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Conference Paper

The Kinetics of Growth of Seed Crystals in Solution

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The theory of growth of seed crystals in critically supersaturated electrolyte solutions is discussed. Techniques of studying crystal growth are reviewed, the application of which yield highly precise and reproducible data. Effects of added foreign substances on the rate of crystallization are emphasized and results, obtained for magnesium oxalate, barium and strontium sulfate crystal growth, discussed.

The formation of crystals in liquid or solid systems, and of liquids in vapor systems, takes place in two steps. The first of these is nucleation, which corresponds to the production of new centers from which spontaneous growth or condensation can occur. In the second, the first particles grow as material from the nutrient medium is deposited on them. The mechanism of crystal growth in solution systems is a problem of great interest with important repercussions in diverse fields such as desalination, cavitation, analytical chemistry, the production and dissolution of bone and tooth minerals and pathological stone formation. The initial stages of nucleation, are difficult to investigate owing to the problems associated with the detection of nuclei of atomic dimensions. By the time an experimental method has responded to nucleation, the new particles are already of microscopic dimensions.

In solution systems, attempts to understand the nucleation process usually follow by analogy with the theories developed for the condensation of a vapor¹. There are, however, a number of additional complicating factors which must be taken into account such as diffusion, solvation of solute ions and desolvation on crystallizing, surface adsorption and double-layer formation. For these reasons, a quantitative treatment of nucleation of salts in supersaturated solution is extremely difficult. The process of nucleation, however, determines the size and size distribution of crystals of precipitate produced, and this is a factor of supreme importance in analytical procedures. In an attempt to make reproducible spontaneous nucleation experiments, efforts are usually made to ensure homogeneous nucleation but it is doubtful if any practical medium of precipitation is sufficiently free from available sites to preclude the possibility of induced nucleation. It has been observed by a number of workers² that repeated purification of reagents and solutions has a marked effect upon the results of subsequent nucleation experiments. This indicates that it is impossible to completely remove from the solutions foreign particles which can act as nucleating sites. In addition, complications arise in deciding whether nucleation and growth occur simultaneously or consecutively. Thus Nielsen³ differs from Turnbull⁴ and Collins and Leinweber⁵ in considering instantaneous nucleation to be unlikely and both

interface⁴ and diffusion⁵ control have been suggested for the subsequent growth process.

For most electrolytes, there exists a relatively well-defined critical supersaturation below which stable supersaturated solutions may be maintained for long periods without crystallization and above which spontaneous precipitation occurs⁶. By careful control of experimental conditions these solutions can be prepared in the laboratory, and when seeded with well characterized crystals of the electrolyte, the rate of growth of the seed crystals may be studied. For very sparingly soluble salts, conductivity methods are well suited for following the course of reaction since a precision of 0.01% in the resistance measurements is relatively easily achieved. The method suffers from the disadvantage, however, of being limited to systems of low ionic strength in which no additional reactions such as hydrolysis accompany the crystal growth. Potentiometric and chemical analysis of the supersaturated solutions may also be used to follow the reactions. Specific ion electrodes should be potentially useful in such experiments but it has been found in some cases that the liquid membrane type tend to induce nucleation on the electrode surface. Radiotracer techniques offer a number of advantages since the solute, at low concentrations may be studied in the presence of higher concentrations of »neutral« or inert electrolyte in order to investigate the effect of changing the ionic strength. Periodic microscopic examination of the growing crystals enables crystal morphology and possible modifications during the growth process to be related to the observed kinetics of the reaction. Studies, such as those outlined above, of the rate of growth of seed crystals in their supersaturated solutions have a number of attractive features. Unlike the more conventional investigations of spontaneous crystallization the method has the great advantage of yielding results which are highly reproducible enabling investigations to be made not only of the mechanism of the growth process but also of the effect of added substances upon the rate of crystallization.

In general, the rate of crystallization will be a function of two variables, the available surface and the concentration of solute, and we may write

$$-dm/dt = ks(m - m_0)^n \quad (1)$$

where n is the order of reaction, s a function of the number of sites available for deposition and k the rate constant. The rate of crystal growth, $-dm/dt$, is expressed in equation (1) as a decrease in molar concentration m . For a number of symmetrical electrolytes, there is now a considerable body of experimental data in support of a kinetic equation (1) with $n = 2$.

$$-dm/dt = ks(m - m_0)^2 \quad (2)$$

The resulting quadratic equation is consistent with a surface controlled mechanism which was originally proposed for the crystal growth of silver chloride⁶. In this, it is assumed that the crystal surface is covered by an adsorbed monolayer of hydrated ions. Formulating the kinetics in terms of the stationary concentrations of lattice ions in the adsorbed phase, crystallization takes place through the simultaneous dehydration of pairs of oppositely charged ions. At equilibrium, the rate of adsorption is just sufficient to maintain the adsorbed layer intact whilst in a supersaturated solution, the excess ions reaching the surface are available for deposition. Experi-

tally, the absence of diffusion control is supported by an observed rate of crystallization which is independent of stirring conditions. In situations in which the lattice ions are present in the supersaturated solutions in non-stoichiometric amounts, the rate of crystal growth can be interpreted in terms of an equation similar to equation (1) by taking into account the electrical potential at the crystal surface which results from adsorption of the lattice ion in excess. The equilibrium value of the potential is such that equal numbers of cations and anions enter the adsorbed monolayer of hydrated ions. The rate equation describing the crystallization of typical sparingly soluble symmetrical electrolyte, ML, made up of M^{a+} and L^{a-} ions is written

$$-dm/dt = ks \{ [M^{a+}]^{1/2} [L^{a-}]^{1/2} - K_{SP}^{1/2} / f_a \}^2 \quad (3)$$

in which K_{SP} is the thermodynamic solubility product and f_a the activity of an a -valent ion. The latter may be calculated from the ionic strength I by means of the equation⁷

$$-\log f_a = Aa^2 [I^{1/2} / (1 + I^{1/2}) - 0.3 I]$$

In solutions in which the lattice ions associate to form complexes, the concentrations of individual ionic species, required for a detailed kinetic analysis of the crystallization, can be obtained from the known thermodynamic association constants and mass balance equations by successive approximation techniques^{8,9}. The crystal growth of magnesium oxalate, in supersaturated solutions containing the relatively strong chelate, MgC_2O_4 , was studied conductimetrically and it was necessary to calculate the concentrations of both the complex and free ions in the solutions in order to interpret the observed rate data¹⁰. Equation (4)

$$dN/dt = -k^1 N^2 \quad (4)$$

where N is the number of moles/l of magnesium oxalate to be deposited before equilibrium is reached, was found to hold over a wide range of supersaturation and lattice ion concentration ratios. A typical plot of the integrated form of equation (4) is shown in Fig. 1. for which the concentration conditions are presented in Table I, and N_i is the initial value of N .

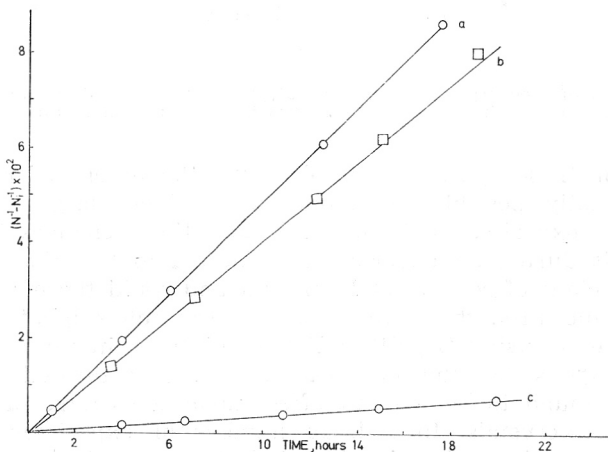


Fig. 1. The crystallization of magnesium oxalate plotted according to the integrated form of equation 4. (see Table I for experimental conditions)

TABLE I
Crystallization of Magnesium Oxalate at 25°C (concentrations in moles l⁻¹)

Experiment Number (see Fig. 1)	[Mg]/[OX]	$N_1 \times 10^2$
a	2	0.167
b	2	0.199
c	4	0.069

A considerable number of studies have been made of the spontaneous precipitation of the sparingly soluble sulphates of bivalent metal ions¹¹. These salts are of particular importance in analytical chemistry and little is known of the mechanism of their nucleation and growth. Conductimetric studies have now been made of the crystallization of barium¹², lead¹³ and strontium¹⁴ sulphate and in each case, the reaction follows, for the greater part of its course the quadratic rate law expressed by equation 2. This is illustrated in Fig. 2 in which the rate of growth — dm/dt is plotted against

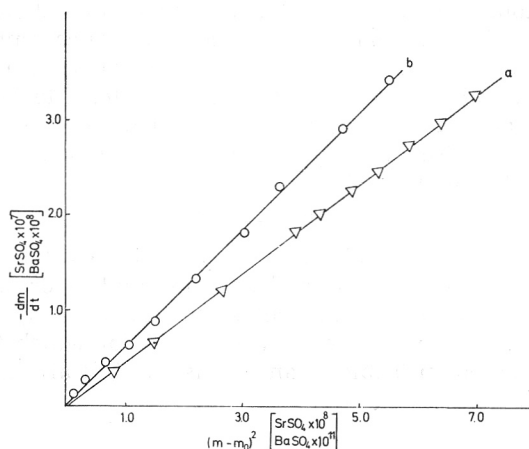


Fig. 2. The growth of seed crystals of barium sulphate (curve a) and strontium sulphate (curve b). Plots of the rate of crystal growth, $-dm/dt$, against $(m - m_0)^2$.

$(m - m_0)^2$. For these sparingly soluble salts, the extent of reaction is such that it is usually possible to employ a relatively large amount of seed crystals in the experiments. Under such conditions, changes in surface area of the crystals during an experiment amounted to less than a few percent of the total weight of seed crystals present and could therefore be neglected. Changes of ionic strength, in the case of strontium sulphate crystallization, could be made by using $\text{Sr}(\text{OH})_2 + \text{H}_2\text{SO}_4$ mixtures in place of the $\text{SrCl}_2 + \text{Na}_2\text{SO}_4$ reagents for the preparation of supersaturated solutions; such changes were found to be without effect upon the course of the growth of the added seed crystals. In a large number of experiments, the rate of crystallization has been found to be independent not only of the rate of stirring, but also independent of the fluid dynamics of the systems. Expe-

periments made in cells of various shapes and sizes using different methods for monitoring the changes of concentration of the lattice ions yielded results for the rate of growth which were effectively independent of the changes made. All the evidence points to a surface reaction mechanism such as that outlined previously. Essentially, the same form of equation (2) is obtained if the concentrations of ions adsorbed on the crystal surface are expressed in terms of a simple Temkin isotherm¹⁵.

In the crystal growth of the bivalent metal sulphates, under conditions of high supersaturation and/or concentrations of inoculating seed crystals below a certain limit, the second order crystal growth is preceded by a growth surge during which the effective reaction order, represented by n in equation (1), is greater than two. In an attempt to explain the surge, experiments were made with seed crystals which had been modified in various ways; (1) by aging for different periods of time, (2) by pre-growing in replenished supersaturated solution immediately before use and (3) by increasing the surface roughness. None of these changes was effective in removing the initial growth surge and it is clear that factors other than surface geometry are responsible for it. An explanation which has been proposed¹² is that of surface nucleation in which case the duration of the initial fast period would be expected to depend upon the number of growth sites available initially and the degree of supersaturation. This has been verified; an increase in the initial supersaturation and the use of smaller amounts of seed crystals increase the duration of the initial surge. It appears, therefore, that for a given supersaturation, a sufficient number of growth sites must be provided initially for uncomplicated second-order growth otherwise new sites must be generated by nucleation. Whether surface or bulk nucleation occurs seems to depend upon the degree of supersaturation. In magnesium oxalate, the supersaturation was high and bulk nucleation was observed¹⁰, whereas for barium sulphate no evidence for this was detected. It is interesting to note that Nielsen¹⁶ postulated a controlling surface nucleation process in the spontaneous crystallization of barium sulphate from solutions in which $m < 4 \times 10^{-4} M$ and found the rate to be dependent upon the fourth power of the supersaturation. A recent kinetic and microscopic study of the growth of calcium sulphate crystals has confirmed that nucleation takes place during the characteristic growth surges¹⁷.

The effect of added foreign substances upon the rate of crystallization is especially interesting. In a number of cases, a trace of adsorbate is sufficient to completely inhibit the growth of seed crystals in their supersaturated solutions. Strontium sulphate appears to be particularly susceptible to impurities and the use of different water preparations is sufficient to affect the course of the reaction. Water, prepared by mixed bed deionization on a column of organic ion exchange resins, reduced the rate of crystal growth and, after a period of time, crystal growth ceased with less than 25% of the reaction completed. It became clear that the source of the inhibiting impurity was the resin matrix itself and the effect was completely removed when the solvent was replaced by doubly distilled water¹⁴. The striking effect of some phosphate additives upon the crystal growth of strontium sulphate is seen in Fig. 3 for the experiments summarized in Table II. At concentrations of sodium pyrophosphate as low as $4 \times 10^{-7} M$, crystal growth

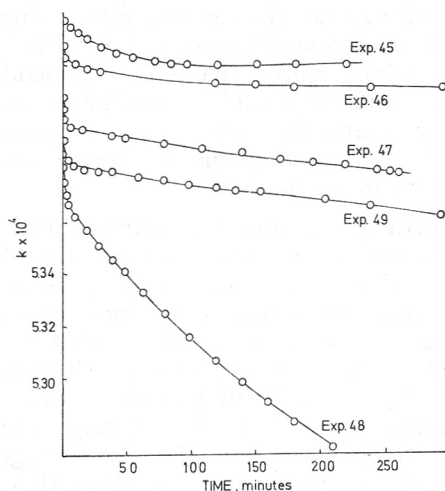


Fig. 3. The growth of seed crystals of strontium sulphate. Plots of specific conductance, k , against time (see Table II for experimental conductors).

TABLE II

Crystallization of Strontium Sulphate in the Presence of Adsorbates

Expt No.	$m_i \times 10^{4a}$ mol/l.	Concn. of adsorbate, M	Seed concn. mg/ml
45	7.500	3.30×10^{-6b}	202
46	7.500	4.30×10^{-7b}	200
47	7.500	4.91×10^{-8c}	178
48	7.500	0.00	91
49	7.500	1.00×10^{-9c}	248

a) m_i = initial concentration of strontium sulphate; b) Sodium pyrophosphate; c) Sodium trimetaphosphate.

is almost completely inhibited (experiment 46). It should be noted, however that in each case the characteristic growth surge upon inoculation of the supersaturated solutions is still in evidence. The amount of observed crystal growth, even with the lowest attainable concentration of additive, is so small that it is not possible to make a quantitative kinetic analysis of the growth curves in Fig. 3. The condensed phosphate anions have also been found to have a marked effect on the stabilization of supersaturated solutions of strontium sulphate^{18,19}. A concentration of sodium triphosphate as low as $3 \times 10^{-5} M$ is sufficient to inhibit completely the nucleation of strontium sulphate in 0.02 M solution, considerably larger than the solubility value¹⁸. The effect could not be attributed to the complex formation between strontium and triphosphate ions because of the low molar ratio of $P_3O_{10}^{5-} : Sr^{2+} = 1 : 670$ in the solution²⁰. Adsorption of the phosphate ions at the crystal surfaces was confirmed radiochemically²⁰.

In the crystal growth of all the bivalent metal sulphates, the reduction in the number of available growth sites effected by the adsorption of the

impurity reduces the over-all rate of crystallization but increases the need for surface nucleation. The results are consistent with the suggestion of Sears²¹ that the impurity reduces the critical free energy for two-dimensional nucleation, causing an increase in surface nucleation. The persistence of the initial surge in the presence of the phosphate additives is further evidence in support of this suggestion.

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IZVOD

Kinetika rasta primarnih kristala u vodenoj otopini

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Kod većine elektrolita postoji relativno dobro definirano kritično presićenje. Ispod te koncentracije presićene je otopine moguće dugo čuvati a da ne dolazi do kristalizacije. Iznad te koncentracije dolazi do spontane kristalizacije. Brižljivom kontrolom uvjeta rada, otopina u kritičnom području presićenja može biti cijepljena kristalom elektrolita. Rast tog kristala moguće je pratiti mikroskopskim metodama. Promjenu koncentracije otopine moguće je pratiti konduktometrijski, potencio-metrijski (pomoću ionsko-selektivnih elektroda), kao i radiometrijski pomoću obilježenih iona.

U radu su opisani matematički izrazi za brzinu rasta kristala, kao funkciju broja mjesta na površini kristala slobodnih za depoziciju, koncentracije konstitu-cionih ionskih vrsta, konstante ravnoteže i faktora aktiviteta. Pokazani su eksperi-

mentalni rezultati za kristalizaciju magnesium-oksalata, barijum i strontium-sulfata. U vrlo čistim otopinama postignuto je odlično slaganje s teorijom. Tragovi adsorbiranih nečistoća (npr. voda propuštena kroz ionsko-izmjenjivačku kolonu za demineralizaciju) mogu inhibirati rast kristala cjepiva. Isto tako djeluje i 4×10^{-7} molarna otopina natrium-pirofosfata koja inhibira rast kristala strontium-sulfata.

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