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Dissolution of calcite crystals in the presence of some metal ions

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A constant composition method has been used for the study of the kinetics of calcium carbonate (calcite) dissolution in which the activities of ionic species in relatively undersaturated solutions are maintained constant. Over a range of relative undersaturation (0.032–0.158) the dissolution reaction appears to be controlled by a bulk diffusion process. The suggestion of a predominantly diffusion-controlled process was supported by the observed low activation energy (2.09 kcal mol^{-1}). The influence of a number of metal ions on the reaction rate has been investigated. The retardation effect of these additives has been attributed to the blocking of active sites by adsorption of metal ions at the crystal surfaces. Inhibition of dissolution by metal ions can be interpreted in terms of a Langmuir isotherm.

1. Introduction

Dissolution and precipitation of solid material from solutions have widespread and universal applications in oceanography, crystallography, metallurgy, ceramics and desalination technology, as well as in a number of biological and environmental precipitation processes [1–4]. Calcium carbonate has probably received the greatest attention in connection with its precipitation and dissolution in natural waters. The reaction is very sensitive to the presence of metal ions which are normally present at relatively high concentrations in biological systems [5–7] and which have been shown to reduce the rate of calcite crystal growth in seawater systems [8]. Factors governing the mechanism of precipitation and dissolution of these salts are therefore of considerable environmental importance, especially the influence of foreign cations which may exert a marked effect on the crystallization and dissolution rates.

In the present work the constant composition method [9] has been used to study the dissolution of calcium carbonate (calcite crystals) in aqueous solutions. The influence of the presence of cobalt, manganese, copper and nickel ions on the rate of dissolution has also been investigated.

2. Materials and methods

Undersaturated solutions of calcium carbonate were prepared using both ultrapure (Alfa Chemical) and reagent grade (J. T. Baker) chemicals with triply distilled deionized water. Solutions were filtered off (0.22 μm Millipore filters) before use. The concentrations of calcium, cobalt, manganese, copper and nickel ions ($\pm 0.2\%$) were determined by atomic absorption (Perkin-Elmer Model 2380) or by exchanging the metal ion for a hydrogen ion on a Dowex 50 ion exchange resin and titrating the liberated acid with standard base.

Calcite seed crystals were prepared by a method similar to that used by Reddy and Nancollas [10] by adding 0.20 mol dm^{-3} calcium chloride to 0.20 mol dm^{-3} sodium carbonate solution at 25 °C. The crystals were aged for at least three weeks before use. The seed material was subjected to X-ray powder diffraction studies and scanning electron microscopy, and the specific surface area of the seed crystals was found to be $0.72 \pm 0.01/\text{m}^2\,\text{g}^{-1}$ (determined by BET analysis using nitrogen).

The experiments were performed at 25 ± 0.1 °C in a 700 cm^3 capacity double-walled Pyrex glass vessel fitted with a Perspex lid with holes for the electrodes and for sampling. Before and after each experiment the combination electrode (9100 Herisau) was standardized with NBS buffers covering the pH range of interest; the buffers were prepared according to the Bates' method [11]. Subsequently, undersaturated solutions of the desired concentration were prepared by slow addition of calcium chloride solution to a sodium hydrogen carbonate solution. Following the introduction of the calcite seed crystals, the activities of the calcium and carbonate ions were maintained at constant levels by the addition of sodium chloride as a diluent monitored by means of a pH-stat (Model 632 Methxom + Impulsomat 614 + Dosimat 665

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+ Labograph 586). The pH of the working solutions was 9.20 ± 0.01.

Additive solutions were also introduced as titrants in order to compensate for dilution effects. In addition samples were periodically withdrawn and filtered (0.22 μm) prior to solution and solid-phase analyses. The data confirmed that the lattice ion and inhibitor concentrations were kept constant to within 1%.

3. Results and discussion

The concentrations of the ionic species in the undersaturated solutions were calculated as described previously [12], using the expressions for mass balance, electroneutrality and thermodynamic equilibrium constant K for the various associated species in equilibrium (see Table I). The computations were made by successive approximations for the ionic strength I, as described previously [12], using the activity coefficients calculated from the extended form of the Debye-Hückel equation proposed by Davies [22].

For many sparingly soluble salts, M_aA_b, the rate of dissolution, normalized for seed surface area, can be expressed by

$$R = d[M_aA_b]/dt = KS\sigma^n \qquad (1)$$

where K is the dissolution rate constant, S is proportional to the number of dissolution sites available on the seed crystals, n is the effective order of reaction and σ is the relative degree of undersaturation, which may be defined by

$$\sigma = (K_{SO}^{1/2} - IP^{1/2})/K_{SO}^{1/2} \qquad (2)$$

where the ionic product IP and the solubility product K_{SO} are expressed in terms of the appropriate activities of the ionic species $[(Ca^{2+})(CO_3^{2-})]^{1/2}$ at time t and at equilibrium respectively. The thermodynamic solubility product 4.723×10^{-9} M^2 was determined by allowing crystal growth and dissolution experiments to proceed to equilibrium. This value is in satisfactory agreement with the value 4.5×10^{-9} M^2 obtained by Nancollas [23].

The results of the dissolution of calcium carbonate (calcite) experiments are summarized in Table II in which T_{Ca} and T_{CO_3} are the molar concentrations of calcium and carbonate ions, respectively. Typical plots of the amount of calcium carbonate dissolved, as a function of time, are shown in Fig. 1. The slopes of these lines, reflecting the rates of dissolution, are summarized in Table II. Since the extent of the dissolution reaction was small (< 5% of the total surface area of the seed crystals) any change in crystal surface area accompanying dissolution could be ignored. The effective order of reaction, determined from the slopes of typical plots of $-\log R$ against $-\log \sigma$ such as that shown in Fig. 2, confirms a first-order dependence on relative undersaturation ($n \sim 1$) in Equation 1, over a range of relative undersaturation, σ,

TABLE I Equilibria taken into account for aqueous solutions of calcium carbonate

n	K; 25 °C	References
$H^+ + CO_3^{2-} = HCO_3^-$	$10^{10.329}$ M^{-1}	[13]
$H^+ + HCO_3^- = H_2CO_3$	$10^{3.76}$ M^{-1}	[14]
$CO_2(aq.) + H_2O = H_2CO_3$	$10^{-2.59}$	[14]
$Ca^{2+} + OH^- = CaOH^+$	$10^{1.37}$ M^{-1}	[15]
$Ca^{2+} + CO_3^{2-} = CaCO_3(aq.)$	$10^{3.20}$ M^{-1}	[16]
$Ca^{2+} + HCO_3^- = CaHCO_3^+$	$10^{1.26}$ M^{-1}	[16, 17]
$H^+ + OH^- = H_2O$	$10^{13.999}$ M^2	[18]
$CaCO_{3(s)}$ (calcite) $= Ca^{2+} + CO_3^{2-}$	$10^{-8.418}$ M^2	[19]
$CO_{2(g)} + H_2O = H_2CO_3^{*a}$	$10^{-1.464}$ M atm^{-1}	[20]
$CO_{2(g)} + H_2O = H^+ + HCO_3^-$	$10^{-7.81}$ M^2 atm^{-1}	[20, 21]

[a] $H_2CO_3^*$ is defined as $CO_2(aq.) + H_2CO_3$.

TABLE II Dissolution of calcium carbonate crystals, $T_{Ca}:T_{CO_3} = 1:1$ with 7 mg seed

$T_{Ca}/10^{-4}$ (mol dm^{-3})	$10^2\sigma$	t (°C)	Rate/10^{-7} (mol min^{-1} m^{-2})
2.18	8.4	15	0.97051
2.03	8.4	20	1.1614
1.77	8.4	30	1.4588
1.66	8.4	35	1.6982
1.75	15.8	25	2.0635
1.80	13.2	25	1.5102
1.86	10.3	25	1.3951
1.90	8.4	25	1.3194
1.94	6.4	25	1.2464
1.97	5.0	25	0.83759
2.01	3.2	25	0.56213

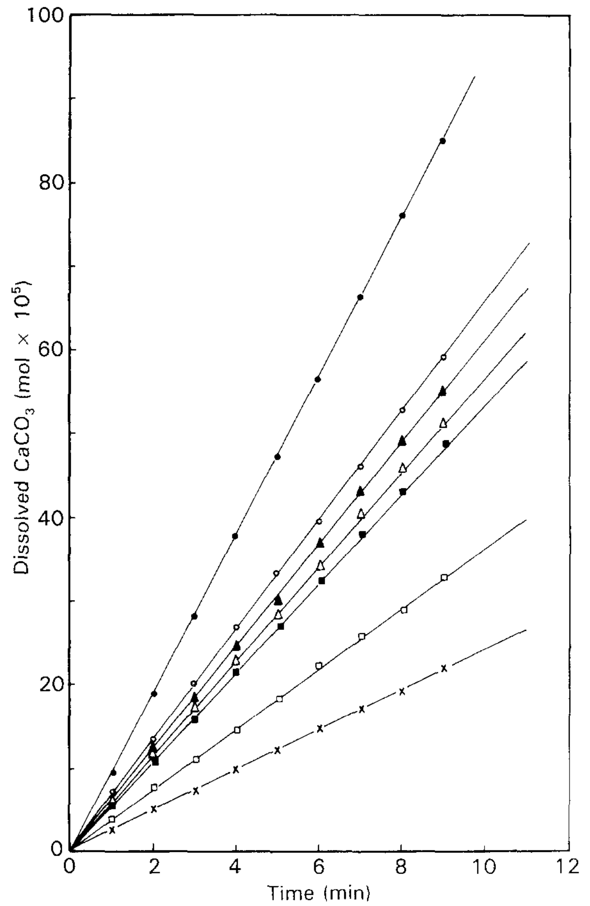

Figure 1 Dissolved calcium carbonate versus time.

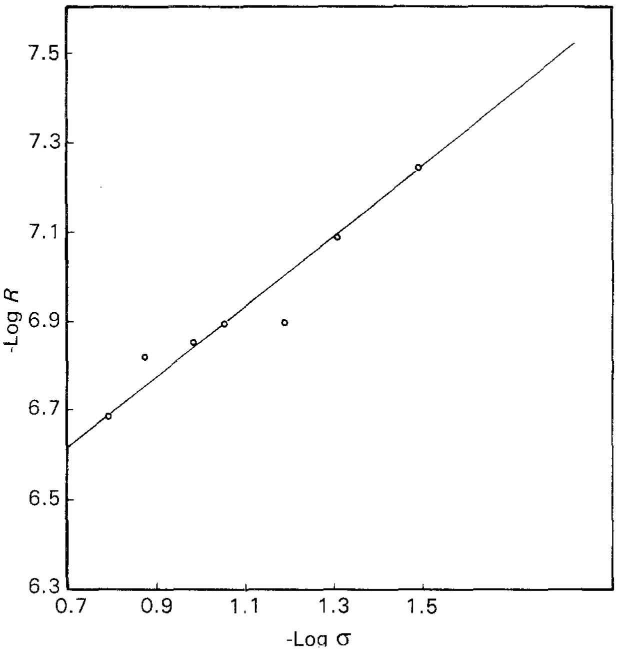

Figure 2 Plots of $-\log R$ versus $-\log \sigma$ for calcium carbonate dissolution.

TABLE III Effect of some metal ions on the rate of dissolution of calcium carbonate crystals, $T_{Ca}:T_{CO_3} = 1:1$; ionic strength $= 0.15\,\text{mol dm}^{-3}$ (NaCl) and 7 mg

$10^2\sigma$	Additive (10^{-7} mol dm^{-3})		Rate (10^{-8} mol min^{-1} m^{-2})	Inhibition (%)
10.3	–	–	13.951	–
10.3	4	Mn	9.549	31.553
10.3	5	Mn	8.731	37.417
10.3	7.5	Mn	7.710	48.606
10.3	10	Mn	6.411	54.046
10.3	20	Mn	4.218	69.766
10.3	30	Mn	2.531	81.858
10.3	2.5	Ni	8.717	37.517
10.3	5	Ni	6.327	54.648
10.3	7.5	Ni	5.230	62.512
10.3	10	Ni	4.218	69.766
10.3	20	Ni	2.206	84.188
10.3	40	Ni	2.109	84.883
10.3	5	Co	10.702	23.289
10.3	7.5	Co	9.279	33.489
10.3	20	Co	6.045	56.670
10.3	30	Co	5.009	64.096
10.3	40	Co	4.471	67.952
10.3	50	Co	3.627	74.002
10.3	5	Cu	8.014	42.556
10.3	7.5	Cu	6.327	54.648
10.3	10	Cu	5.423	61.128
10.3	20	Cu	2.711	80.568
10.3	50	Cu	2.343	83.206
13.2	–	–	15.102	–
13.2	4	Cu	10.402	31.122
13.2	5	Cu	9.796	35.134
13.2	7.5	Cu	8.390	44.444
13.2	10	Cu	7.674	49.186
13.2	30	Cu	4.000	73.513
13.2	50	Cu	3.571	76.354
8.4	–	–	13.194	–
8.4	4	Cu	6.832	48.219
8.4	5	Cu	6.305	52.213
8.4	7.5	Cu	5.373	59.277
8.4	10	Cu	4.438	66.363
8.4	20	Cu	1.915	85.486
8.4	50	Cu	1.600	87.873

0.032–0.158. A value of unity for n might reflect transport of a diffusion-controlled process. The suggestion of a predominantly diffusion-controlled process at relative undersaturations ($0.032 < \sigma < 0.158$) may also be supported by the observed low activation energy (2.09 kcal mol^{-1}).

The influence of the metal ions is especially interesting with respect to industrial application since they are generally not incorporated into the crystal lattice and may markedly influence the rate of precipitation and dissolution. The influence of cobalt, manganese, copper and nickel ions on the dissolution of calcium carbonate (calcite crystals) has been studied in aqueous solutions at sustained relative undersaturation. The results of the dissolution of calcium carbonate experiment in the presence of metal ions are summarized in Table III. It can be seen that concentrations of metal ions as low as 2.0×10^{-6} mol dm^{-3} reduced the dissolution rates by at least 84.19, 80.57, 69.77 and 56.67% compared to that in pure solution at the same relative undersaturation in the presence of nickel, copper, manganese and cobalt, respectively. Thus, in a comparative study, the effectiveness of the metal ion inhibitors at any concentration level was found to be in the order Ni > Cu > Mn > Co. The rate profiles given in Fig. 3 show that the dissolution rates of calcium carbonate in the presence of metal ions (nickel, copper, manganese and cobalt) decrease with successive additions of metal ions. As the concentration of additive molecules increases, the active dissolution sites on the crystal surfaces may be blocked through adsorption and the rate of crystal dissolution decreases.

The adsorption of the molecules at active sites on the crystal surfaces may be interpreted in terms of the Langmuir adsorption isotherm [24]. This requires a linear relationship between the inverse of the relative reduction in rate $R_0/(R_0 - R_i)$ and the reciprocal of the inhibitor concentration, where R_0 and R_i are the rate of dissolution in the absence and presence of the inhibitor, respectively. The applicability of the Langmuir model is demonstrated by the linearity of plots in Fig. 4. The values of the adsorption affinity constants K_L, given by the inverse slopes of the lines in Fig. 4, are 3.00×10^6, 1.52×10^6, 1.25×10^6 and 0.61×10^6 dm^{3}mol for added nickel, copper, manganese and cobalt ions, respectively. Again, the values of adsorption affinity constants reflect the effectiveness of metal ions as inhibitors (Ni > Cu > Mn > Co).

The influence of the dissolution driving force on the degree of inhibition by metal ions is especially interesting. Experiments have also been made in the presence of copper at different relative undersaturation, in order to investigate the influence of dissolution driving force on the degree of inhibition. The data compiled in Table III show that a concentration as low as 5×10^6 mol dm^3 copper ion reduced the dissolution rates by at least 87.87, 83.21 and 76.35% compared to that in pure solution at the relative

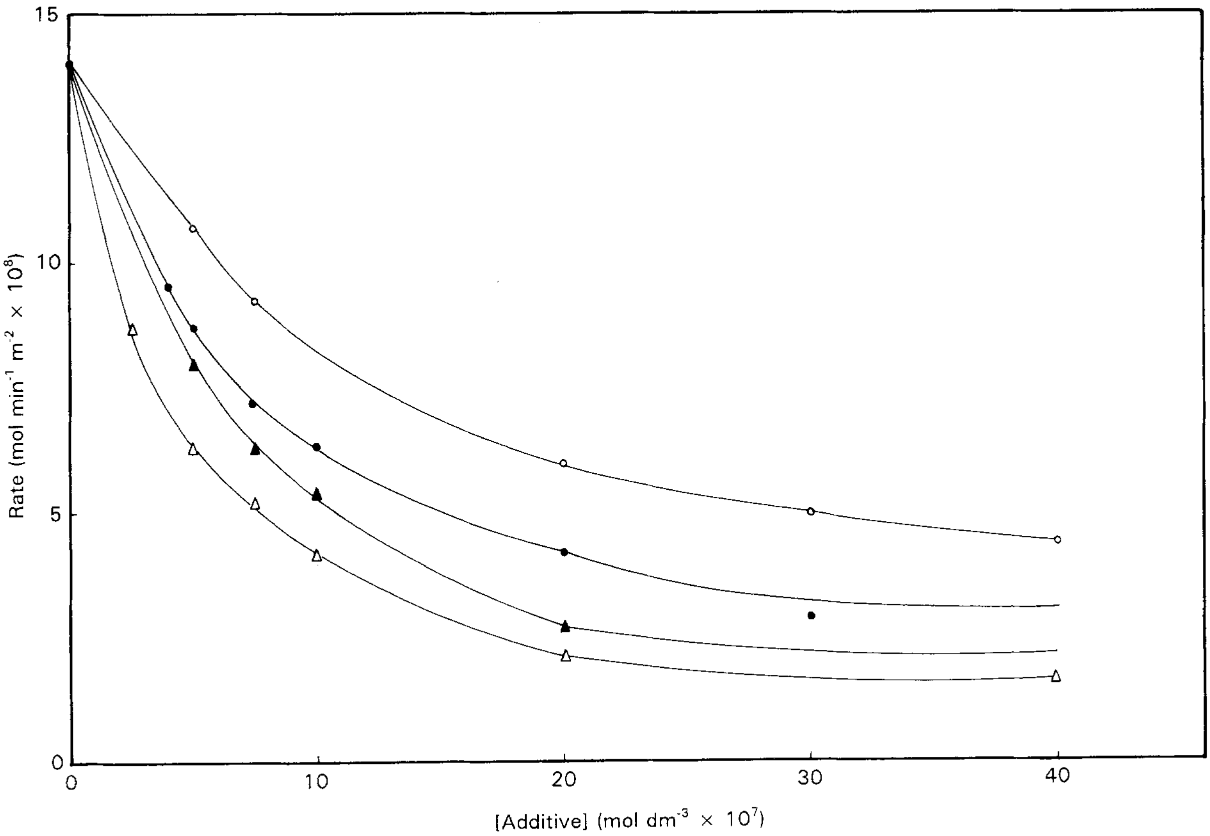

Figure 3 Rate of dissolution versus [additive] for Co (○), Mn (●), Cu (▲) and Ni (△).

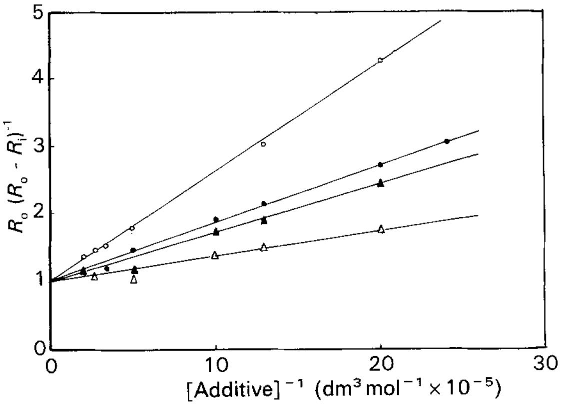

Figure 4 $R_0(R_0 - R_i)^{-1}$ versus $[\text{additives}]^{-1}$ for Co (○), Mn (●), Cu (▲) and Ni (△).

undersaturation $\sigma = 0.084$, 0.103 and 0.132, respectively. Fig. 5 confirms the applicability of the simple adsorption isotherm at all relative undersaturations studied. The values of the adsorption affinity constants are 2.23×10^6, 1.52×10^6 and 1.11×10^6 dm^3 mol^{-1} at relative undersaturations $\sigma = 0.084$, 0.103 and 0.132, respectively. These values reflect the high adsorption affinity at low relative undersaturation in the presence of the copper ion. A similar dependence of the degree of inhibition on change in driving force has been observed for the influence of calcium ions on the rate of dissolution of barium fluoride [25]. The marked dependence on degree of saturation of the effectiveness of growth and dissolution inhibitors has important consequences in

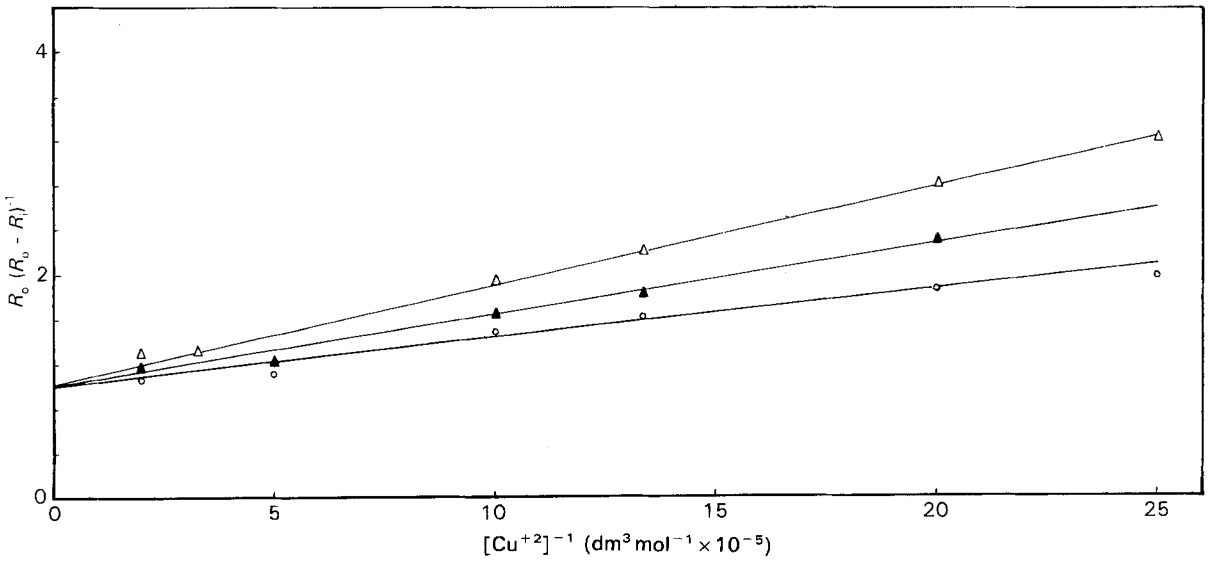

Figure 5 $R_0(R_0 - R_i)^{-1}$ versus $[\text{Cu}^{+2}]^{-1}$ at different relative undersaturations: $\sigma = 0.132$ (△), $\sigma = 0.103$ (▲), and $\sigma = 0.084$ (○).

assessing the usefulness of these compounds for industrial applications such as control of scale.

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