

Controlled Composition Studies of Calcium Carbonate and Sulfate Crystal Growth

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A highly reproducible seeded crystal growth method is described for the study of calcium carbonate and sulfate crystallization reactions in which the solution composition is maintained constant by the potentiometrically controlled addition of reagents. Both hydrogen and calcium specific ion electrodes may be used to control the reactions and the rates are measured with a precision hitherto unattainable even at very low supersaturations. For calcium carbonate, the rate of crystallization is proportional to the square of the relative supersaturation expressed in terms of the activities of the free ion species. The inhibiting influence of a phosphonate additive upon the rate of growth is discussed.

The precipitation and dissolution of calcium carbonate and calcium sulfate are of considerable importance in a wide variety of fields such as limnology (Stumm and Morgan, 1970)¹, oceanography (Cloud, 1965)², and sedimentology (Berner, 1971)³. The formation of these minerals as crystalline scales in geothermal applications, evaporative desalination plants, cooling towers, and petroleum engineering is a persistent problem. In many natural waters, the concentration of calcium carbonate is equal to or greater than the saturation level (Stumm and Morgan, 1970)¹, and as a consequence, calcium carbonate precipitation can take place. The resulting scale formation on heat transfer surfaces may significantly decrease the efficiency of the processes.

Calcium carbonate has probably received the greatest attention in connection with its precipitation and dissolution in natural water systems. The possibility of formation of various polymorphs such as calcite, aragonite and vaterite may markedly influence the course of the reaction. The precipitation is very sensitive to the presence of magnesium ions which are normally present at relatively high concentrations (Traft, 1967)⁴ and it is reported that under these conditions, the formation of the metastable aragonite phase is favored (Kitano, 1965).⁵ The inhibition of calcium carbonate crystal growth by magnesium ions has also been demonstrated in sea-water systems (Pytkowicz, 1965).⁶

Although the formation of calcium carbonate scales can often be controlled by lowering the pH of the solutions contacting the surfaces, the formation of calcium sulfate scales is unaffected. The problem is exacerbated by the

decreasing solubility with increasing temperature and by the fact that the salt can crystallize from aqueous solution in at least three forms: the dihydrate, α - and β - hemihydrates, and the anhydrites. The stability of these phases and the kinetics of transformation from one to another depend upon factors such as the temperature and ionic strength of the solutions. In many practical cases, scaling may take place through the initial formation of calcium carbonate followed by the induced growth of calcium sulfate dihydrate on this surface (Gill and Nancollas, in press).⁷

Although the rates of homogeneous reactions in solution can often be predicted with considerable precision, for heterogeneous processes, discrepancies amounting to orders of magnitude are not uncommon. Crystallization from homogeneous supersaturated solutions can be considered to take place through nucleation followed by the growth of these nuclei to macroscopic dimensions. The initial stages of nucleation are difficult to investigate owing to problems associated with the detection of nuclei of atomic dimensions. It is therefore difficult to design experiments to critically examine the numerous theories which have been proposed for kinetics of homogeneous precipitation (Hahnest and Kleber, 1959;⁸ Stranski, 1928⁹ Becker and Doring,¹⁰ 1935; Becker, 1949¹¹). Despite this fact, such processes continue to be important in natural water systems.

In order to avoid many of the chance nucleation problems associated with attempts to attain homogeneous precipitation conditions, a highly reproducible seeded growth procedure was developed for calcium sulfate (Liu and Nancollas, 1970)¹² and calcium carbonate (Reddy and Nancollas, 1971)¹³. The addition of well-characterized seed crystals to stable supersaturated solutions enabled the rate of growth to be studied by following concentration changes as a function of time. For many sparingly soluble salts, $M_{v+} A_{v-}$, the rate of crystallization can be expressed by an equation of the form

$$\frac{d[M_{v+} A_{v-}]}{dt} = ks \{([M^{m+}]^{v+} [A^{a-}]^{v-})^{1/v} - ([M^{m+}]_o^{v+} [A^{a-}]_o^{v-})^{1/v}\}^n \quad (1)$$

where $[M^{m+}]$, $[A^{a-}]$, and $[M^{m+}]_o$, $[A^{a-}]_o$ are the concentrations of crystal lattice ions in solution at time t and at equilibrium respectively, k is the precipitation rate constant, s is proportional to the total number of available growth sites on the added seed material and $v = (v_+ + v_-)$. The value of n in this phenomenological rate expression is typically two for the crystallization of a number of sparingly soluble salts including calcium carbonate and calcium sulfate (Liu and Nancollas, 1970¹²; Reddy and Nancollas, 1971)¹³. The insensitivity of the reaction rate to changes in fluid dynamics and the observed relatively high activation energy, point to surface controlled crystallization reactions.

An advantage of utilizing the seeded growth technique is that crystal growth occurs on a well-defined surface of known polymorphology, area and morphology. In the field, precipitation invariably takes place on a surface already present either of the mineral itself or of a metal offering available sites for adsorption of lattice ions. The seeded crystal growth methods therefore simulate field conditions much more closely than spontaneous precipitation studies. In experiments in which the rate of growth is determined by measuring the change in concentration of lattice ions as a function of time,

it may be difficult to determine the stoichiometry of the precipitates due to the appreciable reduction in concentrations during the reaction. At each stage, the supersaturated solutions may be metastable with respect to different phases which can form and subsequently redissolve as the concentrations decrease. In the precipitation of calcium phosphates, this probably accounts for the apparent variable stoichiometry and complex kinetics observed experimentally (Tomson and Nancollas, 1978)¹⁴. In the case of calcium carbonate, there is evidence that the initially formed phase rapidly undergoes transformation into calcite crystals (Mullin, J. W., private communication, 1978)¹⁵. Another problem of the conventional seeded growth techniques is associated with the precision of the analytical determinations. Since the rate of crystallization is determined from the differences in lattice ion concentrations as a function of time, it is very difficult to make measurements close to saturation. Often in order to improve the statistical reliability of the results, measurements are made at relatively high supersaturation in order to provide larger concentration differences. However, this can result in a change in the mechanism of the precipitation processes (Nancollas and Tomažič, 1974)¹⁶.

These problems have been overcome in the method reported in the present paper, in which the precipitation is studied under conditions of constant solution composition. The method is particularly useful for investigating the mechanism of crystal growth, since the extent of the reaction at any chosen level of supersaturation can be varied widely. Factors such as secondary nucleation and the influence of foreign ions can also be studied under highly reproducible conditions.

The constant composition method has a number of advantages over the continuous flow crystallizers which are commonly used in industrial processes. Conditions of supersaturation can be selected which, for example, can eliminate undesirable secondary nucleation and in a multi-phase system, the nature of the precipitating solid can be controlled over the whole of the crystallization process. The method has been used to grow hydroxyapatite crystals at very low supersaturation without interference from the normally formed precursor phases (Amjad et al., 1978)¹⁷. The use of conventional seeded bath techniques precludes the possibility of growing appreciable amounts of solid phases since the process is initiated at concentration values close to saturation. In continuous flow crystallizers, nucleation must always occur in order to replace the crystals that are removed as products. A range of size distribution in the product results, and to obtain significant yields of large crystals even at low degrees of supersaturation, equipment is required to separate the large and small fractions. The constant composition method described in the present work enables crystallization to proceed under controlled conditions for long periods yielding products of excellent size uniformity and morphology.

EXPERIMENTAL

Triply distilled, deionised, CO₂-free water was used throughout and crystallization experiments were conducted in a nitrogen atmosphere. Reagent grade chemicals were used and the calcium chloride was recrystallized from aqueous solution. Stock solutions were filtered through Millipore filter pads (0.22 μm) which were pre-washed with water. pH measurements were made with a glass electrode (Beckmann Instruments) which was standardized before and after each of the calcium carbonate experiments using buffer solutions pH = 4.008 and pH = 9.180 prepared by the procedure suggested by Bates (1963)¹⁸. Calcium specific ion electrodes (Radio-

meter Instrument Company) were standardized in calcium chloride solutions of known ionic strength. For the control of pH and pCa, a Metrohm E512 pH meter was used in combination with a Metrohm Impulsomat E473 and Recording Dosimat E415. In order to maintain the composition of the supersaturated solutions at known values during the crystal growth reaction, the Dosimat E415 was modified to deliver up to four solutions simultaneously. Calcium analyses were made either by EDTA titration using murexide as indicator (Schwarzenbach and Flaschka, 1968)¹⁹ or by means of a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer.

Constant Composition Experiments

Calcium Carbonate

Crystal growth experiments were made in a water-jacketed cell maintained at a temperature of 25 ± 0.1 °C. Stable supersaturated solutions of calcium carbonate were prepared by the addition of a known volume of calcium chloride solution (approx 0.05 M) to 500 ml of deionized water and the subsequent careful drop-wise addition of sodium bicarbonate solution (approx. 0.10 M). The mixed solutions were brought to the required pH (normally 8.5–8.78) by the controlled addition of 0.0500 M potassium hydroxide solution. Following confirmation of the stability of the solutions a weighed quantity of calcite seed crystals was introduced. The seed crystals, $0.3 \text{ m}^2 \text{ g}^{-1}$, were prepared by the method described previously (Reddy and Nancollas, 1971)¹³ and were dispersed in 5 ml of saturated calcium carbonate solution and ultrasonicated to break up aggregates. During the crystallization reaction, the pH was maintained constant by the addition of two titrant solutions consisting of 0.1029 M calcium chloride and a mixture of 0.0989 M sodium carbonate and 0.0080 M sodium bicarbonate. These solutions were prepared such that the additional volume contained the same ratio of calcium chloride to calcium bicarbonate at the particular pH of interest as the supersaturated solution. They were added at such a rate so as to replace the calcium carbonate which precipitated. Constancy of calcium concentration during the experiments was verified by withdrawing aliquots, Millipore filtering ($0.22 \mu\text{m}$) and analyzing for calcium by atomic absorption ($\pm 0.3\%$). Additional neutral electrolyte (potassium chloride) was added to the growth solution in order to maintain the ionic strength constant at the desired value. The rate of crystallization was calculated from the volume of titrant solutions added.

In order to investigate the influence of changes in fluid dynamics upon the rate of crystallization of calcium carbonate, a series of experiments were made under the simple chemical and well-defined hydrodynamic conditions of the rotating disc. Natural crystals of calcite (var. Iceland Spar from Chihuahua, Mexico) were centrally set in an inert self-setting acrylic resin («Orthocryl», Stratford-Cookson Co., Yeadon, Pa.) and machined to the feathered edged shape shown in Figure 1 which has been found to be suitable for studying the dissolution of tooth enamel surfaces (Linge and Nancollas, 1973;²⁰ White and Nancollas, 1977).²¹ The exposed calcite surface (area about 1 cm^2) was carefully polished in successive stages on spinning felt impregnated with suspensions of Al_2O_3 having a particle size of 5, 1, and $0.3 \mu\text{m}$ respectively. In a typical experiment, a blank acrylic disc was first placed in the supersaturated solution of calcium carbonate to stabilize the system. The cell also contained a calcium electrode probe in order to control the supersaturation. Any adjustments in supersaturation and pH were made at this time. The blank disc was replaced by the calcite surface and the rate of reaction was observed by following the addition of calcium nitrate and potassium bicarbonate titrant solutions. The disc was rotated at a speed of 401 ± 5 r.p.m.

Calcium Sulfate Crystal Growth

Calcium sulfate dihydrate seed crystals were prepared by precipitation from calcium chloride and sodium sulfate solutions as described previously (Liu and Nancollas, 1970)¹² Supersaturated solutions, stable for long periods, were prepared by mixing calcium chloride and sodium sulfate solutions in the stirred, thermostated cell. The cell also contained a calcium specific ion electrode which was standardized in situ during the initial addition of calcium chloride aliquots in the preparation of the supersaturated solutions. Following the introduction of calcium

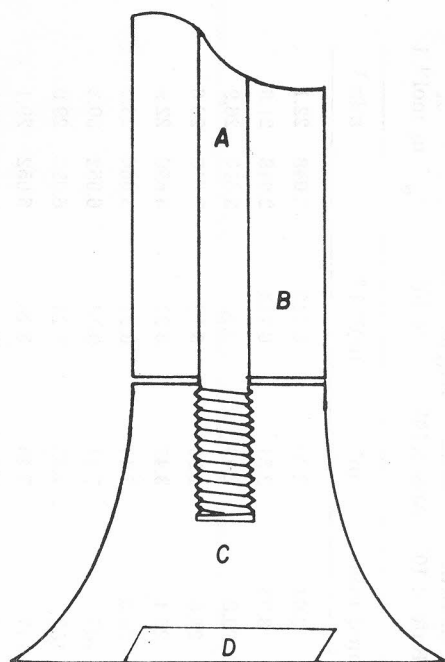


Figure 1. Rotating disc. A, stainless steel shaft; B, teflon sleeve; C, acrylic disc; D, calcite crystal.

sulfate dihydrate seed crystals, the calcium ion activity was maintained constant by the pCa-controlled addition of 0.10 M calcium chloride and 0.10 M sodium sulfate solutions from the mechanically coupled burettes. During the experiments, the calcium concentration, verified by EDTA titration, remained constant to within $\pm 0.5\%$. The gypsum seed crystals had a specific surface area of $0.23 \text{ m}^2 \text{ g}^{-1}$.

RESULTS AND DISCUSSION

The concentration of ionic species in the supersaturated solutions were calculated by taking into account each of the acid-base and ion-pairing equilibria (Nancollas, 1966)²² using the experimental pH or pCa values, and expressions for mass balance, by successive approximation for the ionic strength. Activity coefficients, γ_z , of z -valent ions were calculated using the modified Debye-Hückel equation proposed by Davies (1962)²³.

The calcium carbonate crystal growth experiments are summarized in Table I in which T_{Ca} and T_{C} are the total concentrations of calcium and carbonate, respectively. Figure 2 contrasts the growth curves obtained using conventional pH-stated experiments in which the calcium and carbonate concentrations are allowed to decrease with time (Curve A) and the constant composition experiments in which the activities of all species are maintained at a constant level (Curve B). In the latter case, the concentration of calcium ion remains constant to within $\pm 0.3\%$ during the whole of the crystallization experiment and the rate of crystallization can be very accurately monitored by following the volume of calcium chloride and sodium carbonate/bicarbonate solutions simultaneously added to maintain the pH at the required constant value. Curves of calcite growth as a function of time are shown in Figure 3.

TABLE I
Calcium Carbonate Crystal Growth Experiments

| Exp. | $T_{Ca} \times 10^3$ | | I | Titration Concentration $\times 10^3$ | Addition Rate of Titrant $\times 10^2$ | Growth Rate $\times 10^7$ | Seed Area $\times 10^2$ | $K_{So} (\theta^{1/2} - 1)^{***}$ $\times 10^9$ | K | |
|------|----------------------|---------------|-------|---|--|------------------------------|----------------------------|--|---------------|-----------------|
| | $mol\ l^{-1}$ | $mol\ l^{-1}$ | | | | | | | $mol\ l^{-1}$ | $mol^2\ l^{-2}$ |
| 1 | 1.005 | 0.9851 | 0.007 | 5.03 | 13.0 | 3.94 | 2.50 | 0.713 | 2.048 | 22.1 |
| 2 | 1.005 | 0.9851 | 0.007 | 5.03 | 13.0 | 3.92 | 2.51 | 0.713 | 2.048 | 21.9 |
| 3 | 2.009 | 0.9578 | 0.013 | 10.0 | 34.8 | 20.8 | 2.49 | 3.12 | 3.617 | 26.9 |
| 4 | 2.010 | 0.9511 | 0.013 | 10.0 | 36.0 | 21.5 | 2.59 | 3.12 | 3.617 | 26.6 |
| 5 | 2.500 | 0.9513 | 0.029 | 25.0 | 12.7 | 25.4 | 3.47 | 3.21 | 3.666 | 22.9 |
| 6 | 2.500 | 0.9513 | 0.029 | 25.0 | 12.8 | 25.5 | 3.47 | 3.21 | 3.666 | 23.0 |
| 7 | 1.992 | 3.959 | 0.208 | 100 | 19.2 | 185 | 7.44 | 9.18 | 6.052 | 30.3 |
| 8 | 1.993 | 3.957 | 0.208 | 100 | 18.8 | 180 | 7.43 | 8.18 | 6.052 | 29.6 |
| 9 | 1.986 | 3.964 | 0.208 | 100 | 18.5 | 177 | 7.45 | 8.18 | 6.052 | 29.1 |
| * | 29.05 | 0.7020 | 0.089 | 60.1 | 1.18 | 0.238 | 0.0155 | 5.86 | 5.000 | 26.2 |

* Rotating Disc Experiment

** $\theta = [Ca^{2+}] [CO_3^{2-}]^{1/2} / K_{So}$, $K_{So} = 10^{-8.416} mol^2\ l^{-2}$ at 25 °C

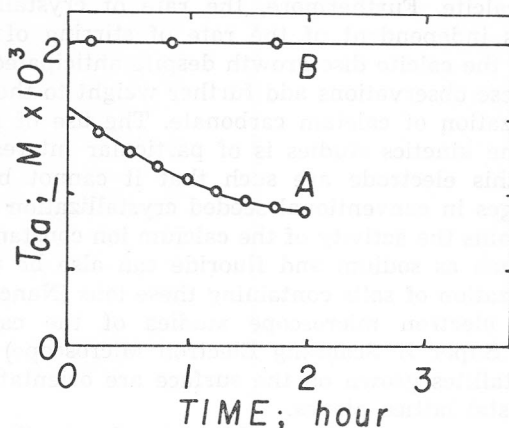


Figure 2. Plots of T_{ca} against time for pH-stat (A) and constant composition (B) experiments.

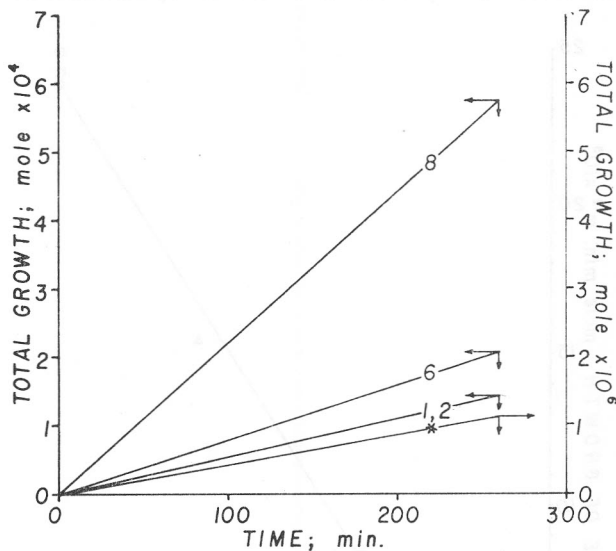


Figure 3. Plots of moles of titrant as a function of time for various surface areas. Experimental numbers (Table I) are indicated on each plot; the starred curve refers to the rotating disc experiment.

The slope of these curves gives the rate of crystallization and the reproducibility of the experiments is indicated by the agreement between the results of experiment 1 and 2. The calcite growth time profiles are indistinguishable for at least 5 hrs.

In the case of the calcite disc, a plot of calcite growth as a function of time during the experiments is also shown in Figure 3. It can be seen in Table I that the rate constant of reaction for both seed crystals and rotating disc methods are in excellent agreement. It is interesting to note that both hydrogen and calcium specific ion electrodes can be used to measure the

crystallization of calcite. Furthermore, the rate of crystallization of calcite seed suspensions is independent of the rate of stirring of the solution and agrees with that of the calcite disc growth despite anticipated widely different fluid dynamics. These observations add further weight to the proposed surface controlled crystallization of calcium carbonate. The use of a calcium specific ion-electrode for the kinetics studies is of particular interest. Typical equilibration times of this electrode are such that it cannot be used to follow concentration changes in conventional seeded crystallization studies. However, it effectively maintains the activity of the calcium ion constant in the solutions. Other electrodes such as sodium and fluoride can also be used to study the kinetics of crystallization of salts containing these ions (Nancollas, unpublished results).²⁴ Scanning electron microscope studies of the calcite disc during crystallization (ISI Super II Scanning Electron Microscope) indicate that the rhombohedral crystallites grown on the surface are orientated parallel to the original calcite crystal lattice planes.

The constant composition method yields rates of crystallization of sufficient precision to be able to choose between the use of activities and concentrations in Equation 1 in order to represent the rate of crystallization. The represen-

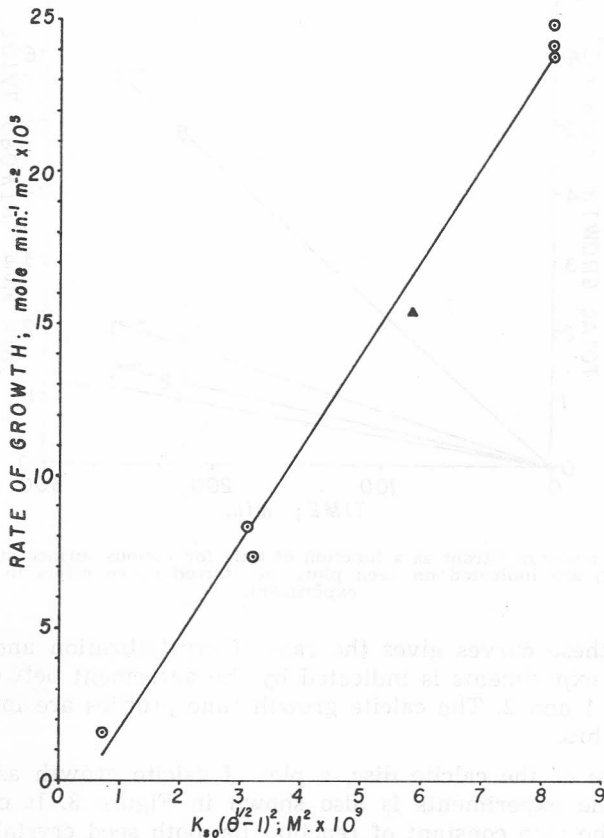


Figure 4. Kinetics plot for calcite growth according to Eqn. 1. O, experiment 1-9; Δ, rotating disc experiment. $\theta = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] y_s^2 / K_{so}$.

tation of growth rates in terms of activity products has recently been discussed (Söhnle and Garside, 1973²⁵; Van Leeuwen, 1979)²⁶. Experiments 1—9 shown in Table I have been made over a range of ionic strength (0.007—0.28 M) and plots of Equation 1, using activities of the free ionic species, shown in Figure 4 indicate that the rate constant is independent of the ionic strength of the solutions.

In the crystallization of calcium sulfate dihydrate, plots of volume of mixed titrant added as a function of time following the addition of well-characterized seed crystals to the supersaturated solutions (0.024—0.030 M calcium sulfate in 0.10 M sodium chloride) are shown in Figure 5. It can be seen that, for the considerably greater calcium concentrations as compared with calcium carbonate, the calcium specific ion electrode can again be used in order to maintain the calcium ion activity in the solutions. The observed rates of crystallization for the experiments shown in Figure 5 are close to the rates of crystallization from conventional seeded experiments published previously (Liu and Nancollas, 1970)¹².

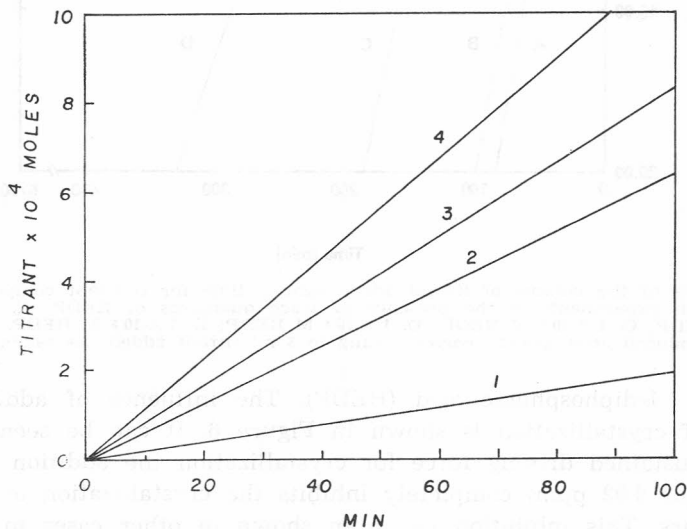


Figure 5. Constant composition growth of calcium sulphate dihydrate crystals in 0.1 M sodium chloride at 25 °C. Calcium sulphate concentrations: 0.0240 M, curve 1; 0.0265 M, curve 2; 0.0275 M, curve 3; 0.0295 M, curve 4.

The constant composition technique has a number of advantages for the study of the influence of trace additives upon the rate of crystallization as compared with the earlier conventional studies (Reddy and Nancollas, 1971)¹³. Deviations from linearity in the plot of volume of mixed solutions added versus time may indicate small changes in the crystallization mechanism induced by the presence of traces of additives. The influence of potential scale inhibiting molecules upon the rate of crystallization of calcite is of particular interest. Additives which are effective at very low concentrations provide a very attractive method for the control of scaling and a substantial number of potential additives have been investigated. In the present work, the constant composition growth of calcite has been studied in the presence of 1-hydroxy-

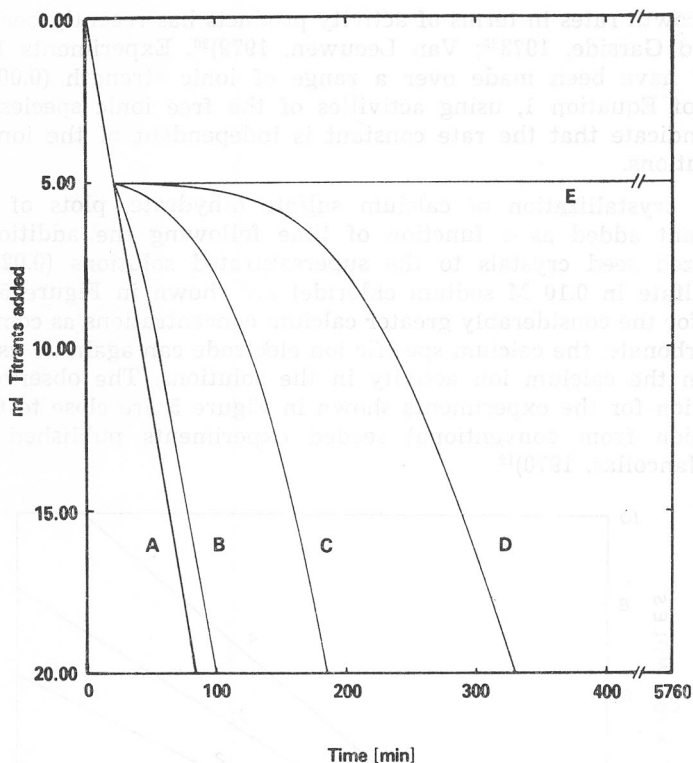


Figure 6. Plots of the volume of titrant added against time for constant composition calcite crystal growth experiments in the presence of trace quantities of HEDP. A, no HEDP; B 5×10^{-8} M HEDP; C, 1×10^{-7} M HEDP; D, 1×10^{-6} M HEDP; E, 1×10^{-5} M HEDP. The inhibitor is introduced after growth corresponding to 5 ml titrant added has taken place.

ethylidene 1,1-diphosphonic acid (HEDP). The influence of additives upon the rate of crystallization is shown in Figure 6. It can be seen that even with the sustained driving force for crystallization the addition of 1×10^{-7} M HEDP (or 0.02 ppm) completely inhibits the crystallization of calcite for about 48 hrs. This inhibition has been shown in other cases to be due to adsorption of additive following a simple Langmuir adsorption isotherm at the crystal surface thus effectively blocking the growing sites. In the present case, after 58 hrs. of reaction, the crystallization commences once more with a rate close to that in the absence of inhibitor. During the long delay period, (Figure 6) there may be sufficient growth of the slow growing phases to cover the adsorbed HEDP molecules on the crystal. The constant composition method allows these effects to be studied under highly reproducible conditions at very low levels of inhibitor concentrations.

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SAŽETAK

Proučavanje rasta kristala kalcijevog karbonata i sulfata metodom kontroliranog sastava otopine

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Opisana je visoko reproducibilna metoda uzgoja kristala kalcijevog karbonata i sulfata iz vodenih otopina, koja započinje unošenjem jezgrića kristalizacije. Sastav otopine kontrolira se potenciometrički uz automatsko doziranje reagensa. Kao indikatorske elektrode mogu poslužiti bilo vodikova ili kalcijeva specifična elektroda, a visoka preciznost postignuta je i kod vrlo niskih presićenja. Brzina kristalizacije kalcijevog karbonata proporcionalna je kvadratu relativne supersaturacije, izraženoj aktivitetom slobodne ionske vrste. Inhibicija rasta kristala 1-hidroksietiliden-1,1-difosfonskom kiselinom opača se samo u početnoj fazi. Tako 1×10^{-7} mol/l otopina inhibitora sprečava rast kristala kroz 48 sati, da bi nakon 58 sati brzina rasta bila jednaka početnoj brzini u neinhibiranom sustavu.

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