of substitution (d.s.) of 0.20 to 1.05 were synthesized.

Sucrose was carboxymethylated using the same procedure as for CMI. Sucrose is the shortest oligosaccharide from the inulin series. CMS with d.s. = 1.36 and with d.s. = 2.00 was prepared.

CMD was obtained by carboxymethylating linear dextrins using the same procedure as for CMI. Linear dextrins were prepared from waxy maize starch using a method described by Besemer (15). After gelatinizing at 100°C, waxy maize starch was incubated at 55°C and a pH of 5 with pullulanase (EC 3.2.1.41, Promozyme; Novo Nordisk A/S, Bagsvaerd, Denmark), resulting in specific hydrolysis of the α-1,6 bonds. The DP of linear dextrins shows a bimodal distribution: 75% consists of a fraction with DP = 15–45, and 25% of a fraction with a DP = 45–75 (15). The d.s. of CMD was 0.81.

CMC, type DT732, was donated by AKZO Nobel Central Research (Arnhem, The Netherlands). The d.s. is 0.57, and the average DP = 300.

PMAA is a copolymer of maleate and acrylate. It was obtained from BASF (Arnhem, The Netherlands) (Sokalan CP 5). The average molecular weight is about 70,000. This product is used as an incrustation inhibitor in detergent formulations (16).

Precipitation of calcium carbonate. Calcium carbonate crystals were precipitated by mixing solutions containing stoichiometric amounts of calcium and carbonate ions in concentrations that suffice to provoke spontaneous precipitation of calcium carbonate. All experiments were performed in duplicate. The solutions were prepared with 0.01 M NaCl dissolved in bidistilled water and were filtered through a Millipore 0.22 μ filter (Millipore Corp., Bedford, MA) before use. The pH was adjusted with a diluted HCl or NaOH solution. After mixing the two solutions, precipitation of calcium carbonate was monitored by measuring the concentration of free Ca^{2+} ions by a calcium-selective electrode (Unicam Analytical Systems, Eindhoven, The Netherlands) and a calomel reference electrode (Unicam Analytical Systems) coupled to a Metrohm 605 pH meter (Metrohm AG, Herisau, Switzerland). At the end of the experiment, the crystals were filtered off using a Millipore 0.22 μ filter and dried at 50°C.

For experiments at pH 10, total Ca^{2+} and CO_3^{2-} concentrations, after mixing, were 2.5 10^{-3} M. For calcium carbonate precipitation at pH 8, these concentrations were 2.5 10^{-2} M. For experiments at pH 7, Ca^{2+} and CO_3^{2-} concentrations after mixing were 2.5 10^{-2} and 0.175 M, respectively.

Characterization of calcium carbonate crystals. The dry crystals were examined by scanning electron microscopy (SEM), using a JEOL JSM-5400 scanning microscope (Yeol Ltd., Tokyo, Japan). Modifications of the crystals were determined using X-ray diffraction (α_1 Guinier Camera, FR522; Enras-Nonius, Delft, The Netherlands).

Constant composition experiments. The constant composition technique is a widely used method to study crystal-growth kinetics at constant supersaturation (7,8,17–20). The apparatus used for the experiments is drawn schematically in Figure 1. A teflon vessel was thermostatted at 25°C. A metastable supersaturated solution was prepared as follows: 470 mL 0.1 M NaCl solution was brought into the vessel. Then 15 mL of solution A (0.02 M $CaCl_2 \cdot 2H_2O$, 0.08 M NaCl) and 15 mL solution B (0.02 M K_2CO_3, 0.08 M NaCl) were added. Then 100 μL solution of the inhibitor in 0.1 M NaCl was added. The pH was adjusted to 10.2 with 0.2 M NaOH. All solutions were prepared with bidistilled water and were filtered with a Millipore 0.22 μ filter. The solution was kept under nitrogen atmosphere to avoid dissolution of air CO_2. Agitation was performed by an overhead teflon stirrer.

Metastability of the solution was verified by an equilibration period of 1 h. The experiments were started by addition of a suspension of calcite seed crystals (about 300 mg). The seeds (Merck Suprapure Calcium Carbonate) were ripened for at least two months before use. Upon addition of the seed crystals to the supersaturated solution, their growth started. Depletion of ions consumed by the growing crystals was compensated by addition of more concentrated calcium and carbonate solutions (solutions A and B) from two burettes (Metrohm 655 Dosimat), which were controlled by a Metrohm 614 Impulsomat used in combination with a calcium-selective electrode (Radiometer Analytical SA, Lyon, France) and a calomel reference electrode, coupled to a Metrohm 605 pH Meter. The added volume of solution A was registered by a computer. Formation of H^+ from HCO_3^- during the crystal growth was compensated by adding a NaOH solution from the third burette (Metrohm 655 Dosimat), which was used in combination with a Metrohm 614 Impulsomat and a Metrohm 605 pH Meter.

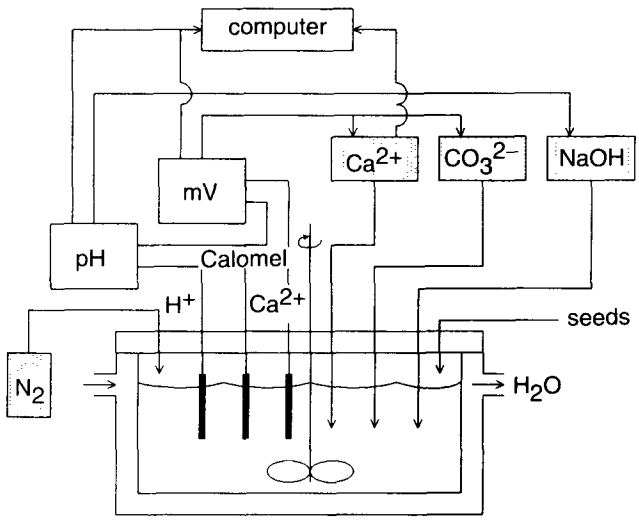

FIG. 1. Apparatus used for constant composition experiments.

To ensure that the supersaturation remained constant during the experiment, the concentration of free Ca ions in the solution after filtration of the crystals was checked by titration with 0.001 M ethylenediaminetetraacetate.

Viscosity measurements. The viscosities of samples of CMI and CMS were determined by subjecting these samples to a shear stress from 0.06 to 700 Pa in a stress viscosity test, using a Bohlin CS Rheometer (Bohlin Reologi AB; Lund, Sweden).

RESULTS AND DISCUSSION

The driving force for calcium carbonate precipitation in aqueous solutions at 25°C. The driving force for crystallization is often expressed by the supersaturation ratio S of the solution, defined as:

$$S = \left\{ \frac{y_2\left[Ca^{2+}\right] \bullet y_2\left[CO_3^{2-}\right]}{K_S} \right\}^{1/2} \quad [1]$$

where y_2 is the ion activity coefficient of divalent ions, and $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of free Ca^{2+} and CO_3^{2-} ions in the solution. K_S is the thermodynamic solubility product of calcium carbonate. Calcium carbonate can crystallize from aqueous solutions in three anhydrous polymorphs: calcite, vaterite, and aragonite (21,22). Calcite has the highest thermodynamic stability at ordinary temperature and pressure. Vaterite and aragonite are metastable modifications, which transform to calcite on aging. While vaterite is formed at low temperatures (<40°C), aragonite is generated at temperatures higher than 50°C. At 25°C the value of K_s for calcite = $4.72\ 10^{-9}$ (23). For vaterite, K_S at 25°C is $1.22\ 10^{-8}$ (3).

In aqueous solutions Ca^{2+} and CO_3^{2-} ions form several soluble complexes with each other and with OH^- and H^+ ions, respectively (3). The equilibrium constants of these equilibria (Table 1) were used in calculating the concentrations of free Ca^{2+} and CO_3^{2-} ions.

Ion activity coefficients y_z for z-valent ions were calculated using the modified Debye–Hückel equation proposed by Davies (27):

$$\log y_z = -0.5091 z^2 \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right) \quad [2]$$

$$\text{with } I \text{ (ionic strength)} = \frac{\sum c_i z_i^2}{2}$$

TABLE 1
Calcium Carbonate Equilibria in Aqueous Solutions and Corresponding Equilibrium Constants at 25°C

Equilibrium	K at 25°C ($dm^3\ mol^{-1}$)	Reference
$H^+ + HCO_3^- \leftrightarrows H_2CO_3$	$2.249\ 10^6$	24
$H^+ + CO_3^{2-} \leftrightarrows HCO_3^-$	$2.133\ 10^{10}$	25
$Ca^{2+} + CO_3^{2-} \leftrightarrows CaCO_3^0$	1412	26
$Ca^{2+} + HCO_3^- \leftrightarrows CaHCO_3^+$	10.0	26
$Ca^{2+} + OH^- \leftrightarrows CaOH^+$	19.95	26

For the calcium carbonate precipitation experiments at pH values of 10, 8, and 7, the initial supersaturation ratio was calculated to be 6.25, 8.05, and 5.24, respectively. These supersaturation ratios were sufficiently high to cause spontaneous nucleation and immediate precipitation of calcium carbonate in the cases where no inhibitor was added.

For the seeded growth experiments, a supersaturation ratio $S = 2.18$ was applied. No spontaneous crystallization of calcium carbonate occurs within the time scale of the experiment. Only growth of the added seeds takes place.

Calcium carbonate precipitation experiments. The influence of the addition of a minor amount of additive on the precipitation kinetics of calcium carbonate was investigated. Supersaturated calcium carbonate solutions were prepared with or without an additive. CMI with different d.s. values (0.36, 0.68, and 1.05) and average DP values (types I and II) were tested and compared with the blank experiment. Effects were also compared with those of a known carboxylate inhibitor (PMAA). Other carboxymethylated saccharides such as CMS, CMC, and CMD (see the Experimental Procedures section) were tested as well. The additives were applied at two concentrations (200 and 10 ppm). The experiments were carried out at pH 10, and the decrease in supersaturation was followed by monitoring the response of the calcium-selective electrode (Fig. 2). When the calcium signal was constant, the experiment was stopped by filtering off the crystals.

In a supersaturated calcium carbonate solution, spontaneous nucleation and subsequent growth take place. At the beginning of the precipitation process, progressive nucleation occurs, and the surface available for crystal growth is very small. At this time the decrease in the concentration of free Ca ions is not measurable. The period in which the concentration of free Ca ions remains practically constant is called induction time (t_{ind}). The induction time depends on the nucleation rate J and the growth rate G according to (28):

$$t_{ind} \sim \frac{1}{\left(J \bullet G^3\right)^{1/4}} \quad [3]$$

After the induction time, the surface available for crystal growth becomes sufficiently high to cause a measurable decrease in the concentration of free Ca ions. This decrease continues until equilibrium is reached or until the growth rate becomes too low to notice further changes in the concentration of free Ca ions, as often happens in the presence of an effective growth inhibitor. Thus the curve of the concentration of free Ca ions vs. time, obtained during a precipitation experiment, normally shows an S shape.

In the blank experiment, no induction time was observed because of high nucleation and growth rates at the high initial supersaturation ($S = 6.25$). However, an S shape can still be recognized (Fig. 2). The concentration of free Ca ions, which was initially $1.81\ 10^{-3}$ M, decreased to the equilibrium concentration $C_{eq} = 4.90\ 10^{-4}$ M.

In cases where an inhibitor was added, an induction period was observed. This can be explained by inhibition of crystal

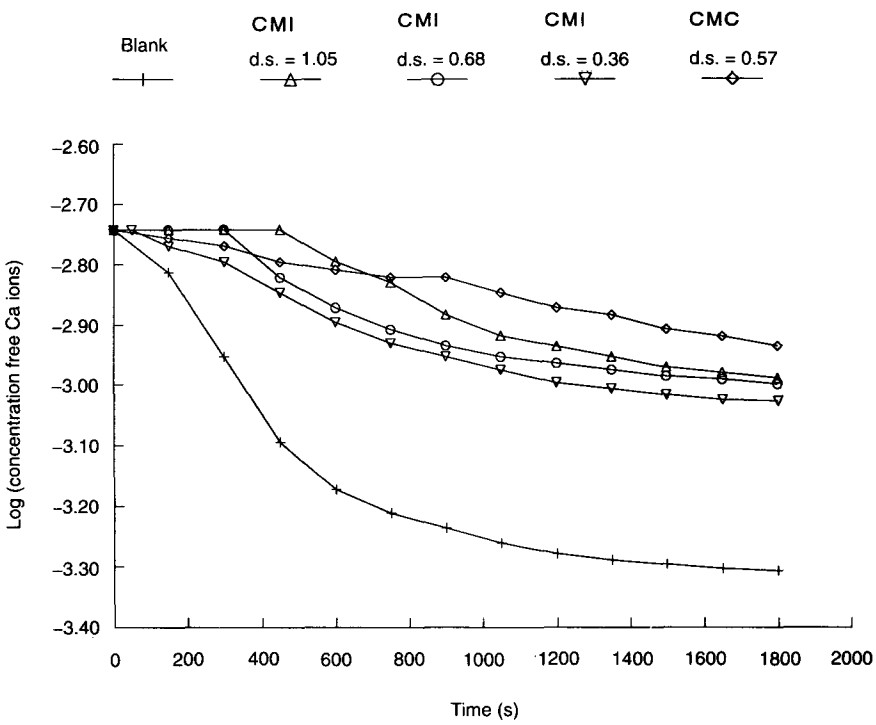

FIG. 2. Response of the calcium-selective electrode during calcium carbonate precipitation experiments (pH = 10; supersaturation ratio $S = 6.25$; concentration of the additives, 200 ppm; CMI prepared with type I inulin). CMI, carboxymethyl inulin; d.s., degree of substitution; CMC, carboxymethyl cellulose.

growth, which influences t_{ind} (Equation 3). Also, the rate of decrease in supersaturation (slope of the curves in Fig. 2) was lower than in the blank experiment. Because of the reduced growth rate, the equilibrium concentration of free Ca ions was not reached within the time scale of the experiment. At the end of the experiment, an apparent equilibrium concentration C_e, which is higher than the equilibrium concentration C_{eq}, was obtained. The effectiveness of an inhibitor can thus be evaluated by three criteria: induction time, apparent equilibrium concentration of free Ca ions, and rate of decrease in concentration. In Table 2 the first two parameters are given for the inhibitors tested.

TABLE 2
Influence of Additives on the Induction Period t_{ind}, and Apparent Equilibrium Concentration of Free Ca Ions, C_e, Observed for Crystallization of Calcium Carbonate from a Solution with pH = 10 and Supersaturation Ratio $S = 6.25$

	10 ppm additive		200 ppm additive	
Inhibitor[a]	t_{ind} (s)	C_e ($\bullet 10^{-4}$ M)	t_{ind} (s)	C_e ($\bullet 10^{-4}$ M)
CMI d.s. = 1.05 (type I)	270	9.55	525	10.30
CMI d.s. = 0.68 (type I)	150	9.33	285	10.00
CMI d.s. = 0.36 (type I)	10	6.30	50	9.40
CMI d.s. = 0.68 (type II)	135	8.33	200	10.00
CMC d.s. = 0.57	—	—	30	11.30
CMD d.s. = 0.81	240	10.00	510	10.63
CMS d.s. = 1.23	0	4.90	0	4.93
CMS d.s. = 2.00	0	4.93	30	4.90
PMAA	760	11.53	—	—

[a]CMI, carboxymethyl inulin; d.s., degree of substitution; CMC, carboxymethyl cellulose; CMS, carboxymethyl sucrose; PMAA, a copolymer of maleate and acrylate.

CMI has an inhibiting effect on the crystallization of calcium carbonate, depending on the d.s. of the products. The induction period observed was longer and the apparent equilibrium concentration C_e was higher when the d.s. was higher. It is generally accepted that polyelectrolytes exert their crystallization-inhibiting properties through adsorption on the crystal surfaces (2). In polycarboxylates (such as CMI) this adsorption is effected by the anionic carboxylate groups. When the carboxylate content (d.s.) is higher, the adsorption on the crystal surfaces increases. PMAA, a polycarboxylate currently used as an effective inhibitor, showed long induction periods, even at a very low concentration (10 ppm). The better performance might be related to its relatively high carboxylic acid content.

The chainlength of the molecule was also important for its performance. CMI prepared with type I inulin was a more effective growth inhibitor than that prepared with type II inulin. CMS, the carboxymethylation product of the smallest inulin oligomer (DP = 2.0), had little or no effect on the observed induction period and apparent equilibrium concentration. Two carboxymethylated polysaccharides, CMC and CMD, with a higher molecular weight than CMI were tested as well. Although addition of CMC caused no long induction period, it is clear from the rate of the decrease in concentration of free Ca ions (see Fig. 2) and the apparent equilibrium concentration that crystallization of calcium carbonate is inhibited. Also, CMD seems to be a good inhibitor. Increased effective-

ness of a compound with a higher molecular weight can be explained by a cooperative action of the carboxylate groups, which results in a higher extent of adsorption (9) and a blockade of a relatively larger crystal surface area. Conversely, it is known from the literature (4,9,29) that effectiveness for crystallization inhibition is less for much higher molecular weight polyelectrolytes. This indicates that not only the extent of adsorption, but also the dynamics of adsorption, play a role. The rate of adsorption is highest for low molecular material, as the diffusion from the bulk solution to the crystal surface is the fastest. The optimum molecular weight for inhibition of crystallization must give a balance between low molecular weight for a high rate of adsorption and high molecular weight for a high extent of adsorption (9). This optimum molecular weight depends on the particular polymer species and is generally lower than 10,000 (4). From our experiments, it is clear that the molecular weight of CMI (about 6,000 for type I inulin) is still below this optimum. For use as crystallization inhibitor, CMI with a high average DP (low content of low molecular weight material) should be chosen.

In contrast to CMI, CMD and, particularly, CMC caused an increase in viscosity of the crystallizing solution (see Table 3). A possible advantage of the use of CMI instead of CMC or carboxymethyl starch is that CMI does not have a great impact on the viscosity of the solution.

Inhibiting properties of CMI were also tested at pH values lower than 10 (pH = 8, pH = 7). Because at these pH values the ratio of free carbonate/total carbonate is very low (see equilibrium constants in Table 1), much higher concentrations of Ca^{2+} and HCO_3^- were needed to get a solution with a comparable supersaturation. In the blank experiments, precipitation of calcium carbonate started immediately. When 200 ppm of CMI (type I, d.s. 1.05) was added, induction periods of at least 300 min were observed. To test the performance of CMI at higher temperatures, an experiment was carried out at 50°C (pH 10). Also in this case an induction period was observed in the presence of CMI in contrast with the blank experiment. Thus it can be concluded that CMI also acts as an inhibitor at neutral pH and at higher temperatures.

To investigate the morphology, the obtained calcium carbonate crystals were examined by SEM. Modifications of the crystals were established using X-ray diffraction.

TABLE 3
Viscosities of Aqueous Solutions of CMI and CMC at 25°C[a]

Inhibitor	d.s.	Concentration solution (wt%)	Viscosity (Pa.s)	Pseudo-plasticy
CMI[b]	0.65	40	0.016	–
CMI[c]	0.68	40	0.012	–
CMC	0.95	2	0.57	+
CMC	0.95	5	26	+
CMC	0.95	10	400	+
CMC	0.57	2	0.40	+
CMC	0.57	5	100	+
CMC	0.57	7	1500	+

[a]Abbreviations as in Table 2. [b]Degree of polymerization (DP) = 30. [c]DP = 10.

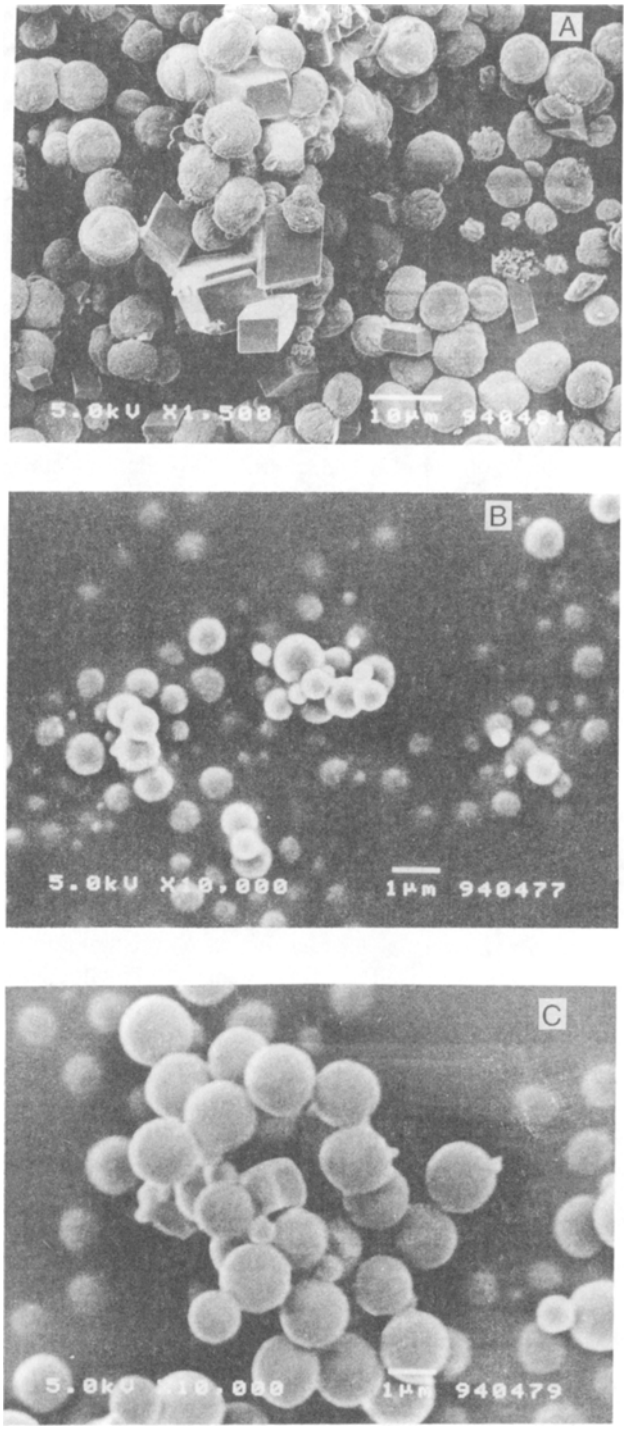

FIG. 3. Scanning electron microscopic views of calcium carbonate crystals precipitated in the presence of 200 ppm of inhibitor: (A) blank, 1,500×; (B) CMI (type I, d.s. = 1.05), 10,000×; (C) CMI (type II, d.s. = 0.68), 10.000×.

Figure 3A shows the crystals obtained in the blank experiment. The crystals are all about the same size (5–7 µm). The majority of the crystals (80%) has the characteristic vaterite morphology (spherulites). A small part (20%) consists of calcite crystals of rhombohedral shape. This vaterite–calcite

composition was confirmed by X-ray diffraction. Calcite crystals result from slow transformation of metastable vaterite, which is formed initially when calcium carbonate crystallizes at room temperature from a solution with a concentration much higher than the solubility product of vaterite (21,22).

Figure 3B shows the crystals obtained when calcium carbonate was precipitated in the presence of 200 ppm CMI (d.s. = 1.05, type I). Crystallization is clearly inhibited. The crystals are much smaller (1 μm) and do not show the typical calcite and vaterite morphology, although it was shown by X-ray diffraction that the crystals consist of vaterite and calcite in about the same ratio as for the blank. The shape of both crystal phases is spherical, which points at inhibition in all directions. Figure 3C shows the crystals, which are formed in the presence of 200 ppm CMI (d.s. = 0.68, type II). Evidently, in this case crystallization is inhibited also: The calcite as well as the vaterite crystals are small (1–1.5 μm) and show a spherical shape. That some rhombohedrals with rounded corners and edges were found shows that inhibition is less pronounced than in the case of CMI with a higher chainlength and a higher d.s. This confirms the results presented in Table 2. Similar effects on the morphology of the calcium carbonate crystals [small vaterite and calcite crystals (1 μm) with a spherical shape] were obtained by addition of PMAA, CMC, and CMD to the crystallizing solution.

CMS had no influence on the calcium carbonate morphology. Vaterite spherulites and calcite rhombi (3 μm) were obtained. The polymeric character of the additives thus seems essential for their performance as inhibitors.

Constant composition experiments. A constant composition experiment is used to study the growth kinetics of seed crystals at constant supersaturation (7,8,17–20). A solution with a low supersaturation of calcium carbonate was prepared, since additional nucleation should be avoided. In addition, the effect of inhibitors is more pronounced at low supersaturations. To this solution, calcite seed crystals were added, which grow due to the supersaturation. The supersaturation was kept at a constant value ($S = 2.18$) by the potentiometrically controlled addition of concentrated calcium and carbonate solutions. To compensate for H^+ ions freed during calcium carbonate growth, the pH was kept constant by addition of NaOH.

By monitoring the volume of the Ca solution added from the burette vs. time, a $V(t)$ curve was obtained. Since the mass of the crystalline material, which is produced during the reaction [$m(t)$], increases continuously, the growth rate can be expressed as the time derivative of this mass [$m'(t)$]. Division by $m(0)$, the initial mass of the added seed crystals, gives the normalized growth rate, which is independent of the amount of added seed crystals. This normalized growth rate can be directly derived from the $V(t)$ function :

$$\frac{m'(t)}{m(0)} = \frac{(c_B - c) \bullet M \bullet V'(t)}{m(0)} \qquad [4]$$

where M = molar mass of calcium carbonate ($kg \cdot mol^{-1}$), c_B = Ca concentration of the solution from the burette, and c = Ca concentration of the bulk solution in the vessel. The outgrowth of the crystals, defined as $m(t)/m(0)$, also follows from the $V(t)$ function:

$$\frac{m(t)}{m(0)} = \frac{(c_B - c) \bullet M \bullet V(t)}{m(0)} \qquad [5]$$

To quantify the influence of an inhibitor, the effectiveness I can be defined as the ratio of the normalized growth rate without and with inhibitor under equal growth conditions (20). Since the growth rate depends on the total surface area of the crystals, growth rates should be compared at the same outgrowth of the crystals, assuming that the inhibitor does not drastically change the shape of the crystals. The effectiveness I of an inhibitor can thus be defined as:

$$I = \frac{\left(\frac{m'(t)}{m(0)}\right)_{\text{blank}}}{\left(\frac{m'(t)}{m(0)}\right)_{\text{inhibitor}}} \qquad [6]$$

under equal conditions of supersaturation, pH, temperature, and outgrowth [$m(t)/m(0)$].

The influence of minor amounts of CMI with different d.s. and DP values was studied by constant composition experiments. PMAA, CMC, CMD, and CMS were also tested. The results are presented in outgrowth vs. time curves (Figs. 4–6). In Figures 7 and 8 the effectiveness I of the different additives at different outgrowth values is shown.

In Figure 4 the influence of the carboxylic acid content (d.s.) of CMI (type I) on crystal growth inhibition is demonstrated. While growth of calcium carbonate in the presence of 5 ppm CMI (d.s. = 1.05) was totally inhibited, addition of the same amount of CMI (d.s. = 0.36) had only little retarding effect on the crystal growth.

The influence of the concentration of the additive is shown in Figure 5. When the concentration of CMI was too low (0.1 ppm, 0.5 ppm), calcium carbonate crystal growth was inhibited for only a short period of time. After this period, the

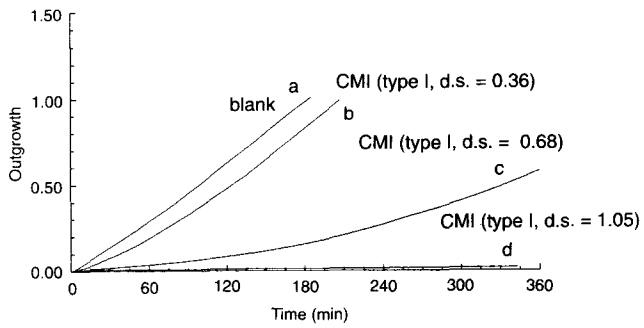

FIG. 4. Growth curves of calcite seed crystals at $S = 2.18$: (a) blank; in the presence of 5 ppm CMI (type I): d.s. = 0.36 (b); d.s. = 0.68 (c); with d.s. = 1.05 (d). Abbreviations as in Figure 2.

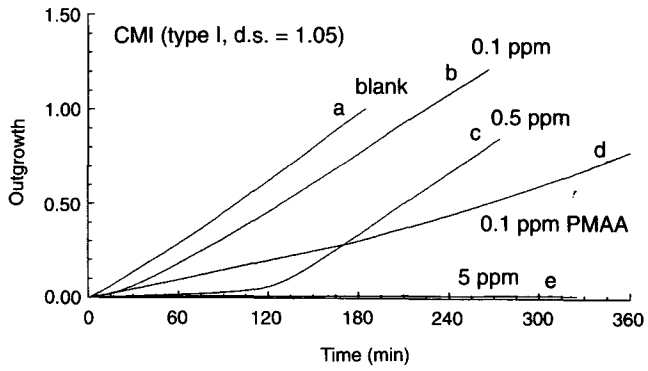

FIG. 5. Growth curves of calcite seed crystals at $S = 2.18$: (a) blank; in the presence of CMI (type I, d.s. = 1.05) with 0.1 ppm (b); with 0.5 ppm (c); with 0.1 ppm PMAA (d); with 5 ppm (e). Abbreviations as in Figure 2; PMAA, a copolymer of maleate and acrylate.

growth rate became the same as for the blank experiment. The effectiveness I was consequently only high at low outgrowth values (see Fig. 7). When 5 ppm of CMI was used instead, the inhibitor effectiveness remained high [log $(I) > 2$] for the duration of the experiment. This behavior may be explained as follows: During the period in which crystal growth is inhibited, most of the growing sites of the crystals are blocked by molecules of the adsorbed additives. As the crystals grow slowly, these blocked sites may be covered by overgrowing layers and the additives incorporated into the growing crystals. Crystallization can then resume at a rate comparable to that of the blank system. A similar behavior was found by Nancollas and Zawacki (2), who used small amounts of a phosphonate as inhibitor for $CaSO_4$ crystal growth.

Addition of PMAA reduced the growth rate during a long period also at a low concentration (0.1 ppm). The better performance of PMAA even at low concentrations might be related to the relatively high carboxylic acid content, as described above.

In Figure 6 growth curves of calcium carbonate in the presence of 5 ppm CMC, CMD (d.s. = 0.81), and CMI prepared with types I and II inulin are shown. The importance of the chainlength is clearly demonstrated. Although CMC has a

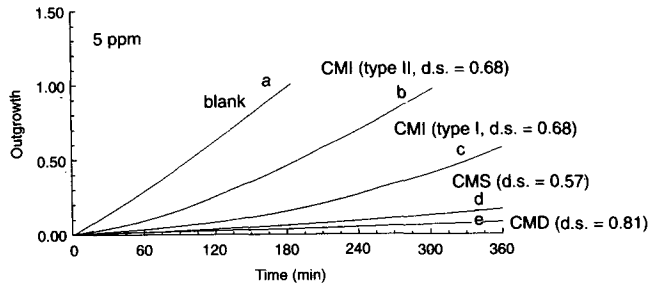

FIG. 6. Growth curves of calcite seed crystals at $S = 2.18$: (a) blank; in the presence of 5 ppm CMI (type II, d.s. = 0.68) (b); with 5 ppm CMI (type I, d.s. = 0.68) (c); with 5 ppm CMC (d.s. = 0.57) (d); with 5 ppm CMD (d.s. = 0.81) (e). Abbreviations as in Figure 2; CMD, carboxymethyl dextrins.

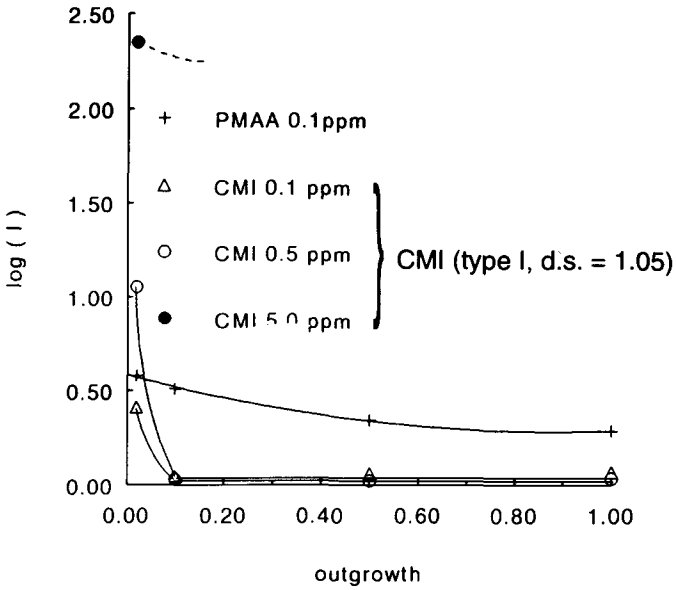

FIG. 7. Inhibitor effectiveness I vs. outgrowth as obtained from the growth curves (CMI: type I, d.s. = 1.05). Abbreviations as in Figures 2 and 5.

lower d.s. (0.57) than CMI (0.68), it showed a better performance. The inhibition effectiveness of CMI prepared with type II inulin (average DP = 10) is lower than the effectiveness of CMI prepared with type I inulin (average DP = 30). Moreover, CMS had no influence on the growth rate of calcium carbonate, even when a highly substituted derivative (d.s. = 2.0) was used. These data confirm the results obtained with the calcium carbonate precipitation experiments described above. In con-

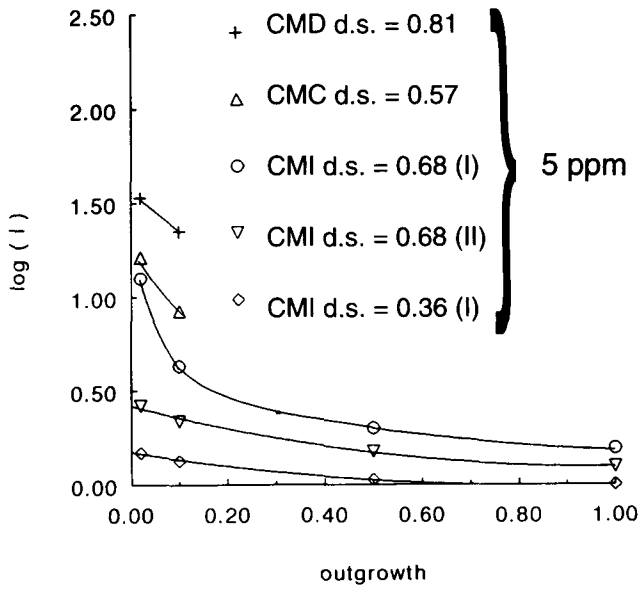

FIG. 8. Inhibitor effectiveness I vs. outgrowth as obtained from the growth curves obtained with 5 ppm of additive. Abbreviations as in Figures 2 and 6.

clusion, calcium carbonate (calcite and vaterite) crystallization inhibition performance of the tested additives can be ordered in the following sequence: PMAA > CMI (type I, d.s. = 1.05) > CMD (d.s. = 0.81) > CMC (d.s. = 0.57) > CMI (type I, d.s. = 0.68) > CMI (type II, d.s. = 0.68) >> CMI (type I, d.s. = 0.36) > CMS (d.s. = 1.36), CMS (d.s. = 2.0).

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