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Influence of some additives on the rate of precipitation of calcite crystals in synthetic sea water

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The precipitation of calcite seed crystals has been investigated in synthetic sea water at 25°C. Over a range of supersaturation, 0.008–0.015, the precipitation reaction appears to be controlled by a surface process which, in contrast to a bulk diffusion reaction, is markedly inhibited by the presence of additives. The influence of a number of polyphosphonates on the rate of reaction has been investigated. The retardation effect of these additives has been attributed to the blocking of active sites by adsorption of phosphonate molecules at the crystal surface.

1. Introduction

Calcium carbonate has probably received the greatest attention in connection with its precipitation and dissolution in natural waters. In many natural waters, the concentration of calcium carbonate is equal to or greater than the saturation level [1], and as a consequence, calcium carbonate precipitation can take place. Calcium carbonate precipitation may play an important role in the carbonate buffering in sea water [2]. In sea water itself, the effect of the various ionic constituents upon the rate of carbonate precipitation may explain the existence of metastable calcium carbonate polymorphs [2, 3].

The formation of scales in geothermal applications, evaporative desalination plants, cooling towers and petroleum engineering is a persistent problem. The resulting scale formation on heat-transfer surfaces may significantly decrease the efficiency of the processes. Much work has been done in an attempt to characterize the formation products of the scale minerals below which solutions will remain metastable and above which catastrophic formation of solids takes place [4].

The problem, in the case of calcium carbonate scale formation is made worse by a decreasing solubility with increasing temperature and by the salt's ability to crystallize from aqueous solution in at least three forms; the factors that govern the mechanisms of precipitation and dissolution of these carbonate salts are, therefore, of considerable interest, especially the influence of foreign cations and anions which may exert a marked effect on the rates of precipitation.

This paper presents a re-evaluation of the kinetics of precipitation in seeded conditions, as well as an examination of the role of some additives on the kinetics of precipitation of calcite crystals. Other factors which are thought to contribute to the kinetics of precipitation, such as the stirring rate, are also studied.

2. Materials and methods

Supersaturated solutions of calcium carbonate were prepared using Reagent Grade (Fisher Scientific Co., and J. T. Baker Co.) chemicals. Solutions were filtered (0.22 µm, Millipore filters) before use. Metal-ion concentrations were determined by passing aliquots through a cation exchange resin (Dowex 50) in the hydrogen form and titrating the eluted acid with standardized sodium hydroxide.

Calcite seed crystals were prepared by a method similar to that used by Reddy and Nancollas [5] by adding 0.20 M calcium chloride to 0.20 M sodium carbonate solution at 25 °C. The crystals were aged for at least 3 weeks before use. The seed crystals were confirmed as calcite crystals by X-ray powder diffraction (Shimadzu XD-3 diffractometer). The specific surface areas (SSA) of the crystals, measured using a single-point nitrogen adsorption apparatus (30% nitrogen, 70% helium, Quantasoeb II, Quantachrome, Greenvale, NY), was 0.63 $m^2 g^{-1}$.

All experiments were done in a thermostatted double walled Pyrex glass vessel at 25 ± 0.1 °C. The total volume of the working solution was 0.500 dm^3, and the synthetic sea water used in this work was prepared from recrystallized NaCl, Na_2SO_4, KCl, $CaCl_2$ and $MgCl_2$ as given by Khoo *et al.* [6] (Table I). The supersaturated calcium carbonate solutions in sea water were prepared by adding appropriate volumes from standardized sodium carbonate stock solution.

The pH of the solutions was measured by a glass/saturated calomel electrode (Metrohm), standardized

TABLE I The composition of synthetic sea water

	NaCl	Na_2SO_4	KCl	$CaCl_2$	$MgCl_2$
mol dm^{-3}	0.4266	0.0293	0.0106	0.0108	0.0552
g kg^{-1} solution	24.061	4.011	0.761	1.153	5.069

before and after each experiment with NBS standard, buffer solutions. The pH of the working solutions was adjusted to 9.50 by the addition of standard sodium hydroxide and it remained constant, indicating lack of any precipitation in the solution.

The mineralization reactions were initiated by inoculation with dry seed crystals, and the total calcium concentrations were measured as a function of time by removing an aliquot, filtering through Millipore filters (0.22 μm), and analysing for total calcium by titration with ethylene diaminetetra (acetic acid) (EDTA), using murexide as indicator [7]. The calcium concentration was also determined indirectly by interpolation between two known calcium concentrations, using the measured experimental change in solution hydrogen-ion activity during precipitation.

3. Results and discussion

The concentration changes of calcium carbonate ionic species in solutions (and hence the rate of precipitation, R) in the absence and presence of the additives were analysed using the following relationship

$$R = \frac{dT_{Ca}}{dt} = ks\,\sigma^n \qquad (1)$$

in which k is a rate constant, s is proportional to the number of growth sites available on the seed crystals, n is the apparent order of the reaction and σ is the degree of saturation for calcium carbonate solutions, which may be defined by

$$\sigma = ([Ca^{2+}][CO_3^{2-}])^{\frac{1}{2}} - ([Ca^{2+}]_0[CO_3^{2-}]_0)^{\frac{1}{2}} \qquad (2)$$

where $[Ca^{2+}]$, $[CO_3^{2-}]$ and $[Ca^{2+}]_0$, $[CO_3^{2-}]_0$ are the supersaturation and saturation molar concentrations of free lattice ions, respectively.

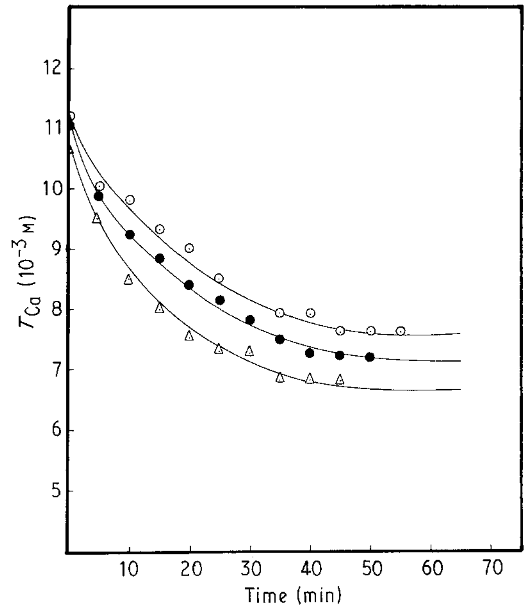

Figure 1 Plots of $[Ca^{2+}]$ against time, Experiments (○) 21, (●) 24 and (△) 28.

The calcium carbonate system is complicated by the relatively slow gas/solution equilibrium $CO_2 + H_2O = H^+ + HCO_3^-$. In the precipitation work, this problem was avoided by keeping to a minimum the volume of the gas space above the solution in the precipitation cell and the effective isolation of the system was verified by the constancy of the pH of the supersaturated solutions for periods of hours in the absence of inoculating seed crystals.

Plots of calcium concentration, T_{Ca}, against time for typical precipitation experiments (Experiments 21, 24, 28) are shown in Fig. 1. The results of the precipitation experiments are summarized in Table II, in which T_{Ca} and T_{CO_3} are the molar calcium and carbonate concentrations. It can be seen that R, normalized for the initial surface area of inoculating seed, is constant, confirming that crystallization takes place on the seed crystals without additional nucleation or spontaneous precipitation.

TABLE II Precipitation of calcite crystals at 25°C[a]. $T_{Ca} = 1.12 \times 10^{-2}$ mol dm^{-3}

Experiment	T_{CO_3} (10^{-2} mol dm^{-3})	$10^3\sigma$	Seed (mg)	Rate (10^{-6} mol min m^{-2})
20	0.572	7.75	100	1.301
21	0.763	8.99	80	1.630
22	1.120	10.95	40	2.290
23	1.120	10.95	60	2.289
24	1.120	10.95	80	2.311
25	1.120	10.95	90	2.317
26	1.120	10.95	100	2.321
27	1.120	10.95	200	2.325
28	1.560	12.93	80	2.981
29	2.010	15.06	80	4.023
30	1.120	10.95	50	2.302
31	1.120	10.95	70	2.313
32	1.120	10.95	100	2.318

[a] Stirring speed 200 r.p.m., with 300 r.p.m. for Experiments 30–32.

TABLE III. Effect of additives on the rates of precipitation of calcite crystals. $T_{\mathrm{Ca}}:T_{\mathrm{CO_3}} = 1:1 = 0.0112\,\mathrm{mol\,dm^{-3}}$, seed = 80 mg, $\sigma = 1.095 \times 10^{-2}$, 25 °C

Experiment	Additives (10^{-7} mol dm^{-3})	Rate (10^{-6} mol min m^{-2})	Inhibition (%)
24	–	2.311	–
40	HEDP 1.50	1.601	30.72
41	HEDP 3.21	1.191	48.46
42	HEDP 6.42	1.042	54.91
43	HEDP 9.60	0.801	65.34
44	HEDP 12.22	0.731	68.36
45	HEDP 16.01	0.710	69.28
46	ENTMP 1.50	1.752	24.19
47	ENTMP 3.21	1.321	42.84
48	ENTMP 6.42	1.073	53.57
49	ENTMP 9.60	0.910	60.62
50	ENTMP 12.22	0.863	62.66
51	ENTMP 16.01	0.810	64.95

In the classical work of Frank and co-workers [8–10], the formation of growth spirals on the crystal surface was postulated. These workers pointed out that real crystals are imperfect and that the growth of singular faces intersected by screw dislocations was quite different from that of perfect faces. The screw dislocations give rise to steps on the crystal surface and as crystallization takes place at the energetically preferential sites offered by ledges, growth spirals develop on the crystal surface. These spirals provide perpetual steps for crystallization and avoid the necessity for two-dimensional nucleation. This model, therefore, is capable of explaining why crystals grow at very low supersaturation. Dehydration or partial dehydration must also take place during the crystallization reaction [10].

The growth data of calcite seed crystals are presented in Fig. 2 as logarithmic plots involving the rates of reaction, R, and degree of saturation, σ. The slope of this linear plot for the growth reaction in the concentration range $0.008 < \sigma < 0.015$ gave a value of $n \simeq 2$. In general it has been shown that for spiral growth, a value $n \simeq 2$ would be expected in Equation 1, while for polynuclear crystallization $n > 2$ [11–16]. A value of unity for n might reflect a transport- or diffusion-controlled process. The observed second-order dependence points to a rate-limiting step involving a surface reaction at the crystal face. Further evidence for the proposed surface mechanism for calcite growth is provided by the observed insensitivity of the rate to changes in the rate of stirring in the precipitation cell [17].

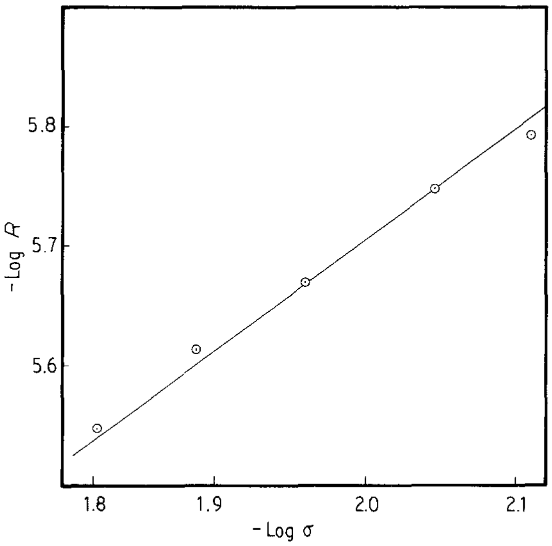

Figure 2 Plots of $-\log R$ against $-\log \sigma$ for the precipitation of calcite crystals.

In general, the rates of precipitation and dissolution of sparingly soluble salts are markedly inhibited by the addition of certain organic molecules [18–22]. The organic phosphonates have been found to be particularly effective in inhibiting scale formation [23, 24], and a number of studies have been made of their influence on the rate of crystal growth of calcite [25]. In the present work, the rate of precipitation of calcite crystals in synthetic sea water was studied in the presence of hydroxyethylidene 1,1-diphosphonic acid (HEDP) and triethylenediaminetetra (methylene phosphonic acid) (TENTMP). Table III summarizes the data at the same supersaturation for each additive; each experiment was made in duplicate or triplicate to ensure certainty. Typical plots of the extent of precipitation as a function of time are shown in Fig. 3. Initial rates of precipitation, plotted against [additive] in Fig. 4, show that the rate of crystallization decreases with successive additions of phosphonates, suggesting that the influence of additives on the precipitation kinetics of calcite may be interpreted in terms of at least two factors: (i) specific adsorption on the crystal surface, and (ii) sequestration of calcium ion in solution. In general, specific inhibition of the rate of crystallization may be expected to be induced at much lower concentrations of additive molecules than for the simple complexation of lattice cations. As the concentration of additive molecules increases, the active growth sites on the crystal surfaces are blocked through adsorption and the rate of crystal growth decreases. Experiments in the presence of phosphonate, summarized in Table III, show that concentrations as low as $9.6 \times 10^{-7}\,\mathrm{mol\,dm^{-3}}$ for each additive (Experiments 43 and 49) reduced the precipitation rates by as much as 65.34% and 60.62% in the

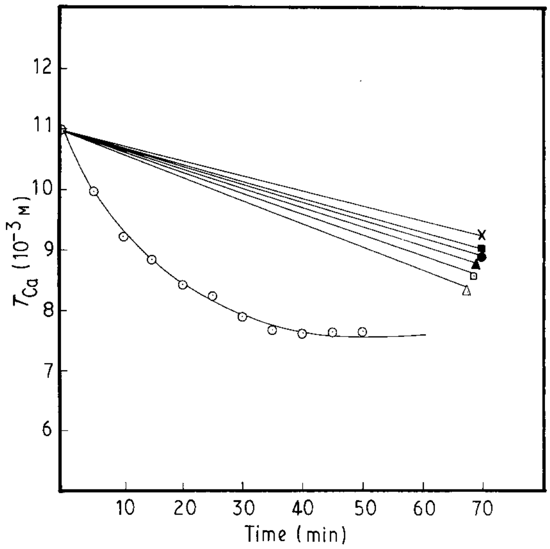

Figure 3 Plots of $[Ca^{2+}]$ against time in the absence and presence of additives, Experiments (○) 24, (△) 41, (□) 42, (●) 45, (▲) 47, (■) 48 and (×) 51.

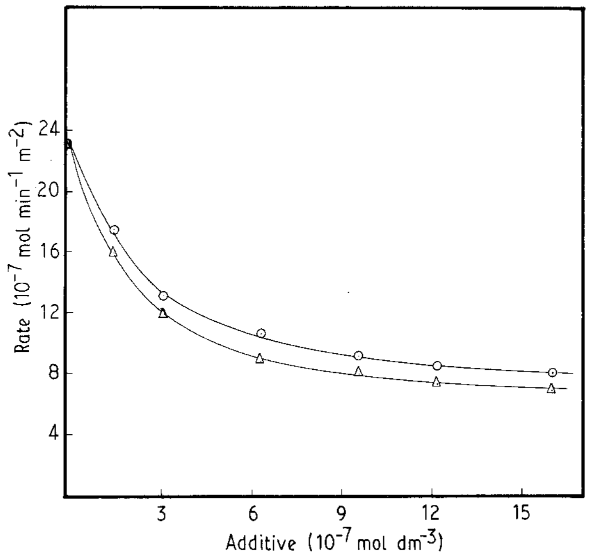

Figure 4 Plots of rates of precipitation against [additive], (△) HEDP and (○) ENTMP.

presence of HEDP and TENTMP, respectively, compared to that in pure solution at the same supersaturation. It can be seen that the efficiency of these phosphonate for the preventation of the precipitation of calcite crystals in synthetic sea water can be represented as follows: HEDP > TENTMP.

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