The Kinetics of the Crystallization of Barium Chromate in Presence of Polyphosphate and Phosphonates

M. N. Ramsis, M. S. Antonious*, E. N. Rizkalla[#], and A. O. Youssef

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

Summary. The inhibiting effect of polyphosphate and phosphonates on the crystallization of barium chromate for both seeded and unseeded systems has been investigated using the changes in ionic conductivity of the lattice ions in supersaturated solutions containing stoichiometric concentrations of barium and chromate at 298 K. The inhibitors studied are sodium tripolyphosphate (STP), ethylenediaminetetramethylenephosphonic acid (ENTMP), and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP). The effect of these inhibitors on the growth of crystals has been studied at several inhibitor concentrations. The influence of these additives on barium chromate crystallization could be interpreted in terms of a Langmuir type adsorption isotherm. The crystallization retarding effect due to inhibitors is in the order HEDP > STP > ENTMP. The inhibitors studied can be used as effective compounds for scale formation control.

Keywords. Kinetics; Crystallization; Barium chromate; Inhibitors.

Kinetik der Kristallisation von Bariumchromat in Gegenwart von Polyphosphat und Phosphonaten

Zusammenfassung. Der hemmende Einfluß von Polyphosphat und Phosphonaten auf die Kristallisation von Bariumchromat sowohl in geimpften als auch in nichtgeimpften Systemen wurde durch Messung der Änderung der Ionenleitfähigkeit der Gitterionen in übersättigten Lösungen stöchiometrischer Mischungen von Barium und Chromat bei 298 K untersucht. Als Inhibitoren wurden Natriumtripolyphosphat (STP), Ethylendiamintetramethylenphosphonsäure (ENTMP) und 1-Hydroxyethyliden-1,1-diphosphonsäure (HEDP) eingesetzt, deren Einfluß auf das Kristallwachstum bei verschiedenen Konzentrationen getestet wurde. Der Effekt dieser Additive auf die Kristallisation von Bariumchromat kann im Sinn einer Adsorptionsisotherme vom Langmuir-Typ interpretiert werden. Die Reihenfolge der Kristallisationsverzögerung lautet HEDP > STP > ENTMP. Die untersuchten Inhibitoren können zur Verhinderung von Ablagerungen eingesetzt werden.

Introduction

Several studies have been reported on the crystal growth of sparingly soluble alkaline earth metal salts in view of their involvement in a wide number of biological,

---

[#] Deceased

industrial, and environmental precipitation processes [1–13]. Barium salts are of particular interest due to their importance in many scale/deposit control applications, industrial water treatment, and from the analytical chemical applications point of view [14–18]. The factors that govern the mechanisms of precipitation of these salts are therefore of considerable interest, especially the influence of foreign species which can exert a marked effect on the rate of crystallization. Phosphorus compounds have been tested for the prevention of barium sulfate scale [19]. *Fernandez-Diaz et al.* [20] had found that phosphoro-modified polyacrylic acid derivatives affect the size of the critical nucleus in barium sulfate crystallization using light scattering studies. *Liu* and *Nancollas* [21] reported that trace amounts of phosphonates can stabilize supersaturated calcium sulfate solutions. The most effective use of inhibitors requires a thorough investigation of the mechanism of action of those ions or molecules at the crystal-water interface.

A previous study of the kinetics of crystal growth of barium chromate in both seeded and unseeded systems with different amounts of seeds and different supersaturation ratios (S) revealed a surface controlled growth mechanism [1]. The growth rate increased by addition of barium chromate seeds with an extent of increase proportional to the amount and type of the seed present.

In the present work, the influence of three commercially available inhibitors (sodium tripolyphosphate (*STP*), ethylenediaminetetramethylenephosphonic acid (*ENTMP*), and 1-hydroxyethylidene-1,1-diphosphonic acid (*HEDP*) on the growth of barium chromate in both seeded and unseeded systems is studied.

Results and Discussion

By analogy with the results of a previous study of the spontaneous growth of barium chromate [1], the concentration changes and hence the rate of crystal growth in the presence of additives (and seeds) were analyzed using the Equation

$$rate = -d[Ba^{2+}]/dt = -d[CrO_4^{2-}]/dt =$$
$$= k_{obs}(([Ba^{2+}]_t[CrO_4^{2-}]_t)^{1/2} - (\pi_s/f_2^2)^{1/2})^2 =$$
$$= k_{obs} \cdot \varDelta^2 \tag{1}$$

where k_{obs} is the observed rate constant, π_s is the thermodynamic solubility product ($= 1.17 \times 10^{-10} \, mol^2 \, dm^{-6}$ [22]), $[X]_t$ is the ionic concentration of species X at time t, and f_2 is the activity coefficient for a z-valent ion obtained by means of the *Davies* Equation [23].

The integrated form of Eq. (1)

$$K_{obs}t = \varDelta_t^{-1} - \varDelta_i^{-1} \tag{2}$$

where $\varDelta_t^{-1}$ and $\varDelta_i^{-1}$ represent the concentration functions at time $= t$ and time $= 0$, respectively, is used to obtain values of K_{obs}.

The small changes in the concentration of barium ions due to their complexation with the additives have been neglected in the rate calculations since their contribution to the total barium contents was at the most less than 0.1%. At all inhibitor concentrations used, precipitation did not commence immediately after adding potassium chromate to barium chloride solution but after an induction time, the duration of which increased with increasing inhibitor and decreasing barium ion concentrations.

Table 1. Effect of inhibitors on the rate of seeded growth barium chromate at 298 K ($T_{Ba} = T_{CrO4}$)

T_{Ba} (10^{-5} M)	Inhibitor	[Inhibitor] (10^{-8} M)	Seed (type)	[Seed] (10^{-5} M)	$k_{obs}/10^3$ (M^{-1} min^{-1})
8.0	–	–	–	–	0.838
8.0	–	–	B	1.6	2.059[a]
8.0	–	–	B	4.8	2.695[a]
8.0	–	–	B	8.0	3.813[a]
8.0	ENTMP	10.0	B	1.6	1.340
8.0	ENTMP	10.0	B	4.8	2.268
8.0	ENTMP	10.0	B	8.0	3.371
8.0	STP	10.0	B	1.6	1.163
8.0	STP	10.0	B	4.8	1.866
8.0	STP	10.0	B	8.0	2.879
8.0	HEDP	10.0	B	1.6	0.977
8.0	HEDP	10.0	B	4.8	1.603
8.0	HEDP	10.0	B	8.0	2.736
10.0	–	–	–	–	1.096
10.0	–	–	A	1.6	1.330[a]
10.0	–	–	B	1.6	3.198[a]
10.0	ENTMP	10.0	–	–	0.583
10.0	ENTMP	10.0	A	1.6	0.928
10.0	ENTMP	10.0	A	4.8	1.580
10.0	ENTMP	10.0	A	8.0	3.093
10.0	ENTMP	10.0	B	1.6	1.850
10.0	ENTMP	10.0	B	4.8	2.688
10.0	ENTMP	10.0	B	8.0	3.973
10.0	STP	10.0	–	–	0.344
10.0	STP	10.0	A	1.6	0.836
10.0	STP	10.0	A	4.8	1.384
10.0	STP	10.0	A	8.0	2.498
10.0	STP	10.0	B	1.6	1.586
10.0	STP	10.0	B	4.8	2.312
10.0	STP	10.0	B	8.0	3.346
10.0	HEDP	10.0	–	–	0.238
10.0	HEDP	10.0	A	1.6	0.749
10.0	HEDP	10.0	A	4.8	1.222
10.0	HEDP	10.0	A	8.0	1.991
10.0	HEDP	10.0	B	1.6	1.411
10.0	HEDP	10.0	B	4.8	2.045
10.0	HEDP	10.0	B	8.0	2.980

[a] Ref. [1]

The effect of inhibitors on the growth of seeded barium chromate was studied for different amounts of both seeds at $S = 9.24$ and for seed B at $S = 7.39$. The supersaturation ratio S is defined as $S = ([Ba^{2+}] \cdot [CrO_4^{2-}]/\pi_s)^{1/2}$. The results obtained are given in Table 1. Plots of the barium ion concentration and the integrated form
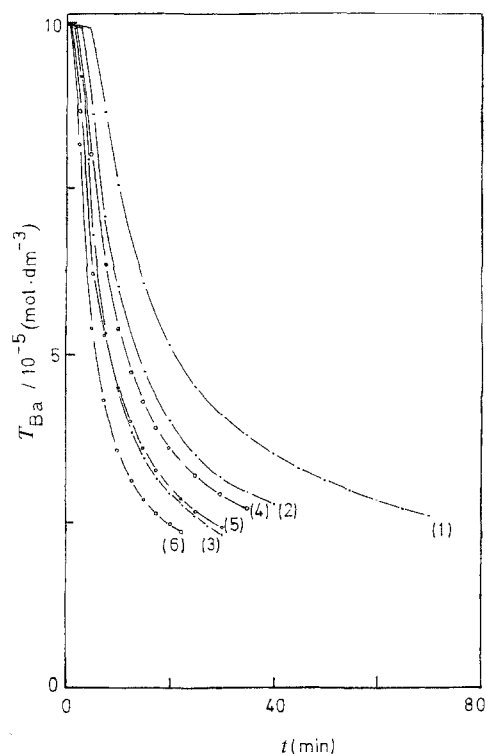
Fig. 1. Growth curves for barium chromate in presence of different concentrations of seeds A and B; $T_{Ba} = 1 \times 10^{-4} M$, $[STP] = 1.0 \times 10^{-7} M$; curve (1): $1.6 \times 10^{-5} M$ seed A; curve (2): $4.8 \times 10^{-5} M$ seed A; curve (3): $8.0 \times 10^{-5} M$ seed A; curve (4): $1.6 \times 10^{-5} M$ seed B; curve (5): $4.8 \times 10^{-5} M$ seed B; curve (6): $8.0 \times 10^{-5} M$ seed B

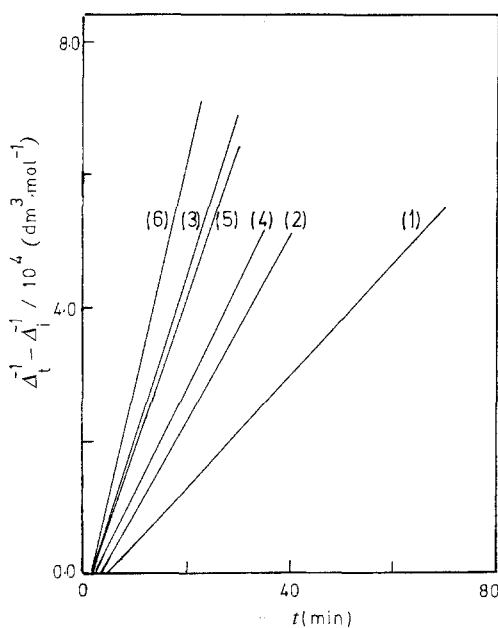**Fig. 2.** Plots of the integrated form of Eq. (1) for different concentrations of seeds A and B; $T_{Ba} = 1 \times 10^{-4} M$; $[STP] = 1.0 \times 10^{-7} M$; curve (1): $1.6 \times 10^{-5} M$ seed A; curve (2): $4.8 \times 10^{-5} M$ seed A; curve (3): $8.0 \times 10^{-5} M$ seed A; curve (4): $1.6 \times 10^{-5} M$ seed B; curve (5): $4.8 \times 10^{-5} M$ seed B; curve (6): $8.0 \times 10^{-5} M$ seed B

of Eq. (1) for seeded systems in presence of STP, as a representative example, are given in Figs. 1 and 2.

The results obtained are consistent with crystallization kinetics of second order as indicated from the Figures. This is in agreement with the previous results obtained for the growth of barium chromate from pure and seeded solutions [1].

Attempts to apply *Nielsen*'s chronomal analysis [24] to interpret the kinetic results were successful only in presence of inhibitors and seed B over a limited range of θ, where θ is the degree of reaction. Thus, for a diffusion or surface controlled reaction of order p, the growth rate can be experessed by the following integrals:

$$I_D = K_D t = \int \theta^{-1/3}(1 - \theta)^{-1}\,d\theta \tag{3}$$

$$I_P = K_P t = \int \theta^{-2/3}(1 - \theta)^{-P}\,d\theta \tag{4}$$

where K_D and K_P are constants related to the final particle size and the initial concentrations of the reactants. Plots of I (obtained from θ) against time are expected to be linear for a given mechanism. The results obtained are illustrated in Fig. 3 for systems containing inhibitors and inhibitors and seeds. As mentioned previously, none of the curves completely fulfills the conditions of Eqs. (3) and (4) for systems containing inhibitors only or inhibitors and seed A. The linearity condition is fulfilled in presence of inhibitors and seed B with an order equal to 2. The linearity conditions appear to be limited to the late stages of growth ($\theta = 25$–85%). The nonlinearity in the low θ ranges may be due to (i) a more complex mechanism, *i.e.* a combination between both surface and diffusion controlled mechanisms and (ii) to the hypothesis behind the chronomal analysis which presumes homogeneous nucleation and the formation of uniformly shaped particles. The second possibility seems to be the explanation for observing a linear plot for I_2 in case of presence of inhibitors and seed B; in this case, the added seed presents suitable sites for uniform growth due to the way of its preparation which leads to better crystalline perfection and cleaner seed facets. This is in contrast to seed A which was separated directly from its mother liquor during its preparation, thus leading to a relatively imperfect crystalline structure and an unhomogeneous growth. This kind of growth is the same as that also found in absence of seeds, since inhibitors present are adsorbed on the barium chromate surface, thus leading to a defective crystalline structure.
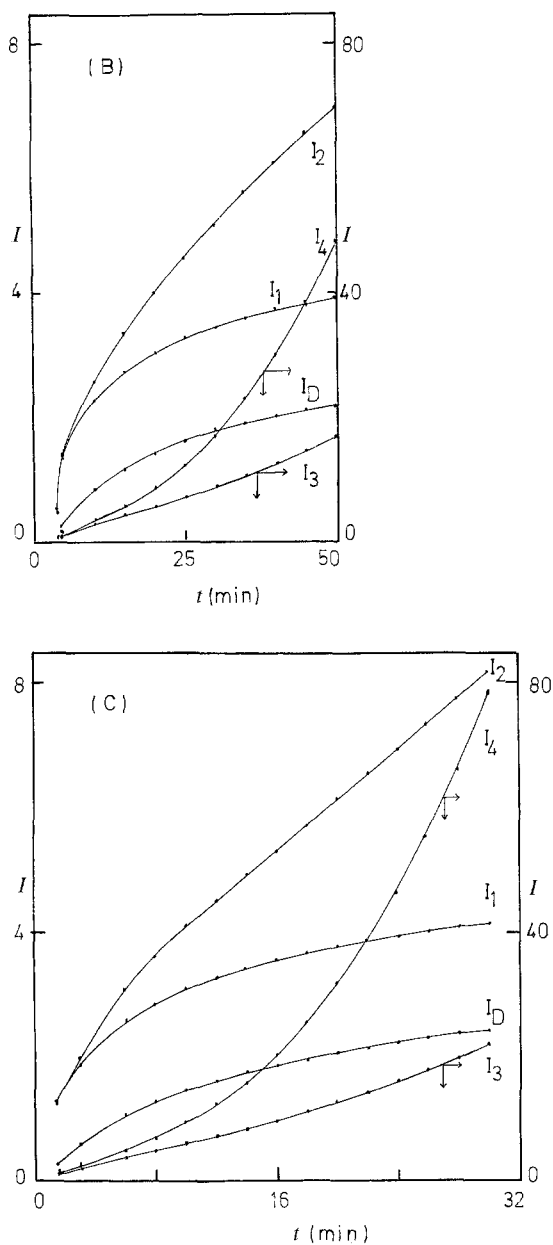
1104 — M. N. Ramsis et al.
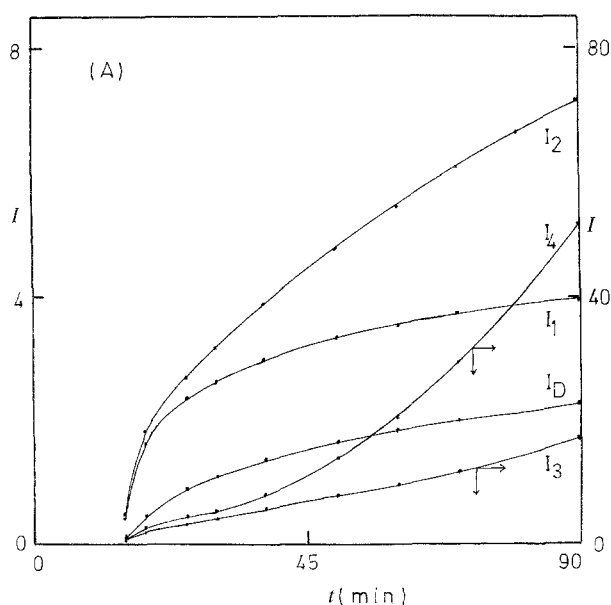
Fig. 3. Plots of I_D and I_P ($P = 1\text{–}4$) chronomals as a function of time for barium chromate precipitation in presence of $1 \times 10^{-4} M$ barium ions and $1.0 \times 10^{-7} M$ STP; (A): no seeds; (B): $1.6 \times 10^{-5} M$ seed A; (C): $1.6 \times 10^{-5} M$ seed B

Inhibitors are able to retard or to block the crystallization process even if added in vestige amounts. Their effect 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 former reason cannot be the case since free barium ions in solution can be partially complexed and may be adsorbed at the surface dislocations. Due to the relatively high concentration of free barium ions used with respect to inhibitor 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. The latter reason may be interpreted in terms of the *Langmuir* adsorption
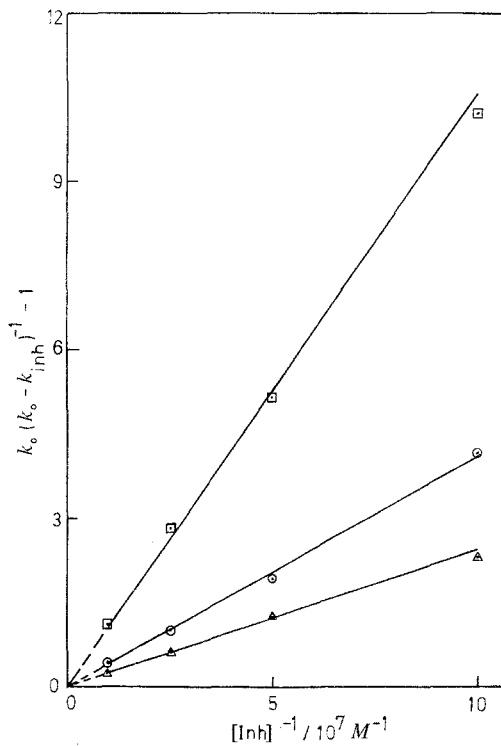
Fig. 4. _Langmuir_ adsorption isotherms in presence of ($\square$) $ENTMP$, ($\bigcirc$) STP, and ($\triangle$) $HEDP$; $T_{Ba} = 1 \times 10^{-4} M$

isotherm. Thus, the plot of the inverse of the relative reduction in rate, $k_0(k_0 - k_{inh})^{-1}$, and the reciprocal of the inhibitor concentration should yield a straight line where k_0 and k_{inh} are the rates of crystallization in the absence and presence of inhibitor, respectively. The results show that the growth of barium chromate in the presence of inhibitors for both spontaneous and seeded growth systems distinctly indicate a marked inhibitory effect. Figure 4 illustrates the above relationship for barium chromate growth in presence of $ENTMP$, STP, and $HEDP$. This Figure confirms that the inhibitory effect of these inhibitors is due to adsorption at active growth sites following the _Langmuir_ adsorption isotherm. As indicated from the Figure, the inhibitory effect of the additives is in the order $HEDP > STP > ENTMP$. From Fig. 4, the adsorption affinity constants can be calculated to be 10×10^6, 27×10^6, and 36×10^6 dm³/mol for $ENTMP$, STP, and$HEDP$, respectively. These values reflect a strong adsorption of $HEDP$ at the interface relative to other inhibitors.

Increasing the inhibitor concentration will lead to a decrease in the growth rate due to the blocking of the active sites of crystallization on the crystal surface. No crystallization can occur if the amount of inhibitor is sufficient to be adsorbed at the surface of the whole crystal. Our results indicate that an inhibition of 46.8, 68.6 and 78.2% is found for $1 \times 10^{-7} M$ $ENTMP$, STP, and $HEDP$, respectively. Complete inhibition of the crystallization was found, and no decrease in the measured conductance within 24 hours was detected when the concentration of the inhibitors increased to more than $2 \times 10^{-7} M$. This stabilization action can be due to an increase in the energy of formation of the critical nuclei as a result of the endothermal

adsorption of the inhibitor on the surface of the nucleus, thus leading to the breakdown and disintegration of a number of the available embryos before further growth can take place [25].

From the structures of the inhibitors added, one molecule of each inhibitor is capable of interacting with one active metal site. Thus, at the same molar concentration, STP, $ENTMP$, and $HEDP$ are capable of inhibiting the same number of embryos. Accordingly, differences in the inhibiting action of additives can be attributed to structural factors such as their size. Adsorption rate measurements of STP on strontium sulfate precipitated from pure solution have shown that adsorption of STP takes place immediately after the birth of $17\,\text{Å}$ nuclei in a solution containing polyphosphate [25]. Extending this conclusion to other phosphonate systems, it would be expected that adsorption of the larger molecule $ENTMP$ is likely to take place after the birth of larger aggregates of the host lattice, whereas with the $HEDP$ molecule nuclei of smaller dimensions would fulfill the adsorption requirements. This order holds well with the results obtained for the three inhibitors studied in this work and with the results obtained by *van Rosmalen et al.* [26] who found that in most cases $HEDP$ behaves as one of the most efficient inhibitors in the class of phosphonate compounds.

In presence of seeds, the additives were found to have the same order of inhibition as those found in case of unseeded systems. Thus, $1 \times 10^{-7}\,M$ of $ENTMP$, STP, and $HEDP$ led to 30.2, 37.1, and 43.6% and 42.1, 50.4, 55.8% inhibition for $1.6 \times 10^{-5}\,M$ of seeds A and B, respectively, in the presence of $1 \times 10^{-4}\,M$ barium ion concentration. Decreasing the barium ion concentration to $8 \times 10^{-5}\,M$ with the same concentrations of additives and seed B led to 34.9, 43.5 and 52.5% inhibition for the above mentioned inhibitors, respectively.

The greater inhibitory action of additives on seeds of type B may be due, as mentioned before, to its greater crystalline perfection which will be more affected by the presence of additive than the imperfect crystalline structure of seed A.
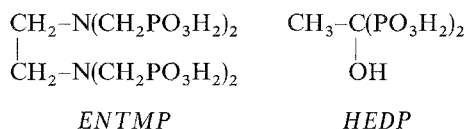
As anticipated, decreasing the fraction of the surface area of seeds covered by inhibitor will result in a decrease in the inhibitory action. This is due to an increase in the number of active sites available for crystal growth. Thus, $1.6 \times 10^{-5}\,M$, $4.8 \times 10^{-5}\,M$, and $8.0 \times 10^{-5}\,M$ of seed B in the presence of $1 \times 10^{-7}\,M$ $ENTMP$ and $8.0 \times 10^{-5}\,M$ barium ions led to a decrease in the inhibition percentage of 34.9, 15.8, and 11.5, respectively. Other inhibitors behave similarly as can be seen from Table 1.

As a conclusion, the experimental results validate that the action of phosphate and phosphonates as crystal growth inhibitors may be explained by adsorption of these inhibitors at active growth sites of the crystal surface. Kinetic data were found to fit a simple *Langmuir* model from which a measure of the affinity between additive and substrate could be obtained. On the basis of kinetic data, the effectiveness of the inhibitors for barium chromate growth follows the order $HEDP > STP > ENTMP$ in both seeded and unseeded systems.

Experimental

Barium chloride and potassium chromate were of AR grade. Commerical grade STP was crystallized four times from a methanol-water mixture [27]. The purity of the final product ($Na_5P_3O_{10} \cdot 6H_2O$) was

checked by elemental analysis. The organic phosphonates *ENTMP* and *HEDP* were kindly provided by Monsanto Industrial Chemicals, Brussels, Belgium.

$$\begin{array}{ll} CH_2-N(CH_2PO_3H_2)_2 & CH_3-C(PO_3H_2)_2 \\ \;\;| & \;\;| \\ CH_2-N(CH_2PO_3H_2)_2 & OH \end{array}$$

$$\qquad ENTMP \qquad\qquad\qquad HEDP$$

Stock solutions were prepared in doubly distilled deionized water (conductivity $< 10^{-6}$ mho) and diluted as required. Solutions were always freshly prepared before use.

Details of the preparation of seeds and kinetic measurements have been described before [1]. Barium chromate seeds were prepared by two different methods. Seed A was obtained as the spontaneously precipitated solid formed by direct addition of $10^{-2} M$ barium chloride to $10^{-2} M$ potassium chromate solutions; seed B was prepared precisely as seed A, followed by aging of the solid for about three weeks with the mother liquor. In both cases the solid was filtered, washed, and dried at 383 K. Scanning electron microscopy (SEM) indicated that barium chromate seeds are present in the form of microcrystallites, and that seed B is more ordered than seed A. X-ray diffraction studies showed that seeds of type B exhibit a higher degree of crystallinity relative to those of type A. Surface area measurements gave surface areas of 0.9 and 1.7 m^2/g for seeds A and B, respectively [1].

All measurements were performed at 298 K (constant temperature water bath). A typical growth experiment involved the addition of prethermostated potassium chromate solution to the barium chloride solution in such a way that the required concentration was reached with the final volume of 250 cm^3. Both barium and chromate ion concentrations were equal throughout the work. Inhibitors and seeds, if present, were always added to the barium chloride solution. The kinetics of growth were monitored conductometrically using a YSI model 32 conductance meter.

The changes of concentration in the solution were calculated using a constant equivalent conductivity of barium chromate of 139.9 ohm^{-1} equiv^{-1} cm^2 at 298 K [22]. Correction of conductivity due to potassium chloride is taken into consideration. For experiments conducted in presence of additives, a blank experiment was necessary to correct for their contribution to the total conductance.

References

[1] Antonious MS, Ramsis MN, Youssef AO (1996) Monatsh Chem **127**: 15

[2] De Vreugd CH, Witkamp GJ, Van Rosmalen GM (1994) J Crystal Growth **144**: 70

[3] Grases F, Kroupa M, Costa-Bauza A (1994) Urol Res **22**: 39

[4] Amjad Z (1993) Langmuir **9**: 597

[5] Callegas-Fernandez J, Martinez-Garcia R, De Las Nieves Lopez FJ, Hidalgo-Alvarez R (1993) Solid State Ionics **63–65**: 791

[6] Verdoes D, Kashchiev D, Van Rosmalen GM (1992) J Crystal Growth **118**: 401

[7] Amjad Z (1991) Langmuir **7**: 600

[8] Grases F, Genestar C, Palou J (1990) Colloids and Surfaces **44**: 29

[9] Kralj D, Brecevic L, Nielsen AE (1990) J Crystal Growth **104**: 793

[10] Hamza SM, Abul-Rahman A, Nancollas GH (1985) J Crystal Growth **73**: 245

[11] Rizkalla EN, Moawad MM (1984) J Chem Soc Faraday Trans 1, **80**: 1617

[12] Bochner RA, Abul-Rahman A, Nancollas GH (1984) J Chem Soc Faraday Trans 1, **80**: 217

[13] Shyu LS, Nancollas GH (1980) Croat Chem Acta **53**: 281

[14] Antonious MS (1996) Phosphorus, Sulfur and Silicon **112**: 235

[15] Amjad Z (1994) Water Treat **9**: 47

[16] Symeopoulos BD, Koutsoukos PG (1993) Appl Radiat Isot **44**: 894

[17] Van der Leeden MC, Kashchiev D, Rosmalen GM (1992) Colloid Interface Sci **152**: 338

[18] Prieto M, Putnis A, Fernandez-Diaz L (1990) Geol Mag **127**: 485

[19] Weijnen MPC, Van der Leeden MC, Rosmalen GM (1987) In: Rodriguez R, Thardy Y (eds) Geochemistry of the earth's surface and mineral formation Madrid: CSIC, pp 753–776
[20] Fernandez-Diaz L, Putnis A, Cumberbatch T (1990) Eur J Mineral **2**: 495
[21] Liu ST, Nancollas GH (1973) J Colloid Interface Sci **44**: 422
[22] Weast RC (ed) (1993) Handbook of Physics and Chemistry, 74th edn. CRC Press, Boca Raton
[23] Davies CW (1962) Ion Association. Butterworths, London
[24] Nielsen AE (1964) Kinetics of Precipitation. Pergamon Press, Oxford
[25] Naono H (1967) Bull Chem Soc Japan **40**: 1104
[26] Van Rosmalen GM, Van der Leeden MC, Gouman J (1980) Krist Tech **15**: 1269
[27] Quimby QT (1954) J Phys Chem **58**: 603