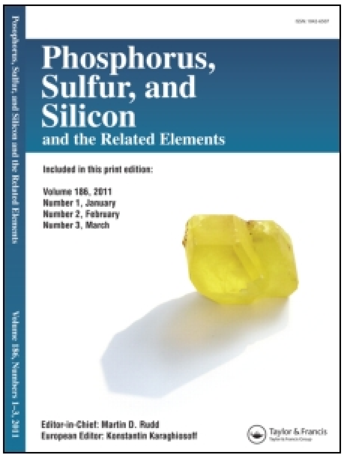

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EFFECT OF ADDITIVES ON THE CRYSTALLIZATION OF BARIUM SULPHATE

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The kinetics of crystallization of barium sulphate for both seeded and unseeded systems in presence of additives have been studied by following the changes in ionic conductivity in supersaturation solutions containing stoichiometric concentrations of the lattice ions at 298 K. The additives investigated include: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), hexa methylenediaminetetramethylenephosphonic acid (HMNTMP), ethylenediaminetetramethylenephosphonic acid (ENTMP) and nitrilotrimethylenephosphonic acid (NTMP). The effect of these additives on the growth kinetics has been studied at several inhibitor concentrations. The retarding effect of these inhibitors is interpreted in terms of adsorption of inhibitor ions at the active crystal growth sites following the Langmuir isotherm. The order, in terms of decreasing the inhibitory effect on the rate of growth of barium sulphate of the studied additives is HEDP > HMNTMP > ENTMP > NTMP. This order holds for both seeded and unseeded systems.

Key words: Additives, barium sulphate, phosphonates, kinetics.

INTRODUCTION

The crystal growth of sparingly soluble alkaline earth metal salts is of great importance due to their participation in a wide number of biological, industrial and environmental precipitation processes.[1-12] Of special interest are the barium salts because of their importance in the petroleum industry, as well as from the analytical chemical applications point of view.[13-16] The mechanisms of precipitation of these salts are therefore of great interest especially in the presence of additives which may exert considerable effects on their crystallization process.

Retardation and inhibition of crystal growth by additives are interesting phenomena and have wide applications in fields such as medicine and industry[17,18] and several implications in stereochemistry and materials science.[19-22] Of particular interest is the phosphonates. Although numerous studies have been reported on the effect of inhibitors on crystal growth yet the mechanism of inhibition is not well understood in most cases.

Previous study of the kinetics of crystal growth of barium sulphate revealed both diffusion and surface controlled growth mechanisms.[12] At high supersaturation ratios, the reaction was found to be determined by the rate of diffusion of the reacting species to the surface of the crystal, whereas at lower supersaturations the rate is controlled by polynuclear surface-growth mechanism. The diversity in the order of the reaction from 1 to 7 in case of barium sulphate crystallization[14,23-28] has led Nancollas and his group[29,30] to study this system using seeded growth technique. Their results indicated second order kinetics and a surface-controlled mechanism even at a supersaturation ratio as high as 56.

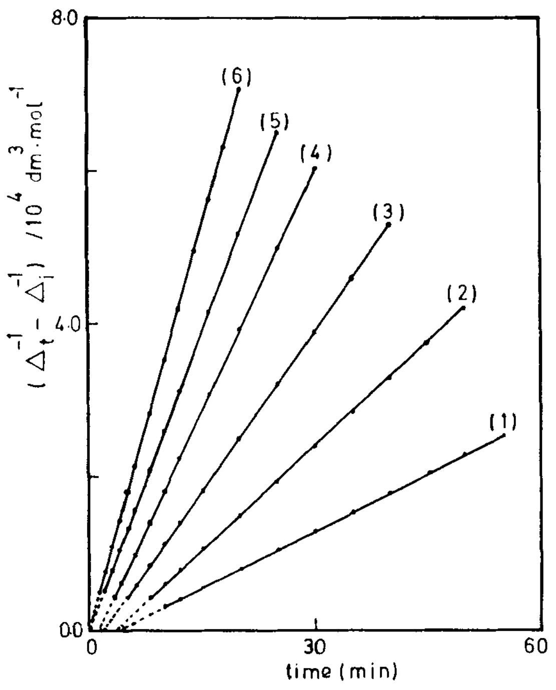

FIGURE 1 Plots of the integrated form of Equation 1 for the growth of $BaSO_4$ at different supersaturation values at 298 K; $T_{Ba} = T_{SO_4}$; curve (1) S = 15.07, curve (2) S = 20.10, curve (3) S = 25.12, curve (4) S = 30.15, curve (5) S = 35.17 and curve (6) S = 40.20.

This contribution is designed to present a detailed systematic study of the role of different additives; namely: 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), hexa methylenediaminetetramethylenephosphonic acid (HMNTMP), ethylenediaminetetramethylenephosphonic acid (ENTMP), and nitrilotrimethylenephosphonic acid (NTMP) on the kinetics of growth of barium sulphate in both seeded and unseeded systems.

RESULTS AND DISCUSSION

By analogy with the results of previous crystallization study on barium chromate,[1] the rate of crystal growth, R, in absence or presence of additives (and seeds) were analyzed using the equation

$$\begin{aligned} R &= -d[Ba^{++}]/dt = -d[SO_4^{--}]/dt \\ &= k_{obs}\{([Ba^{++}]_t[SO_4^{--}]_t)^{1/2} - (K_{sp}^0/f_2^2)^{1/2}\}^2 \\ &= K_{obs}\Delta^2 \qquad (1) \end{aligned}$$

where k_{obs} is the observed rate constant, K_{sp}^0 is the thermodynamic solubility product (taken as 9.9×10^{-11} [31,32]), $[X]_t$ is the ionic concentration of species X at time t and f_2 is the activity coefficients for a z-valent ion obtained by means of the Davies equation[33]

TABLE I

Effect of supersaturation ratio (S) on the rate of growth of barium sulphate at 298 K ($T_{Ba} = T_{SO_4}$)

T_{Ba} /10^{-4}M	S	$k_{obs}/10^3$ $M^{-1}.min^{-1}$
1.5	15.07	0.501
2.0	20.10	0.915
2.5	25.12	1.416
3.0	30.15	2.071
3.5	35.17	2.614
4.0	40.20	3.543

TABLE II

Effect of additives on the rate of growth of barium sulphate at 298 K ($T_{Ba} = T_{SO_4} = 4.0 \times 10^{-4}$ M)

[Additive] /10^{-8}M	k_{obs} /10^3 $M^{-1}.min^{-1}$ (% Inhibition)			
	HEDP	HMNTMP	ENTMP	NTMP
1.0	2.748 (22.4)	2.299 (35.1)	2.148 (39.3)	1.620 (54.2)
2.0	2.249 (36.5)	1.690 (52.3)	1.543 (56.4)	1.039 (70.6)
5.0	1.452 (59.0)	0.943 (73.3)	0.838 (76.3)	0.493 (86.0)
10.0	0.931 (73.7)	0.580 (83.6)	0.437 (87.6)	0.262 (92.6)
20.0	0.545 (84.6)	0.356 (89.9)	0.250 (92.9)	0.131 (96.3)

$$-\log f_2 = Az^2[\sqrt{I}(1 + \sqrt{I}) - 0.3I] \qquad (2)$$

where I is the ionic strength.

The integrated form of Equation (1);

$$k_{obs}t = \Delta_t^{-1} - \Delta_i^{-1} \qquad (3)$$

where Δ_t^{-1} and Δ_i^{-1} represent the concentration functions at time = t and time = 0, respectively, is plotted in Figure 1 for different supersaturation ratios, S, where S is defined as

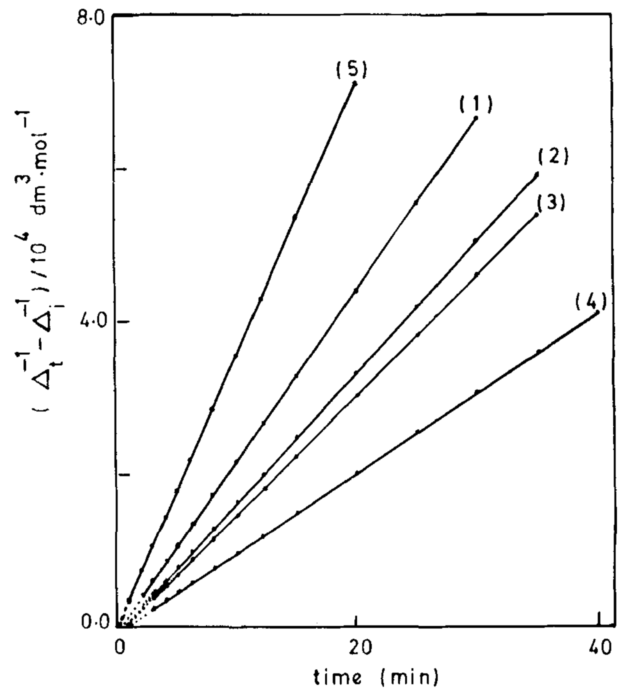

FIGURE 2 Plots of the integrated form of Equation 1 for the growth of $BaSO_4$ in presence of additives at 298 K; $T_{Ba} = T_{SO_4} = 4.0 \times 10^{-4}$ M; [Additive] = 2×10^{-8} M; curve (1) HEDP, curve (2) HMNTMP, curve (3) ENTMP, curve (4) NTMP and for comparison, curve (5) without additives.

$$S = ([Ba^{++}][SO_4^{--}]/K_{sp}^0)^{1/2} \tag{4}$$

The results obtained from Figure 1 for the observed rate constant values are depicted in Table I. The results obtained are consistent with a second order crystallization kinetics as indicated from the figure. This is in agreement with the previous results obtained by Nancollas *et al.* for the growth of barium sulphate from pure solutions.[29,30]

The effect of additives on the kinetics of growth of barium sulphate was studied for different concentrations of additives at S = 40.2. The results obtained are given in Table II. The small changes in concentration of barium ion due to its complexation with the additives were neglected in the rate calculations since its contribution to the total barium contents was at the most less than 0.13%. Plots of the integrated form of Equation (1) for systems containing 2×10^{-8} M additives, as a representative example, are given in Figure 2, thus consisting the same order of reaction.

For all the inhibitor concentrations used, precipitation did not commence immediately after adding potassium sulphate to barium chloride solution but began after an induction time, the duration of which increased with increasing inhibitor concentration. The induction time was also observed in absence of additives, by the decrease of the supersaturation ratio in the spontaneous growth experiments as indicated in Figure 1.

In spite of the world-wide application of additives as growth and dissolution inhibitors, their mechanism of inhibition is still largely obscure. Inhibitors are able to

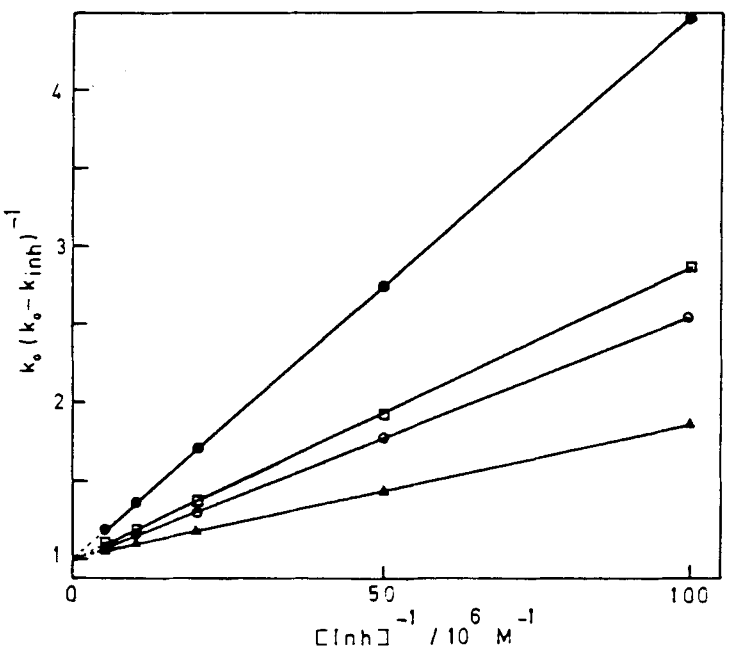

FIGURE 3 Langmuir adsorption isotherms in presence of (●) HEDP, (□) HMNTMP, (○) ENTMP and (△) NTMP; $T_{Ba} = T_{SO_4} = 4.0 \times 10^{-4}$ M.

TABLE III

Effect of additives on the rate of growth of barium sulphate at 298 K ($T_{Ba} = T_{SO_4}$); [additive] = 2×10^{-8} M

$T_{Ba}/10^{-4}M$	$k_{obs}/10^3\ M^{-1}.min^{-1}$ (% Inhibition)			
	HEDP	HMNTMP	ENTMP	NTMP
1.5	0.197 (60.6)	0.125 (75.0)	0.110 (78.0)	0.065 (87.0)
2.0	0.425 (53.5)	0.284 (68.9)	0.251 (72.5)	0.152 (83.3)
2.5	0.736 (48.0)	0.514 (63.7)	0.459 (67.5)	0.287 (79.7)
3.0	1.171 (43.4)	0.844 (59.2)	0.765 (63.0)	0.489 (76.3)
3.5	1.578 (39.6)	1.161 (55.5)	1.053 (59.7)	0.703 (73.1)
4.0	2.249 (36.5)	1.690 (52.3)	1.543 (56.4)	1.039 (70.6)

retard or to block the crystallization process even if added in trace amounts. Their intended consequence can only be explained either by complexation of the inhibitor with the lattice cation or by adsorption of the molecules at active sites of the crystal surface. The results obtained for barium sulphate growth in the presence of additives for spontaneous growth systems distinctly indicate a marked inhibitory effect as shown in Table II. The inhibition increases with increasing additive concentration.

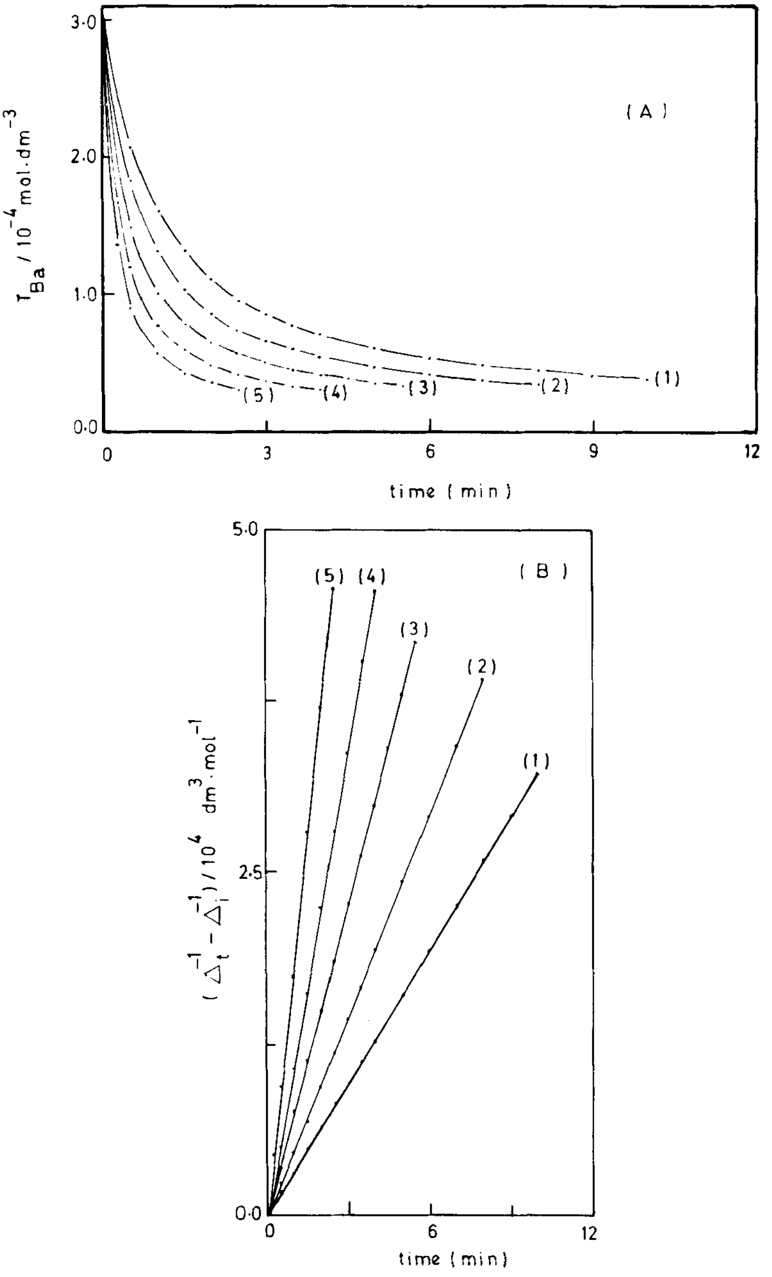

FIGURE 4 (A) Growth curves for $BaSO_4$ in presence of different amounts of seeds at 298 K; $T_{Ba} = T_{SO_4} = 3.0 \times 10^{-4}$ M, curve (1) 44.0 ppm, curve (2) 83.0 ppm, curve (3) 129.0 ppm, curve (4) 167.0 ppm and curve (5) 213.0 ppm. (B) Plots of the integrated form of Equation 1 for the growth of $BaSO_4$ in presence of different amounts of seeds at 298 K; $T_{Ba} = T_{SO_4} = 3.0 \times 10^{-4}$ M, curve (1) 44.0 ppm, curve (2) 83.0 ppm, curve (3) 129.0 ppm, curve (4) 167.0 ppm and curve (5) 213.0 ppm.

TABLE IV
Effect of the amount of seed on the rate of growth of barium sulphate at 298 K ($T_{Ba} = T_{SO_4} = 3.0 \times 10^{-4}$ M)

[Seed] ppm	$k_{obs}/10^3$ $M^{-1}.min^{-1}$
44.0	3.273
83.0	4.865
129.0	7.586
167.0	11.350
213.0	18.407

Assuming that the retarding action of the additive anions is mainly a result of their adsorption on crystal surfaces or embryos[34,35] thus preventing their further growth, then the Langmuir adsorption isotherm should be valid. If the absorbed inhibitor covers a fraction α of the total surface available, then the rates of adsorption and desorption are expressed as $k_a(1 - \alpha)$[Inhibitor] and $k_d\alpha$ where k_a and k_d are the rate constants for adsorption and desorption, respectively. At equilibrium, it can be shown that

$$k_0(k_0 - k_{inh})^{-1} - 1 = k_d/k_a[\mathrm{Inh}]^{-1} \quad (5)$$

where k_0 and k_{inh} are the rate constants in absence and presence of inhibitors, respectively. Thus the plot of the inverse of the relative reduction in rate and the reciprocal of the inhibitor concentration should yield a straight line. Figure 3 illustrates the above relationship for barium sulphate growth in presence of HEDP, HMNTMP, ENTMP and NTMP. This figure confirms that the inhibitory effect of these additives is due to adsorption at active growth sites. As indicated from the figure, the inhibitory effect of the additives is in the order HEDP > HMNTMP > ENTMP > NTMP. From Figure 3 the adsorption affinity constants are calculated to be 2.87×10^7, 5.48×10^7, 6.48×10^7 and 12.05×10^7 dm^3/mol for HEDP, HMNTMP, ENTMP and NTMP, respectively. These values reflect strong adsorption of HEDP at the interface relative to other inhibitors. As the concentration of additive increases, the active sites for crystallization on the crystal surface are blocked through adsorption and consequently the growth rate decreases. If sufficient inhibitor molecules are adsorbed at the surface of the whole crystal, no crystallization can occur. Our results indicate that an inhibition of about 85%, at least, is found in case of the presence of 2×10^{-7} M additive. When the concentration of additive increased to more than the above mentioned value, no decrease in the measured conductance was detected within 24 hours and the precipitation was completely inhibited. This phenomenon has been discussed by Naono[35] who attributed the stabilization action to an increase in the energy formation of the critical nuclei as a result of the endothermal adsorption of the inhibitor on the surface of the nucleus. This eventually

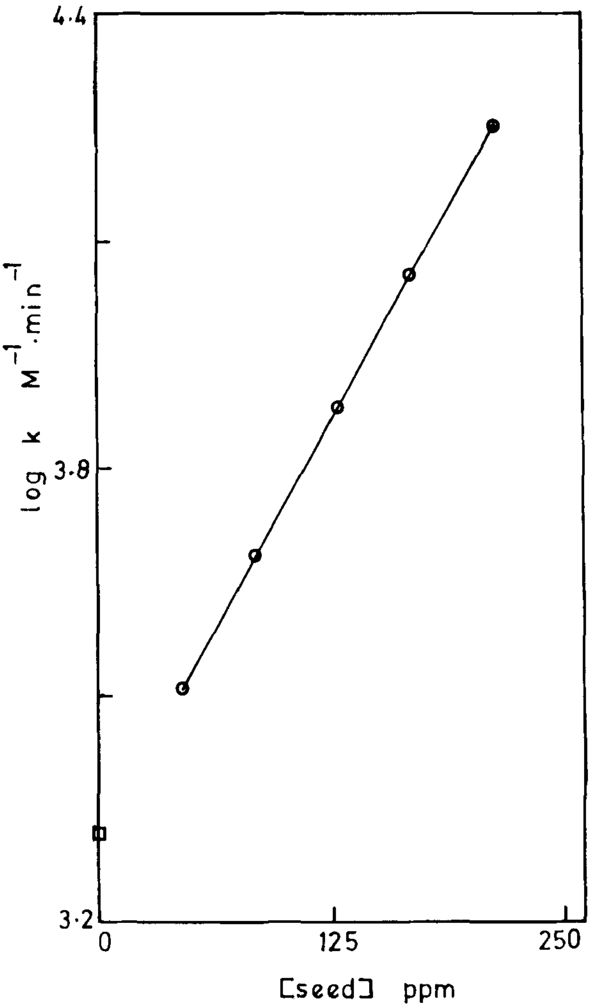

FIGURE 5 Plot of log k for $BaSO_4$ vs different amounts of seeds at 298 K; $T_{Ba} = T_{SO_4} = 3.0 \times 10^{-4}$ M. The value of log k for unseeded system is given as (□).

leads to the breakdown and disintegration of a number of the available embryos before further growth can take place.

Experiments in presence of all additives at different supersaturation values have also been performed in order to investigate the influence of the precipitation driving force upon the degree of inhibition. The results are given in Table III. For all of the added additives, it can be seen from Table III that the degree of inhibition decreases with increasing the driving force of precipitation. This is due to the fact that solute molecules moving from the bulk to an eventual incorporation in the crystal lattice must find a suitable incorporation site. This site is a critical-sized embryo. At low supersaturation ratios the number of these embryos are small and the additives are easily adsorbed thus showing a great inhibitory action. Inhibition of crystallization thus occurs by preferential adsorption of the additive molecules at the edges of the

TABLE V

Effect of additives on the rate of seeded growth barium sulphate at 298 K ($T_{Ba} = T_{SO_4}$); [additive] = 1.0×10^{-7} M

[Seed] ppm	$k_{obs}/10^3$ $M^{-1}.min^{-1}$ (% Inhibition)			
	HEDP	HMNTMP	ENTMP	NTMP
44.0	1.159 (64.5)	0.972 (70.3)	0.889 (72.8)	0.678 (79.2)
129.0	3.291 (56.6)	2.870 (62.1)	2.402 (68.3)	1.927 (74.5)
213.0	10.227 (44.4)	9.317 (49.3)	7.785 (57.7)	6.190 (66.3)

sub-critical etch pits formed on the surface thus preventing their development beyond the critical size. At high supersaturation values, the number of embryos are large and although the additives can be adsorbed on the crystal surface, yet the crystallization can proceed easily provided that the adjacent adsorbed molecule will be now separated by a distance greater than that of the length of the critical etch pit.

The results of crystal growth experiments made in presence of varying amounts of barium sulphate seeds are shown in Figure 4 and the results are summarized in Table IV. The results indicate that the rate of crystallization of barium sulphate is directly proportional to the amount of seed crystals added initially (see Figure 5). Figure 4 indicates that the induction time, which was a characteristic parameter in spontaneous precipitation and in precipitation in presence of inhibitors, is now vanished. The explanation of this is that in pure solutions a fraction of the lattice ions is consumed in forming the embryos which function as a base for the actual growth stage, whereas in seeded systems the added seeds present suitable sites for direct growth thus diminishing the slow surge observed in the integrated rate plots in case of spontaneous growth.

In the presence of seeds, the added additives were found to have the same order of inhibition as that found in case of unseeded systems (Table V). Thus at the level of 44 ppm barium sulphate and with S = 30.15, 1×10^{-7} M of HEDP, HMNTMP, ENTMP and NTMP led to 64.5, 70.3, 72.8 and 79.2% inhibition, respectively.

As expected, increasing the amount of seeds in presence of a given amount of additive led to a decrease in the inhibitory action. Thus 129 and 213 ppm of the barium sulphate seeds with S = 30.15 and in presence of 1×10^{-7} M HEDP led to a decrease in the inhibition percentage to 56.6 and 44.4%, respectively. Other inhibitors behave similarly. The reason of this is due to the increase in the active sites present for crystal growth by increasing seed amounts with the decrease of retardation action of inhibitor due to its fixed amount, i.e., the fraction of surface area of seeds covered by inhibitor decreases.

Finally, we can infer that the main reason for inhibition by phosphonates is due to adsorption of these molecules on the surface of the crystal. Chelation at the surface with barium ions may also be probable at certain dislocations on the crystal surface. These reasons prevent further deposition of barium sulphate and decreases the rate of crystallization. Free barium ions in solution can be partially complexed and may be adsorbed at the surface dislocations but due to the relatively high concentration of free barium ions used with respect to additive concentrations, the minute amounts of complexed cations would not be expected to compete with the barium ions present in the bulk for the crystal growth sites.

EXPERIMENTAL

Barium chloride and potassium sulphate used were of AR grade. The organic phosphonates HEDP, HMNTMP and ENTMP were provided by Monsanto Industrial Chemicals, Brussels, Belgium and NTMP was provided by Aldrich Co, Milwaukee, USA.

Stock solutions were prepared in doubly distilled deionized water (conductivity $<10^{-6}$ mho) and diluted as required. Solutions were always freshly prepared before use. The exact molarities of both barium and sulphate ions were checked using standard analytical methods.[31]

Barium sulphate seed was obtained as the spontaneously precipitated solid formed by direct addition of 10^{-2} M barium chloride to 10^{-2} M potassium sulphate. The solid obtained was filtered, washed and dried at 383 K.

Details of the kinetics procedure are the same as that described before.[1] All measurements were performed under controlled temperature of 298 ± 0.1 K by means of a water circulating constant-temperature bath. A typical growth experiment involved the addition of prethermostated potassium sulphate solution to the barium chloride solution so as to maintain the required concentration with the final volume of solution 250 cm^3. Both the barium and sulphate ion concentrations throughout the work were equal. Additives, and seeds if present, were always added to the barium chloride solution. The kinetics of growth were monitored conductometrically using a WPA CMD 400 digital conductivity bridge with a limiting accuracy of 10^{-7} mho.

The changes of concentration in the solution were calculated using a constant equivalent conductivity of barium chloride equals to 139.9 $ohm^{-1}equiv^{-1}cm^2$ at 298 K.[32] Correction of conductivity due to potassium chloride is taken in consideration. For experiments conducted in presence of additives (and seeds), a blank experiment was necessary to correct for their contribution to the total conductance.

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