EFFECT OF THE PRESENCE OF SOME ANIONS ON THE CRYSTAL GROWTH OF CALCITE IN AN ARTIFICIAL SEAWATER

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ABSTRACT

Effect of the presence of inorganic phosphate, sulfate, fluoride and urate on crystal growth of the precipitated calcite in an artificial seawater at 25°C, pH=8.5 and salinity $=35^0/_{00}$ has been studied. The crystal growth of calcite crystals is markedly inhibited by the presence of each of these additives except sulfate. The degree of inhibition increases with the successive addition of anions and with decrease of saturations. The effect of the studied inhibitors (phosphate, fluoride and urate ions) have been attributed to the blocked active sites on the crystal surfaces by adsorption of these anions. The reduction in precipitation rates can be interpreted in terms of Langmuir – type adsorption isotherm.

1. INTRODUCTION

Mineralization and demineralization of sparingly soluble salts in aqueous solutions are of considerable importance in a wide variety of fields. Calcium carbonate precipitation may play an important role in the carbonate buffering of seawater (Koutsoukos *et al.*, 1981). The formation of scales in geothermal applications, evaporative desalination plants, cooling towers and petroleum engineering is a persistent problem; the calcium carbonate scale formation is made worse by a decreasing solubility with increasing temperature. A scale deposit will form an insulating blanket on transfer surfaces, which greatly impedes the flow of heat, causing a reduction in capacity or efficiency or both. From industrial experience corrosion and scale formation perform a synergistic action. So, the influence of foreign cations and anions may exert a marked effect on the rate of precipitation of calcite crystals. However, this problem has been overcome by adding inhibitors like acids.

The crystal growth of the precipitate was initiated by the introduce of a weighted amount of calcite seed crystals in a super-saturated synthetic seawater. The influence of presence of some anions as inorganic phosphate, sulfate, fluoride and urate upon the rate of the crystal growth of calcite has been investigated.

2. MATERIALS AND METHODS

2.1. Materials

Solutions of calcium chloride, sodium bicarbonate, sodium phosphate, sodium sulfate, sodium fluoride, sodium urate, potassium hydrogen phethalate and sodium hydroxide were prepared in triply distilled deionized water using Reagent Grade chemicals. These solutions were filtered through (0.22 μm Millipore membrane filters) before use. Concentrations of solutions 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 (Hamza *et al*., 1993).

Calcite seed crystals were prepared by a method similar to that used by (Reddy and Nancollas, 1971) by adding 0.20 M calcium chloride to 0.20 Na-bicarbonate solution at 25°C. The seed crystals were aged for at least 3 weeks before use. The seed crystals were confirmed as calcite crystals by scanning electron microscopy and by x- ray powder diffraction (Phlips Powder Diffraction Apparatus with Copper Kα Radiation with Ni Filter). The specific surface areas (SSA) of the crystals, measured using a single – point nitrogen adsorption apparatus (Quantachrome Corporation, Greenvale, NY) was 0.52 m^2/g.

2.2. Methods

Precipitation experiments were made in pyrex glass vessels of approximately 500 ml capacity. The artificial seawater used in this work was prepared according to that mentioned by (Grasshoff, 1976) as shown in Table 1. The super – saturated calcium carbonate solutions in artificial seawater were prepared by adding appropriate volumes from standardized sodium carbonate stock solution. The solutions were maintained at an appropriate temperature 25±0.1°C by circulating thermo stated water. Working solutions were always magnetically stirred, and nitrogen gas was bubbled throughout the experiment, the pH was adjusted at 8.50 and at fixed salinity 35‰.

During the precipitation process, samples were withdrawn at random times, filtered through membrane filters (0.22 μm Millipore) and the filtrates were analysed for calcium by EDTA using Eriochrome Black T indicator. While the solids collected by filtration were examined as calcite by x-ray diffraction.

Table (1): The composition of synthetic seawater.

Composion	g/Kg
NaCl	23.939
MgCl	5.O79
NaSO$_4$	3.994
CaCl$_2$	1.123
KCl	0.667
KBr	0.098
H$_3$PO$_4$	0.O27
SrCl$_2$	0.024
NaF	0.003
NaHCO$_3$	0.196

3. RESULTS AND DISCUSSION

The concentrations of ionic species in these solutions were calculated from mass – balance and electroneutrality expressions as described by (Nancollas, 1966). Activity coefficients were calculated from the extended form of the Debye – Huckel equation proposed by
Davies (1962).

The relative super – saturation, σ, is defined by:

$$\sigma = I^{1/2} - I_0^{1/2} / I_0^{1/2} \qquad (1)$$

in which I is molar concentration product of calcium carbonate in the solutions and I_0 the solubility value at the same concentration.

For many sparingly soluble salts, M_aA_b the rate of precipitation R, normalized for seed surface area can be expressed by equation 2:

$$R = d [M_a B_b] / dt = ks\sigma^n \qquad (2)$$

in which k is the crystallization rate constant, s is proportional to the number of growth sites available on the seed crystal surface and is the effective order of reaction.

The calcium carbonate systems are 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 super-saturated solutions for periods of hours in the absence of inoculating seed crystals.

A series of precipitation experiments covering a range of additives concentrations and initial relative super-saturation has been performed. The first 5 experiments were done without the addition of any anions with the purpose of determining whether the growth rate was dependent on the initial super-saturation. The solutions even containing additives were all stable at all super-saturated, prior seed addition. The results of the precipitation experiments summarized in at Table 2. It can be seen that R, normalized

for the initial surface area of inoculating seed, is constant, confirming that precipitation takes place on the seed crystals surfaces without additional nucleation or spontaneous precipitation.

The rate of precipitation of calcite crystals was again studied but in the presence each of other anions phosphate, sulfate, fluoride and urate. The effect of the added other anions ions on the precipitation reactions is illustrated from the rate profiles shown in (Fig.1). Where the precipitation rates of calcite in the presence of the other ions (phosphate, sulfate, fluoride and urate) decrease with successive additions of the additive ions. It can be seen that the effectiveness of the inhibition is in the following orders : phosphate > fluoride > urate, while almost little effect has been motioned in case of sulfate; may be because artificial seawater contain sulfate (3-4g/Kg) that is why the addition of sulfate ions showed little or no affection the inhibition. Experimental data in the presence of anions ions, show that concentrations as low as 40×10^{-6} mol/l for each additive reduced the precipitation rates by as least as 72.6, 61.2, 49.6, and 10.6% compared to that in pure solution at the same relative super-saturation ion for the presence of phosphate, fluoride, urate and sulfate, respectively. As the concentration of additives ions increases, the active growth sites on the crystal surfaces become blocked through adsorption and lead to decreases the rate of precipitation of calcite. In general, the rates of precipitation and dissolution of sparingly soluble salts are markedly inhibited by the addition of certain additives (Hamza, 1990; Hamza and Hamdona, 1991; Hamdona et al., 2005). A number of studies have been made in the presence of some anions and cations on the rate of crystal growth and dissolution of calcite (House, 1987; Hamza and Hamdona, 1992; Hamdona and khader, 1944; Salem et al., 1994).

Table (2): Effect of some anions on the rate of precipitation on calcite crystals, seed 50 mg and 25°C.

σ	Additives 10^{-6}mol/l		Rate 10^{-6} mol/min m	Inhibition %
0 .90	-	---	1.630	---
1.10_a	-	-	2.311	-
1.29	-	-	2.981	-
1.51	-	-	4.023	-
1.71	-	-	4.764	-
2.35	-	-	8.222	-
2.35	5	PO_4	6.123	25.53
2.35	10	PO_4	4.691	42.95
2.35	20	PO_4	3.141	61.80
2.35	30	PO_4	2.450	70.20
2.35	40	PO_4	2.253	72.59
2.35	50	PO_4	2.150	75.61
2.35	5	F	5.611	16.05
2.35	10	F	4.289	31.15
2.35	20	F	3.497	47.84
2.35	30	F	3.092	57.47
2.35	40	F	2.670	61.23
2.35	50	F	3.045	63.24
2.35	5	Ur	6.351	13.62
2.35	10	Ur	5.102	23.24
2.35	20	Ur	4.455	37.95
2.35	30	Ur	4.042	45.82
2.35	40	Ur	3.663	49.62
2.35	50	Ur	3.922	52.53
2.35	5	SO_4	7.752	4.36
2.35	10	SO_4	7.501	5.72
2.35	20	SO_4	7.377	8.77
2.35	30	SO_4	7.351	10.28
2.35	40	SO_4	7.305	10.59
2.35	50	SO_4	7.300	11.15

An experiments at $\sigma = 1.10$ at different seeds.
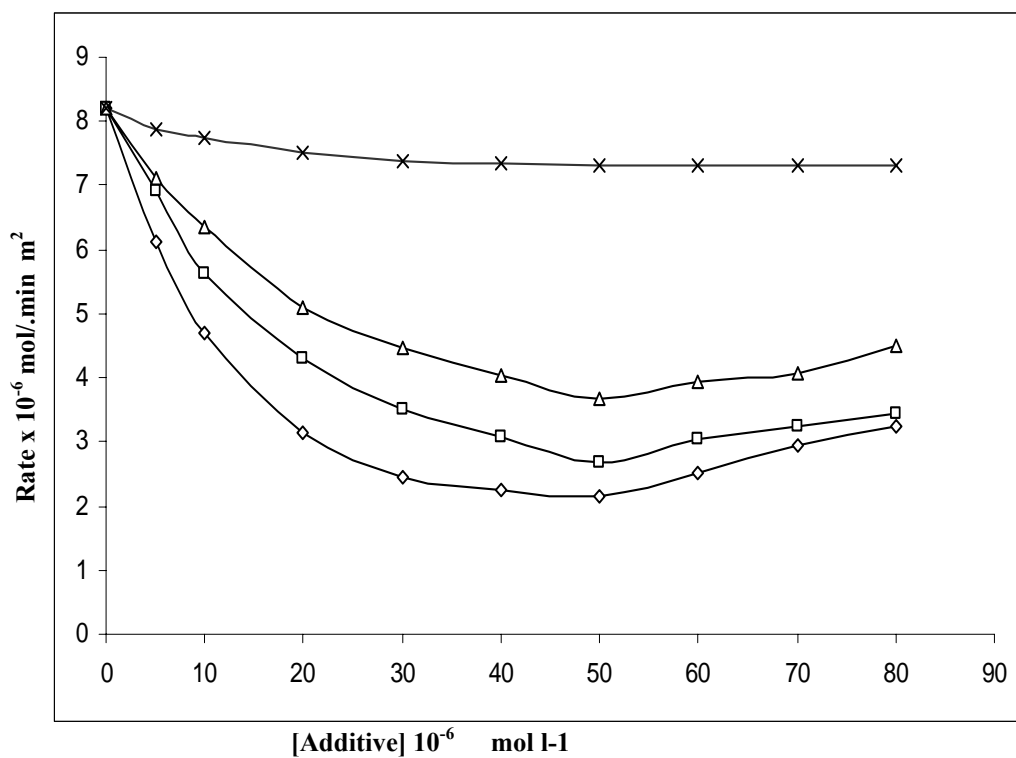
Fig. (1). **Rate of precipitation versus additive of each of phosphate (◇), fluoride (▢), urate (△) and sulfate (×) ions.**

There are several possible mechanisms by which an additive can inhibit the crystal growth reaction. An additive may form stable complexes with one of the precipitating ions and decreases the solution super-saturation. In the present study, Phosphate, sulfate, fluoride and urate ions form moderately stable complexes with calcium ions. Relevant to the systems, the results of speciation calculations obtained by using literature constant values show that in super-saturated solutions with 1.0×10^{-6} mol/L inhibitor, less than ≈ 3 % of the total dissolved calcium is bound as calcium inhibitor containing complex. Also, the calculation shows that, the effect of ion-pair formation on kinetics is virtually negligible. The assumption that the inhibitory effect of the additives is mainly due to adsorption and subsequent blocking of the active growth sites, was tested by using the Langmuir adsorption model.

The adsorption of the additives at active sites on the crystal surfaces may by interpreted in terms of the Langmiur adsorption isotherm, 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 (Kousoukos $et\ al$, 1981) where R_0 and R_i are the rate of precipitation in the absence and presence of the inhibitor, respectively. The applicability of the Langmuir model is demonstrated by the linearity of plots in Fig. 2. The values of the adsorption affinity constants K_L, are 7.44×10^4, 4.52×10^4 and 2.87×10^4 l/mol for added phosphate, fluoride and urate ions, respectively. The results of the present study indicate that sulfate ion does not interact with calcite surfaces sufficiently to retard their growth rate or alter their morphology development (Reddy and Nancollas, 1976) or not it's

bound as Ca inhibitor containing complex. Again, the values of adsorption affinity constants reflect the effectiveness of the anions as inhibitors for the precipitation of calcite.

The influence of driving forces on the degree of inhibition of calcite precipitation by these anions is interesting. Experiments also, have been made in the presence of phosphate at different relative super-saturation, in order to investigate the influence of driving force on the degree of inhibition. The data compiled in Table 3 showed that a concentration as low as 40×10^{-6} mol/L phosphate ion reduce the precipitation rates by at least 87.26, 72.59 and 60.42% compared to that in pure solution at the same relative super-saturation $\sigma = 2.10$, 2.35 and 2.62, respectively. Fig. 3 confirms the applicability of the simple adsorption isotherm at all relative super-saturations studied. The values of the adsorption affinity constants are 15.38×10^4, 7.44×10^4 and 4.01×10^4 L/mol at relative super-saturation $\sigma = 2.10$, 2035 and 2.62, respectively. These values reflect the high adsorption affinity at low relative super-saturation in the presence of phosphate ion. A similar dependence of the degree of inhibition on change in driving force has been observed for the influence of polyphosphonate on the rate of precipitation of calcite (Hamza and Hamdona, 1992).

The marked dependence upon the degree of saturation of the effectiveness of precipitation inhibitors has important consequences in assessing the usefulness of these compounds for industrial applications such as the control of scales. It is clearly insufficient to base such selections on the results of a limited number of threshold precipitation experiments.

Table (3): Precipitation of calcite in the presence of phosphate ions at different degree of saturation.

σ	PO_4^{2-} x 10^{-6} Mol/l	Rate x 10^{-6} Mol/min m^{-2}	Inhibition %
2.10	--	6.729	-
2.10	5	4.252	36.81
2.10	10	2.611	61.20
2.10	20	1.874	72.15
2.10	30	1.255	81.35
2.10	40	0.857	87.26
2.10	50	0.758	88.74
2.10	60	0.823	87.77
2.10	70	0.992	85.26
2.10	80	1.379	79.51
2.35	--	8.222	--
2.35	5	6.123	25.53
2.35	10	4.691	42.95
2.35	20	3.141	61.80
2.35	30	2.450	70.20
2.35	40	2.253	72.59
2.35	50	2.150	75.61
2.35	60	2.518	73.82
2.35	70	2.952	64.10
2.35	80	4.253	48.27
2.62	--	10.592	--
2.62	5	8.251	22.10
2.62	10	7.587	28.37
2.62	20	5.926	44.05
2.62	30	5.123	51.63
2.62	40	4.192	60.42
2.62	50	4.662	55.99
2.62	60	4.368	59.76
2.62	70	4.703	55.60
2.62	80	5.062	52.21
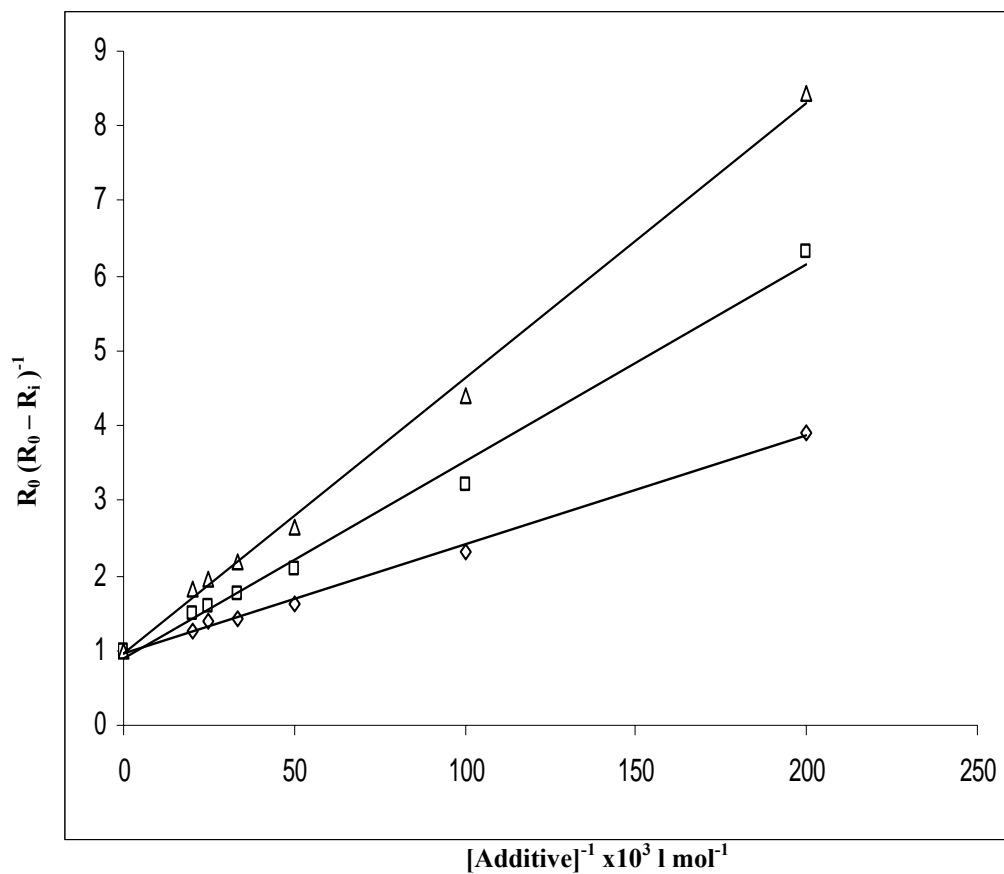
Fig. (2): $R_0(R_0 - R_i)^{-1}$ **versus [additive]$^{-1}$ for phosphate ($\diamondsuit$), fluoride ($\square$), and urate ($\triangle$).**
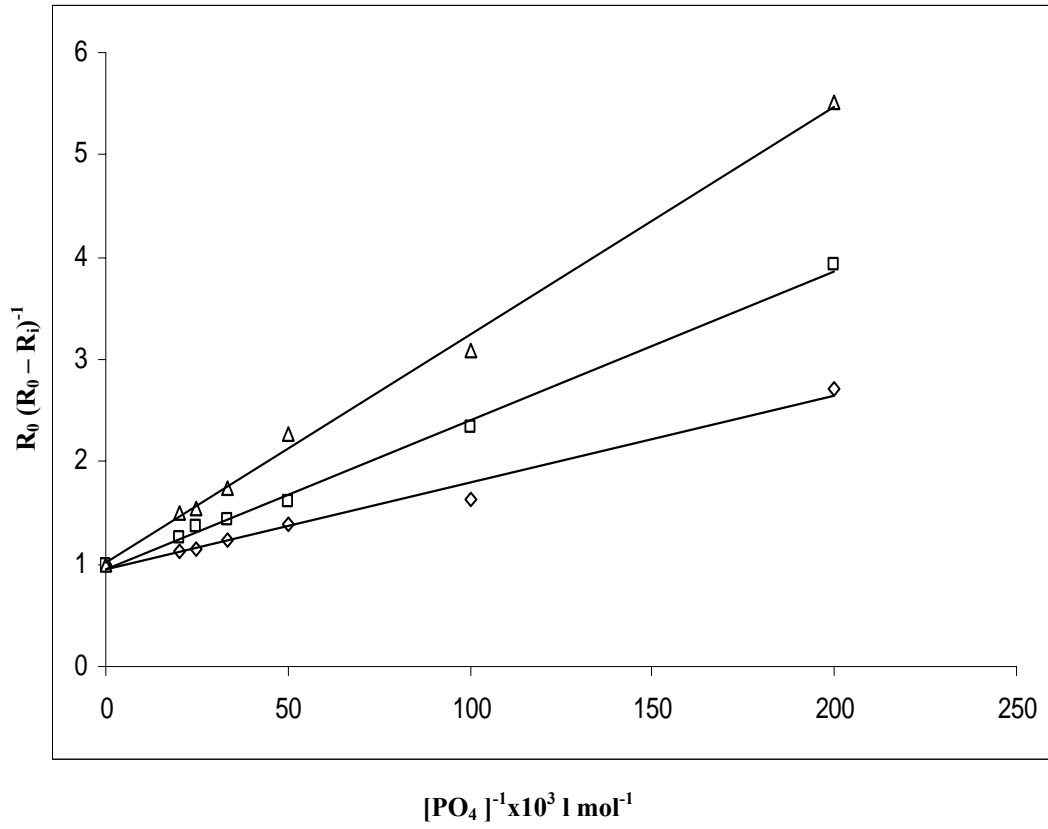
Fig.(3): $R_0(R_0 - R_i)^{-1}$ versus $[PO_4]^{-1}$ at different relative super- saturation : $\sigma = 2.10$ (◇), $\sigma = 2.35$ (□) and $\sigma = 2.62$ (△).

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4. CONCLUSIONS

The present study indicated that the presence of inhibitors, phosphate, sulfate, fluoride and urate ions at low concentrations can markedly inhibit the precipitation rate of calcite crystals, except the sulfate ion, which almost no effect has been observed because artificial seawater contains sulfate (3-4 g/Kg). On the basis of the kinetic data, effectiveness of the inhibitors follows the order: phosphate > fluoride > urate >>> sulfate. Degree of inhibition increases with decreases of the degree of saturation. The inhibition effect of the inhibitors may be explained by the adsorption of inhibitor ion at growth sites in terms of Langmuir-type adsorption isotherm.

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FIGURE LEGENDS

Figure 1. Rates of precipitation versus additives ions: phosphate ($\Diamond$); fluoride ($\square$); urate (Δ) and sulfate ($\times$).

Figure 2. $R_0 (R_0 - R_i)^{-1}$ versus [additive]$^{-1}$: phosphate ($\Diamond$) ; fluoride ($\square$) and urate (Δ).

Figure 3. $R_0 (R_0 - R_i)^{-1}$ versus [PO_4] at different relative super-saturation : $\sigma = 2.10$ ($\Diamond$) ; $\sigma = 2.35$ ($\square$) and $\sigma = 2.62$ (Δ).