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Mechanism of precipitate formation during spontaneous crystallization from supersaturated aqueous solutions

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The models of formation of salt precipitates during crystallization from supersaturated aqueous solutions are analyzed. The results of theoretical simulations and experimental studies are compared. The attention is focused on the processes of crystal aggregation and agglomeration. The data on the mechanism of crystal intergrowth under conditions of mass crystallization of salts from supersaturated aqueous solutions are considered. The intergrowth process is shown to be described most reliably by the model based on the Polak theory according to which in supersaturated solutions, connecting nucleus-bridges are formed within aggregates between the closest faces of neighbouring crystals.
The bibliography includes 159 references.

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I. Introduction

In this review, an attempt is made to generalize the data accumulated in recent decades on the mechanism of formation of the crystal size distribution during crystallization. Emphasis is placed on the spontaneous isothermal crystallization the rules of which hold also for the continuous and non-isothermal crystallization processes. Gaining insight into the mechanism of crystallization in this particular (and simplest) case will allow for more reliable prediction of the parameters and mechanisms of other more complicated crystallization processes.

In this review, we do not discuss the nucleation of crystals in salt solutions because this is a separate deep subject matter. Attention is focused on the next stage of crystallization in which the crystals formed begin to grow, form aggregates and agglomerates and are partly broken due to collisions with one another, the stirrer or crystallizer walls. The processes of aggregation and agglomeration of crystals during crystallization, the mechanism of crystal intergrowth under conditions of mass crystallization, the most popular models of crystallization processes are considered and the new studies in this field are analyzed.

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II. Early concepts on the mechanism of formation of the crystal size distribution during crystallization

Up to recently, development of the crystal size distribution during spontaneous crystallization was assumed to be a result of two almost simultaneous processes: the nucleation of crystals and their further growth. The aggregation and agglomeration of crystals during crystallization were ignored as well as their fragmentation and attrition. An early model was proposed by Todes and Roginskii,[1,2] who assumed that in the first stage of crystallization, nuclei of crystals are formed (as this takes place, the solution supersaturation does not virtually decrease), while in the second stage, only the growth of crystals from their nuclei occurs. They also proposed that the number of salt crystals formed in the initial period remains unchanged during the whole crystallization process and the crystal growth obeys the first order equation with respect to solution supersaturation.[2]

Thus, with these suppositions and with the assumption that the crystals are spherical, the following equation was proposed [2, 3] for determining the total surface area (S) of crystals that grow in solution:

$$S = 3\left(\frac{4\pi}{3}\right)^{1/3} \frac{N^{1/3} v^{2/3}}{\rho^{2/3}} (C_{\text{in}} - C)^{2/3} = N\pi \left[\frac{6(C_{\text{in}} - C)v}{\pi\rho N}\right]^{2/3} \quad (1)$$

where N is the total number of salt crystals in solution, v is the solution volume/m^3; ρ is the density of salt crystals/kg m^{-3}; C_{in} is the initial mass concentration of the supersaturated salt solutions/kg m^{-3}; C is the mass concentration of the crystallizing (dissolved) substance (salt) in the solution/kg m^{-3}.

As was noted above, in this case, N is set to be constant throughout the whole crystallization process; hence, $N = N_0 = \text{const}$ (where N_0 is the total number of salt crystals in solution immediately after the end of the induction period of crystallization or in the instant when the nucleation of new crystals in solution stops).

In the general case, when the supersaturations is not too high, the rate of decrease in solution supersaturation is described by the well-known empirical equation

$$-\frac{dC}{d\tau} = \frac{S\rho}{v} k_g (C - C_0)^z = \frac{S}{v} K (C - C_0)^z \quad (2)$$

where τ is the time/s; k_g is the mean rate coefficient for crystal growth; C_0 is the mass concentration of the saturated salt solution/kg m^{-3}; z is the order of the crystal growth equation (usually, $z = 1-2$); $K = k_g \rho$ is the mass transfer coefficient.

Substitution of Eqn (1) into expression (2) for $z = 1$ and $N = N_0$ leads to the formula

$$-\frac{dC}{d\tau} = \frac{K}{v} N_0 \pi \left[\frac{6(C_{\text{in}} - C)v}{\pi\rho N_0}\right]^{2/3} (C - C_0) \quad (3)$$

Integration of Eqn (3) affords a rather complicated mathematical expression.

Deryabina and Mishchenko [3] verified this model experimentally for spontaneous isothermal crystallization of calcium sulfate from its supersaturated aqueous solutions. They have demonstrated that, in principle, Eqn (3) describes satisfactorily the experimental data on the kinetics of decrease in solution supersaturation; however, at the end of the crystallization process, they observed systematic deviations of experimental points from the theoretical curve towards higher (as compared with expected) values of the residual supersaturation. The authors explained these deviations by low accuracy of measurements. However, from our point of view, it is more reasonable to attribute them to either deceleration of crystal growth as the crystal size increases (the diffusion growth mode) or the effect of crystal aggregation during crystallization, resulting in a decrease in the total surface area of the growing crystals. This decreases the rate of supersaturation decrease and gives rise to the observed deviations from the calculated curves. Note also that the deviations from theoretical curves caused by insifficient accuracy of measurements would be random and located on both sides of the curve, *i.e.*, resulting in both overrated and underrated supersaturation values.

In their model, Roginskii and Todes [2] assumed that the growth rates of crystals in solution are equal, which should have led to the monodisperse crystallization product, and this contradicts the experimental data.

Later, the cellular model of spontaneous crystallization was put forward [4–9] according to which the total volume of the supersaturated solution is split into a certain number of equal unit cells. One nucleus is formed in each cell. The nuclei appear in different moments but the crystal growth law is the same for all cells. The cells are assumed to be isolated from one another; hence, the crystals grow only due to supersaturation of the solution present in a given unit cell. It is quite clear that under these assumptions, all the crystals formed should be of the same size, *i.e.*, the size distribution of crystals should be monomodal and the crystals should be monodisperse. However, this is not the case in reality. Moreover, it is rather difficult to prepare monodisperse crystals by spontaneous crystallization.

To eliminate the drawbacks of the cellular crystallization model, Kharin [7–9] has introduced several modifications. He assumed that during crystallization, the solute concentration changes uniformly throughout the solution volume, *i.e.*, the cells are not isolated. Also, whereas the mass of the crystal was earlier determined only by the growth time, being independent of the nucleation time, in the new model, the mass of the crystal was assumed to depend also on this parameter. In other words, the mass of the crystal became also dependent on the current supersaturation in solution at the moment of nucleation.

Based on these assumptions, Kharin analyzed his own experimental data on the isothermal crystallization of calcium carbonate and saccharose, in particular, the curves of crystal size distribution at the end of an experiment. To reach agreement between the theory and the experiment, he has introduced the arguable assumption that the nucleation process is not steady-state in the initial period of crystallization.[8, 9] Note that the assumption that nucleation is not steady-state during the induction period when supersaturation remains virtually unchanged contradicts some experimental data. Thus, the initial stage of gypsum crystallization on a heated metal surface was studied by direct microscopic measurements *in situ*.[10–12] No non-steady-state period was observed for the surface nucleation of calcium sulfate crystals. The experimental data were adequately described by equations of the classical nucleation theory. Earlier, a similar result was obtained [13] for potassium chloride crystallization.

Serebryakov [14] reported a detailed verification of Kharin's model: comparison of the calculated and experimental dependences failed to confirm the cellular model. To explain somehow the experimental curves observed, the author [14] has assumed that at the initial moment of crystallization, a certain fixed number of primary crystals are formed in solution and afterwards only their growth occurs, which is in line with the Roginskii–Todes model.[2] The calculations based on this assumption resulted in the considerably smaller deviation between calculated and experimental dependences and confirmed the theoretical concepts of Todes,[1] according to which the crystal nuclei are formed in the very beginning of isothermal crystallization and the subsequent nucleation during the crystallization process can be neglected.

Berliner [15] proposed a somewhat different model. Particularly, in contrast to the classical thermodynamic theory

of Gibbs – Volmer,[16 – 22] he took the power law dependence of the nucleation rate (J) on supersaturation that was proposed by Mayer [23, 24]

$$J = \beta_1 (C - C_m)^{z_1} \quad (4)$$

where β_1 is rate constant for nucleation in solution; C_m is the solution concentration at metastable equilibrium; z_1 is the order of the nucleation rate equation.

With these assumptions, a complicated system of differential and integral-differential equations was formed which, as admitted by the author himself, was difficult to solve by even numerical methods. However, the system can be solved by numerical methods provided that several simplifications are introduced. The dependences of the relative supersaturation of solution during crystallization, calculated in terms of this model, proved to be S-shaped, which is typical of spontaneous crystallization. The Roginskii – Todes equation [2, 3] turned out to be a special case of this model. An algorithm was proposed for experimental testing of this model;[15] however, no comparison with experimental data was carried out.

In their later joint studies, Berliner and Melikhov [25, 26] tried to refine the model described above. Into the initial system, they introduced the equations for the spatial continuity of crystal sizes and the balance equation for the substance being crystallized in solution. After several transformations, they solved these equations numerically to afford asymptotic formulas for predicting the kinetics of crystallization and also determined the rate constants for nucleation and crystal growth.[25] This model was refined by introducing the function that accounted for the fluctuations in the crystal growth rate.[26] According to the authors, these fluctuations make a prinounced contribution to the crystal size distribution observed at the end of crystallization. The selection check of the relationships derived carried out with the use of experimental data from the classical study by Fisher [27] has demonstrated than the found parameters of crystallization differ somewhat from the data of other researchers.[28 – 30] The authors of the aforementioned model [26] attributed this difference to specific features of the method for treatment of experimental results the other researchers used.[28 – 30] In addition, they suggested that for low solution supersaturations, the model they proposed should be supplemented by taking into account the secondary nucleation.† Some other, analogous crystallization models were also proposed.[34 – 46]

The general drawback of the above models is that all of them ignored the processes of aggregation and intergrowth of crystals during crystallization. Thus, Roginskii and Todes [2] admitted that one of the reasons for the experimentally observed Gaussian size distribution of crystals was indeed their agglomeration. To explain the non-monomodal size distribution of crystals, Kharin [7 – 9] had to assume that the nucleation process is not steady state in the induction period of crystallization, while the authors of the later models [25, 26, 40] took into account the fluctuations in the crystal growth rate (nevertheless, these fluctuations certainly do affect the form of curves of crystal size distribution).

† In our opinion, the secondary nucleation should also be taken into account at higher surpersaturations, because as the solution supertsaturation increases, the rate of secondary nucleation also increases and its effect should become stronger.[31 – 33]

III. Aggregation and agglomeration of crystals during crystallization

1. Experimental data on the aggregation and agglomeration of crystals. Formation of pseudo-single crystals

As was noted above, the crystal aggregation during crystallization was ignored for a long time. However, experimental results showed that crystallization of salts from solutions involves their aggregation and agglomeration‡ in addition to crystal nucleation and further growth.

To date, extensive experimental evidence that aggregation and agglomeration of crystals occur during crystallization of various salts has been accumulated. Below, we consider only some of these studies, namely, the studies that, on our opinion, have made the largest contribution to description of these processes.

An early indication of crystal aggregation during crystallization was obtained by Pozdner,[47] who studied the isothermal crystallization of several poorly soluble salts by the nephelometric method. He has shown that the kinetics of variations in the scattered light intensity during crystallization can be described by the Smoluchowski equation [48] for coagulation of colloids. However, as was shown by Chepelevetskii,[49] the change in the solution opacity during crystallization does not contradict the concepts of simultaneous nucleation and growth of crystals. In view of this, the data by Pozdner could be recognized as convincing evidence for crystal aggregation during crystallization.

The direct proof of aggregation and agglomeration of crystals was obtained later when studying crystalline deposits after the completion of the crystallization process. Thus, Matusevich and Shabalin [50] observed the formation of agglomerates of KNO_3 and $K_4[Fe(CN)_6] \cdot 3\,H_2O$ crystals. The agglomeration of crystals of various highly soluble salts was also studied by other authors.[50 – 53] The aggregation was observed during crystallization of poorly soluble salts.[54 – 69] Thus, in a study of calcium carbonate precipitation, the crystal agglomerates were visualized by a microscope.[57] A comparison of the crystal size distribution in the final crystalline product calculated within the framework of the Randolph – Larson model,[41] which disregards the possibility of crystal aggregation during crystallization, revealed a considerable deviation between the results of calculations and experimental data. Later, the formation of coarse agglomerates from finer $CaCO_3$ crystals was observed by other scientists. For instance, it was shown [58]

‡ It deserves mention that in publications (especially, earlier) devoted to crystallization, the processes of aggregation and agglomeration were not distinguished, namely, the aggregation was often referred to as agglomeration and *vice versa*. At present, it is generally accepted that the aggregation is integration of crystals (or particles) into a single large particle under the effect of electrostatic forces (heterocoagulation) or due to the van der Waals and like forces. For instance, it is aggregates that are formed upon coagulation of colloids. Agglomeration is further intergrowth of crystals within the aggregate to become a whole unit (*i.e.*, the crystals in the agglomerate are bound by chemical rather than van der Waals forces). Certainly, in the studies of crystallization, it is difficult to experimentally determine the moment when a crystal aggregate is transformed into an agglomerate. This complicates investigation of the mechanism of crystal intergrowth. However, the initial stage of agglomeration, *i.e.*, aggregation, can be easily monitored by the decrease in the concentration (or in the total number) of crystals in solution during crystallization.

that the agglomerates formed were spherical and consisted of very fine crystals of calcium carbonate.

The aggregation of crystals during crystallization of barium sulfate and carbonate was studied in detail by Melikhov *et al.*[59–62] The isothermal crystallization of barium sulfate was examined in a rapid-mixing unit.[59,60] Solution supersaturation was created by feeding equimolar solutions of $BaCl_2$ and K_2SO_4 into an Y-shaped mixer. Electron microscopic examination of the precipitates in different stages of the crystallization process has shown that, first of all, a large number of barium sulfate ultramicrocrystals (nanocrystals) were formed in solution to be later joined into well-ordered ring-shaped aggregates.[59–61] In turn, the ring-shaped aggregates were also combined into larger conglomerates and so on, up to the formation of pseudo-single crystals (Fig. 1). Similar results were also obtained for crystallization of barium carbonate.[62] It should be noted that this is, perhaps, the first experimental proof of the appearance of pseudo-single crystals upon crystallization of salts in solutions.

Still more convincing evidence that pseudo-single crystals are formed was obtained by Melikhov *et al.*[63] while studying the crystallization of calcium sulfate semihydrate. In this case, too, the complex multistage mechanism of crystalline precipitate formation was revealed. Like the crystallization of barium sulfate and carbonate,[59–62] the crystallization of $CaSO_4 \cdot 0.5\,H_2O$ started with the formation of a large number of nanocrystals, which were later joined into aggregates shaped as hexagonal prisms outwardly indistinguishable from single crystals.[63,64] These pseudo-single crystals were later joined into coarser crystals (macrocrystals) with the internal structure exposable by mild etching in water (Fig. 2).

The agglomeration of crystals of calcium sulfate semihydrate was observed during crystallization from supersaturated sulfuric-acid phosphate solutions which mimicked the phosphoric acid production.[65,66] The experiments were carried out at 90 °C and a constant concentration of phosphate ions but different excessive amounts of sulfuric acid. The kinetics of crystallization was monitored by collecting samples of the suspension. The method of moments was used in describing this process.[65,66] It was shown that taking into account agglomeration provided coincidence of calculated and experimental data.

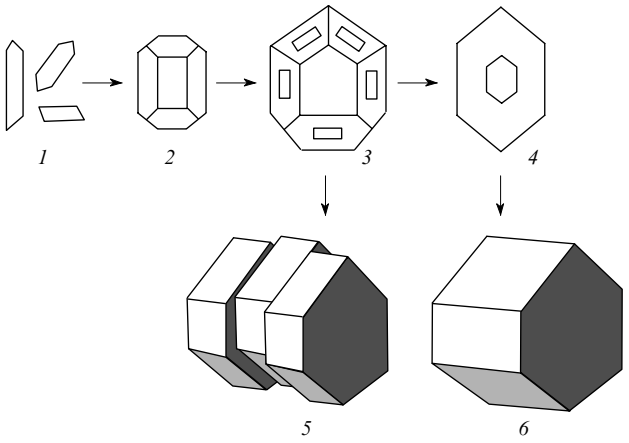


Figure 1. Illustration of the formation of barium sulfate precipitate.[61]
(*1*) Original filamentary nanocrystals; (*2*) original ring-shaped agglomerates of nanocrystals; (*3*, *4*) secondary ring-shaped agglomerates (conglomerates) immediately after their formation and after subsequent morphological ordering; (*5*, *6*) results of the stage of pseudo-single crystal formation.

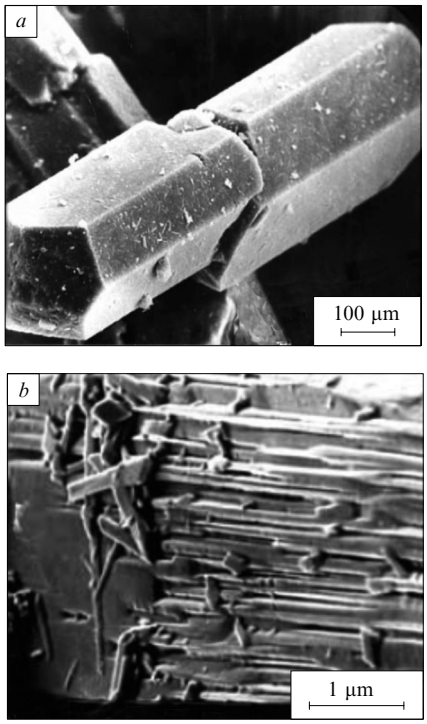


Figure 2. Microimages of pseudo-single crystals of calcium sulfate semihydrate (*a*) and its internal structure after slight etching in water (*b*).[64]

When studying the aggregation and agglomeration of calcium oxalate monohydrate crystals, successive formation of a hierarchical complex structure of the crystalline precipitate comprising calcium oxalate monohydrate crystals, primary aggregates (agglomerates) of these crystals and the secondary agglomerates of primary aggregates was observed.[67,68] In another study,[69] nanosized pseudo-single crystals of cadmium sulfide were detected during the formation of nanocrystalline films of this salt.

Attention is drawn by the fact that the formed agglomerates are often of a regular shape and outwardly almost indistinguishable from single crystals of precipitating salts. As was demonstrated,[70–76] the reason for the appearance of pseudo-single crystals lies in the hydrodynamical and morphological selection of aggregates in the course of agglomerate formation, which results in predominance of regularly shaped particles with low hydrodynamic resistance. For motion velocities higher than a certain threshold value, regularly shaped aggregates of similarly sized crystals joined according to the 'peer-to-peer' principle are accumulated in the suspension. Note that other authors have also arrived at this conclusion.[77]

To date, the formation of pseudo-single crystals was observed for a large number of poorly soluble compounds.[77–91] Moreover, a new name, mesocrystals, was invented for them and the formation as such agglomerates which proceeds through oriented aggregation of primary crystals is now referred to as the non-classical crystalliza-

tion. The studies on the non-classical crystallization were surveyed by Niederberger and Cölfen.[90]

2. Dynamics of crystal aggregation

After the discovery of crystal aggregation in the course of crystallization of various salts, attempts were made to study this process in more detail and elucidate its kinetics. Thus, Melikhov *et al.*[92] proposed a model of aggregation according to which microcrystals of a monodisperse suspension join into floccules where they are held together (probably, by van der Waals forces; the authors did not indicate the cause of binding) but retain mobility with respect to one another. The floccules may both form and break, being in quasi-equilibrium with individual microcrystals in solution. Within the floccules, microcrystals may intergrow to form primary crystal aggregates (nuclei). It was postulated that the primary aggregation process is hindered whereas the further addition of new microcrystals to already formed aggregates is fast.[92] The model is described by a complex system of integral and differential equations with a lot of unknown parameters, analogously to the system used in the earlier studies.[25, 63] The authors [92] have analyzed the following possible types of aggregation:

— intrafloccular — crystal aggregates form within the floccule volume;

— interfloccular — crystal aggregates form only outside the floccules;

— mixed — aggregates migrate many times from the solution to the floccules and back.

This model was tested in a study of the crystallization of calcium sulfate semihydrate by an experimental method similar to that described earlier [63] according to which the suspension was sampled during crystallization and the collected samples were filtered through a carbon-graphite cloth or a thermostatically controlled glass filter. The examination of precipitates (from suspension samples after filtering) included analysis of the mutual arrangement of microcrystals and aggregates and also their morphological features. It was found that with time, the number of crystals in aggregates increased. Moreover, the proportion of aggregates in the precipitate progressively increased while the number of individual mirocrystals decreased. In the late stages of crystallization, no individual microcrystals were observed at all in the filtered precipitates. The aggregation proceeded in two stages. In the first stage, the primary faceted aggregates were formed to be combined into the secondary chain aggregates in the second stage.

The authors of the above study [92] concluded that the primary aggregates were formed outside the floccules while the secondary aggregates appeared within the floccules. The clusters of secondary aggregates observed on the carbon-graphite cloth served as not very convincing evidence that floccules were formed. The debatable character of this proof was due to the fact that the filtration conditions could distort the true picture of this process, so that the observed clusters of aggregates and crystals could result from non-uniform filtration of suspension samples through the carbon-graphite cloth. At the same time, the authors believed that the observed formation of aggregates shaped as hexagonal prisms pointed to the preferential addition of primary microcrystals to the aggregate surface at the sites where microcrystals could stick by two (or more) faces.

In another study, Melikhov *et al.*[93] explored the effect of supersaturation on the aggregation of calcium sulfate semihydrate crystals by using the same experimental procedure. The aggregation process was studied under isothermal conditions at the constant solution supersaturation. The original suspension of $CaSO_4 \cdot 0.5\,H_2O$ crystals was obtained by mixing H_2SO_4 and $Ca(H_2PO_4)_2$ solutions followed by long-term keeping in the mother solution with vigorous stirring. During this period, calcium sulfate semihydrate crystallized, the equilibrium was established in solution and the size of $CaSO_4 \cdot 0.5\,H_2O$ crystals was stabilized. Then the reactants were added to the solution at a constant rate in order to create a persistent constant supersaturation. It was shown experimentally that the aggregation of crystals in solution began immediately after the onset of supersaturation (before the introduction of reactants into suspension, the concentration of crystals remained unchanged) and, in the initial period of crystallization, the concentration of solid phase particles (crystals and aggregates) in the suspension markedly dropped down. Then the concentration of solid phase particles in solution was stabilized and remained almost constant up to the end of the experiment (although the solution remained supersaturated) or changed very slowly (Fig. 3). On the whole, the decrease in the concentration of solid-phase particles in the suspension after the onset of solution supersaturation was described by the following empirical formula:[93]

$$\frac{n}{n_1} = 1 - B\Big\{1 - \exp[-\beta(\tau - t_0)]\Big\} \qquad (5)$$

where n is the total concentration of solid-phase particles in the solution /m^{-3}; n_1 is the concentration of primary crystals in the solution ($n = n_1$ for $\tau = t_0$), m^{-3}; B, β are empirical constants.

Experimental studies [92, 93] clearly demonstrated that the processes of crystal aggregation and agglomeration under conditions of mass crystallization proceed only in supersaturated solutions; moreover, the rate of these processes sharply drops with the increase in the size of solid-phase particles. The strong dependence of agglomeration of aluminium hydroxide on the solution supersaturation was also observed earlier.[94, 95]

It is evident that hydrodynamic conditions of crystallization should have a substantial effect on the aggregate formation process. On the one hand, the intensification of solution stirring should increase the rate of collisions

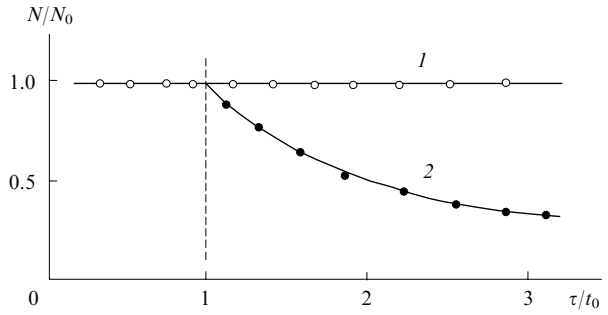


Figure 3. Variation of the number of particles in the calcium sulfate suspension in aqueous solution.[61, 93]
(*1*) Saturated solution; (*2*) supersaturated solution; t_0 is the time of beginning of reactant addition for creating solution supersaturation.

between crystals,[96–98] thus accelerating the aggregation. On the other hand, as the stirring intensifies, the time of crystal contact on collisions decreases (which apparently lowers down the probability of their intergrowth) and the rates of breakage and crushing of crystals and agglomerates on their collisions with one another, the stirrer and crystallizer walls increase.[99–102] As was shown by Matusevich and Shabalin,[50] more vigorous stirring of the solution during crystallization leads to a decrease in both the average size of crystals formed and the degree of their agglomeration. This changes the habit of crystals, *i.e.*, agglomerates are formed from more precisely attached and finer crystals. At high stirring velocities, the crystal aggregation and agglomeration cease altogether and the processes of crystal destruction and mechanical attrition are intensified, which results in smoothed corners and rounded faces.[50] Similar results were obtained in later publications.[58, 99, 103, 104]

The main complication faced by the studies of aggregation during crystallization lies in the difficulty of determination of the concentration of crystals in solution during salt precipitation. In particular, this concerns readily soluble salts that crystallize very quickly. The experimental procedures that imply collection of suspension samples during crystallization can produce distorted or unreliable results because the sampling process is not instantaneous and the salt concentration may change during the sampling time; moreover, destruction or formation of new agglomerates and crystals may occur in the sample. Yet another source of distortions is filtration of suspension sample, which can also be accompanied by similar changes in the crystal size distribution and the salt concentration in solution. Hence, to obtain reliable data on the kinetics of crystal aggregation and mechanism of crystalline product formation, one has to use procedures for monitoring of all the process parameters *in situ* without interfering into the process. One component of these methods is turbidimetry (and also nephelometry), which was among the first methods applied to study crystallization.[47, 49] However, it was mainly used to find the length of induction periods of crystallization[47, 49, 105] or the precipitate concentration.[106] Later, this method was used to elucidate the volume fraction of the solid phase during salt crystallization[104, 107, 108] and also the size distribution.[108]

Yet another possible component of *in situ* procedures is conductometry. By continuous measurement of solution conductivity during salt crystallization, one can monitor the removal of solution supersaturation; moreover, the solution samples need not be taken out for measurements because electrodes of the conductometer are immersed directly into the crystallizing solution. Like turbidimetry and nephelometry, the conductometric method was used earlier to study crystallization of various salts (especially, poorly soluble salts, *e.g.*, see Ref. 3); however, the simultaneous use of the turbidimetric and conductometric methods for studying the kinetics of spontaneous crystallization was described only relatively recently.[104, 109–112] In a study of crystallization kinetics of ammonium chloride by these methods, coarse aggregates (70–200 μm) built of fine NH_4Cl crystals with the diameter below 5 μm were detected.[104] As the stirring velocity increased, the average size of aggregates decreased. The authors also assessed the changes in the volume fraction of precipitated ammonium chloride crystals, but the changes in the concentration of ammonium chloride crystals formed in solution during the crystallization were not estimated.

A somewhat different experimental method was also reported.[109–112] The experiments were carried out on two almost similar (with minor non-essential differences) setups with automatic measurement and recording of the conductivity and optical transmittance of supersaturated solutions during spontaneous isothermal crystallization of a salt. The supersaturation was achieved by using the following two procedures:

— a salting-out agent was added to the solution; in its presence, the solubility of the salt decreased and the solution became supersaturated; ethanol was used as the salting-out agent;

— the supersaturated solution was prepared by the thermal method, *i.e.*, by cooling a saturated solution down to the temperatures corresponding to its supersaturation.

The salt concentration in the solution during crystallization was determined by means of calibration plots based on the data on solution conductivity. The salt crystallization began spontaneously with continuous stirring of the solution so that all the crystals formed were in the suspended state.[109–112] The experimental data were treated by the well-known dependence analogous to the Bouguer–Lambert–Beer law for coloured solutions, according to which the absorbance of a suspension at low solid-phase concentrations is directly proportional to the total surface area of solid particles contained in the solution [113]

$$D_0 = \log\frac{I_0}{I} = K_f S \qquad (6)$$

where D_0 is the absorbance of the salt solution in the course of crystallization; I_0 , I are the optical transmittance of the salt solution in the initial moment and moment τ, respectively (%); K_f is the optical absorption constant of the salt / m^{-2}. Formula (6) forms the basis of the photosedimentation analysis of the dispersion composition of dusts and powders.[113]

After the end of salt crystallization (when the optical transmittance and conductivity of solution cease to change), the stirrer was switched off and the curve of variation of optical transmittance during sedimentation of the formed salt crystals was recorded. This curve was used to calculate the crystal size distribution of the crystalline product and the optical absorption constant K_f for the salt under study (for the calculation method, see a monograph [113]).

Thus, the experimental procedure used in the cited studies[109–112] provided thorough *in situ* monitoring of the kinetics of salt precipitation without interruption of the crystallization process and also served to elucidate the crystal size distribution after the end of crystallization directly in the solution without withdrawing the precipitate. The thus obtained combined data on the solution absorbance and conductivity variations made it possible to calculate the dynamics of changes in the total number and diameter of the crystals formed in solution and also other crystallization parameters. The use of this experimental method to study the spontaneous crystallization of a series of salts,[109–112] namely, $NaNO_3$, $CaSO_4 \cdot 2H_2O$, KNO_3, NaCl, KCl, $NaNO_2$, K_2SO_4 and $Ba(NO_3)_2$ has shown that despite the different solubility and other physicochemical properties of these salts, their crystallization proceeds by the common patterns. Thus, it turned out that the largest

number of crystals of any salt under study was formed in the very beginning of crystallization immediately after the induction period, which confirmed the theoretical estimates by Todes.[1] The crystals formed during this period were of the micrometre size.[109–112] This result is in adequate agreement with the data of other scientists (see Refs 104 and 114). For instance, the studies of the spontaneous crystallization of calcium sulfate[114] revealed the presence of micrometre-sized gypsum crystals in solution at the end of the crystallization induction period.

During crystallization, the total number of crystals present in solution of any studied salt progressively decreased, which pointed to their aggregation.[109–112] However, the aggregation of crystals ceased when the solution was no longer supersaturated and became saturated,[109–112] which agrees with the data by several researchers.[93–95] In describing the kinetics of crystal aggregation, the Smoluchowski equation[48] for colloid coagulation was used. Indeed, for both coagulation of colloids and spontaneous crystallization, the predominant type of collisions is binary (*i.e.*, the interaction of only two particles, whereas the simultaneous collision of three and more crystals or colloid particles is much more rare and can be neglected). For crystal aggregation, the Smoluchowski formula[48] for colloid coagulation was transformed as follows:[109–112]

$$N = \frac{N_0}{1 + K_a N_0(\tau - \tau_0)} \qquad (7)$$

where K_a is the rate coefficient for crystal aggregation /s^{-1}; τ_0 is the time after which only the growth of already formed crystals takes place (nucleation of crystals has already stopped or is insignificant) /s. In many experiments, τ_0 corresponded to the end of the induction period of crystallization.[109–112] Note that in this equation, by N is meant the total number of crystalline particles, including not only crystals but also aggregates (agglomerates) of crystals, *i.e.*, an aggregate (or an agglomerate) is considered as a single crystalline particle.

Figures 4 and 5 show the typical kinetic dependences of aggregation of $NaNO_2$, $Ba(NO_3)_2$ and KCl salts plotted in the coordinates of Eqn (7). It is seen that these plots are linear in the initial period of crystallization. However, as the equilibrium is approached, gradual deviation from linearity is observed, which is apparently due to the fact that the rate coefficient for aggregation K_a decreases as the solution supersaturation is gradually decreased, because this lowers down the probability of crystal intergrowth.[95] Nonetheless, Eqn (7) can be used for the approximate description of the kinetics of aggregation of crystals during spontaneous crystallization (correlation coefficient 0.60–0.99) (see Refs 109–112). A detailed microscopic study of one of the obtained precipitates has shown that it indeed consisted of crystal agglomerates.[112]

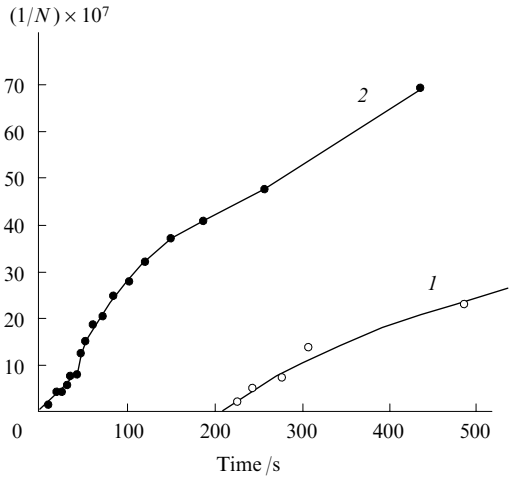


Figure 4. Kinetic dependences of aggregation of $NaNO_2$ (*1*) and $Ba(NO_3)_2$ (*2*) crystals in the coordinates of Eqn (7).[109]

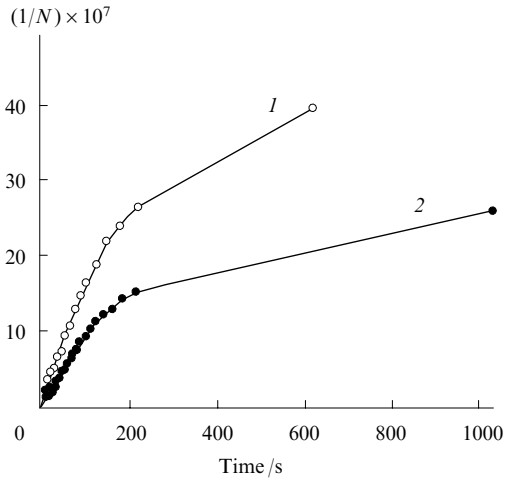


Figure 5. Kinetic dependences of aggregation of KCl crystals in the coordinates of Eqn (7).[110]
Experiment: (*1*) 3; (*2*) 5.

IV. Formal consideration of the crystal aggregation process during crystallization

One of the first models describing the formation of a crystalline precipitate taking into account the aggregation of crystals was proposed by Baker and Bergougnou.[115] The model assumed that the crystal growth proceeds exclusively due to aggregation and subsequent intergrowth within aggregates (the growth of crystals themselves both in solution and within aggregates was ignored) and that the formed aggregates are not destroyed. The mechanism of crystal intergrowth within aggregates (*i.e.*, the formation of agglomerates from aggregates) was not analyzed. Based on results of other authors,[116, 117] it was assumed that the rate constant for aggregation remains invariant throughout the whole aggregation process (although the theoretical analysis predicts that in stirred solutions this constant should change with increase in the size of colliding particles,[96–98] *i.e.*, as the crystals and agglomerates grow). The stages of nucleation and subsequent growth of primary crystals were not analyzed either. This model was developed for a continuous process. The balance equation took into account the rates of the following processes: formation of agglomerates from primary crystals, formation of secondary agglomerates from primary agglomerates, and withdrawal of all types of agglomerates from the system. The comparison of this model with experimental data was carried out only on the qualitative level.

In a monograph,[118] the crystallization process is considered taking into account the possible agglomeration of crystals and also the changes in the number of crystals due to both their destruction and introduction of seed crystals into the solution. No comparison of the derived balance equation with experimental data was carried out.

Halfon and Kaliaguine[94,95] simplified the well-known balance equation describing a continuous process[41–43,45] for the case of isothermal periodic crystallization with due regard to the possible formation and destruction of crystal agglomerates. In doing this, they assumed that the nucleation rate is described by Eqn (4) in which the quantity C_0 has been substituted for C_m and the linear rate of crystal growth (V) is described by the well-known empirical formula

$$V = k_g(C - C_0)^z \tag{8}$$

The mass balance equation for the substance being crystallized in terms of the classical version of this model (which disregards the formation and destruction of aggregates) was compared with the experimental data obtained[94] for the kinetics of crystallization of aluminium hydroxide. The best agreement between theory and experiment was observed for $z = 2$, $k_g = 3.55 \times 10^{-4}$ (for the crystal growth rate expressed in micrometres per hour and the solution concentration calculated for Al_2O_3 and expressed in grammes per litre) under the assumption that crystallization proceeds without the nucleation of new crystals in the solution.

The crystallization of aluminium hydroxide was carried out in the presence of seed crystals in solution; for low concentrations of these crystals, long induction periods were observed. All experiments were carried out in industrial aluminate solutions. The best agreement between theoretical curves and experimental data was observed for experiments where the crystallization proceeded without the induction period. Moreover, comparing these results with the experimental data obtained for simulated industrial solutions prepared from pure chemicals[119,120] revealed the deviation in the average rate coefficient for crystal growth, particularly, a higher value $k_g = 8 \times 10^{-4}$ was found. Therefore, the authors[94,95] concluded that some corrections for the secondary nucleation should be introduced into the model. However, they did not analyze the presence of induction periods in their experiments with sufficiently large amounts of seed crystals (seed ratio of 15%–25%). Meanwhile, this suggests that either the crystals used as the seeds were not identical to the crystals formed in the solution under the given experimental conditions (some other modification) or the solution contained some dissolved impurities that could block the kinks and other sites of crystal growth on the surface of seed crystals. These very factors could give rise to the induction periods of crystallization. Insofar as the seed crystals were prepared from the industrial aluminate solution,[94,95] the second factor appears to be more likely. This was confirmed by the observation that as the number of seed crystals in solution increased, the induction periods of crystallization disappeared (probably because the impurities failed to completely block the surface of seed crystals). This was also indirectly confirmed in a study[121] devoted to sodium carbonate crystallization from an industrial aluminate solution in which a very low growth rate of seed crystals was observed (seed crystals were prepared from the same solution under similar experimental conditions, which ruled out their non-conformity to the crystallization conditions). It was also noted[121] that one of the reasons for the extremely low growth rate of sodium carbonate crystals could be the presence of a dissolved impurity in the industrial aluminate solution, capable of inhibiting the growth.

The proposed model was compared[95] with the experimental size distribution curves of crystals recorded in different stages of the crystallization process using a Coulter counter. The comparison took into account the possible aggregation and disintegration of crystals during crystallization. It was also postulated that the probability of crystal intergrowth upon collisions is determined by a power law dependence on solution supersaturation described by a formula analogous to formulas (4) and (8). Processing of experimental data in terms of this dependence has revealed that the exponent is 4. The use of this value in further calculations led to the satisfactory agreement between experimental and theoretical dependences.[95] However, the controversial nature of these calculations deserves mention. Thus, some parameters and dependences of the crystallization process were found by comparing experimental data with the results of theoretical calculations carried out based on the mass balance equation for the substance being crystallized, which ignored the crystal aggregation and destruction during crystallization[94] and adequately described the kinetic curves. Moreover, for the better agreement, the secondary nucleation was also taken into account (the correctness of the latter was already called in question above). The other parameters of the crystallization process were found using another balance equation which did take into account the crystal agglomeration and destruction.[95]

To take into account the crystal aggregation in the model of mass crystallization of salts from solutions, Moshinskii[122] has introduced the corresponding modifications into the crystal volume distribution function. The destruction of aggregates during crystallization was ignored. The crystal growth rate was set by formula (8) for $z = 2$. The rate coefficient for aggregation (in terms of Moshinkii, the coagulation kernel) was taken to be constant throughout the whole process, *i.e.*, it did not depend on either solution supersaturation or the size of colliding particles. Different solutions of the derived equation were considered; no comparison of calculated and experimental data was carried out.

A simple method of theoretical assessment of the expected crystal size distribution at the end of the crystallization process was proposed.[110,111] In these studies, it was shown (see above) that the kinetics of crystal aggregation during crystallization can be described by the Smoluchowski equation for coagulation of colloids; this is why it was assumed that the size distribution of crystals also obeys the same laws. Thus, in line with the Smoluchowski theory, when considering the crystal aggregation, the number of crystal aggregates N_k comprising k primary particles is determined by the expression[110,111]

$$N_k = \frac{N_0\left[K_a N_0(\tau - \tau_0)\right]^{k-1}}{\left[1 + K_a N_0(\tau - \tau_0)\right]^{k+1}} \tag{9}$$

The size of crystal aggregates and their mole fraction in the precipitate can be calculated, in the first approximation, according to the equations [110, 111]

$$d = d_k = \left(\frac{6m_k}{\pi\rho}\right)^{1/3} \tag{10}$$

$$Q_k = \frac{100 m_k N_k}{m} \tag{11}$$

$$Q = \sum_k Q_k \tag{12}$$

where d_k is the diameter of a crystal or a crystal aggregate composed of k primary crystals /m; m_k is the mass of a crystal aggregate composed of k primary crystals /kg; m is the total mass of the salt deposited from solution /kg; Q_k is the mass fraction of crystals or crystal aggregates comprising k primary crystals, in the precipitate (%); Q is the total mole fraction of all crystals and crystal aggregates containing one to k primary crystals (%). Note that here, by the primary crystals are meant the salt crystals present in solution immediately after the end on the induction crystallization period, before the beginning of the aggregation process.

According to the results of several studies,[109–111] the average number of crystals in crystal aggregates did not exceed 20. Hence, for the growth of primary crystals within aggregates, their effect on the growth of one another (for instance, due to overlap of their surfaces) was minor so that even in the first (rough) approximation, the growth of primary crystals within aggregates could be described as if they had grown in the solution bulk. In this case, the mass of a primary crystal at the end of crystallization should be equal to m/N_0 and the mass of an aggregate of k primary crystals is, correspondingly,

$$m_k = \frac{km}{N_0}$$

Taking into account the changes in the salt concentration in solution during crystallization, formulas (10) and (11) take the following form: [110, 111]

$$d_k = \left[\frac{6(C_{\text{in}} - C)vk}{\pi N_0 \rho}\right]^{1/3} \tag{13}$$

$$Q_k = \frac{100\, k[K_a N_0(\tau_{\text{cr}} - \tau_0)]^{k-1}}{[1 + K_a N_0(\tau_{\text{cr}} - \tau_0)]^{k+1}} \tag{14}$$

where τ_{cr} is the duration of the crystallization process /s.

Figure 6 shows the results of calculations [110, 111] according to Eqns (12)–(14). As can be seen, good agreement between experimental points and calculated curves was observed. However, certain differences were present. Indeed, the deviation between experimental and theoretical data in the region of small d can apparently be explained by the disintegration of crystals and the secondary nucleation. The deviations in the region of high d values (see Fig. 6 *b*) are apparently due to the simplifying assumptions made in calculating the size of crystal aggregates. For instance, if the number of primary crystals in coarse aggregates exceeds 20, then their growth cannot be considered as if it took place in the solution bulk. Hence, it is necessary to take into account

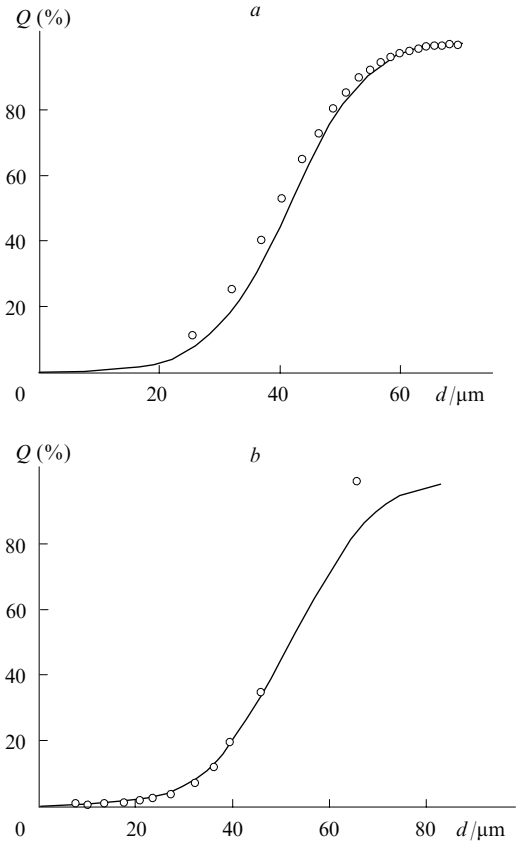


Figure 6. Size distribution of KCl (*a*) and NaCl (*b*) crystals after the completion of crystallization.[110]
Points correspond to experiment; curves correspond to calculations by expressions (12)–(14).

the overlap of surfaces of primary crystals (for a part of primary crystals within this aggregate, the growth ceases in a certain moment because their surface is completely blocked by other primary crystals). In the above simplified calculations of the size of crystal aggregates, this fact was ignored so that the size of such aggregates was overestimated (see Fig. 6 *b*).

The above calculations [110, 111] operated with K_a values found by treatment of the kinetic data on crystal aggregation according to formula (7). Although the approximation of non-linear dependences (Figs 4 and 5) by straight lines is rather rough, this is seen (see Fig. 6) to provide adequate agreement with experiment. Naturally, the agreement would be better if a functional dependence of K_a on the crystallization conditions, *i.e.*, on the current solution supersaturation, was found. So far, one has to assume that K_a is constant throughout the whole crystallization period and to find the K_a value from experimental data.[109–111]

From the presented brief (far from being complete) survey of crystallization models proposed by different scientists, it is evident that all these models are of the formal and descriptive nature rather than predictive. When one or another theoretical model was compared with experimental data, the inverse problem was always solved, *i.e.*, the model parameters for which the model best matched the experimental results were determined. Most often, the equations describing the growth, nucleation, aggregation and agglom-

eration of crystals were introduced *a priori* or on the basis of very scarce data. Thus, in the majority of cases, the nucleation rate was described by Eqn (4) with C_m being replaced by C_0 and the crystal growth rate was described by Eqn (8). Without any experimental substantiation, it was assumed that the rate of crystal intergrowth (agglomeration rate) is described by a formula analogous to dependences (4) and (8). Moreover, due to the large number of unknown parameters, their fitting to particular experimental conditions was inevitable, which made these models local, *i.e.*, capable of describing the crystallization process only under the particular experimental conditions. It can also happen (as noted in Ref. 123) that two analyses of experimental data on the crystallization of one and the same salt carried out by different scientists in the framework of different models lead to opposite conclusions. For instance, in a study of the crystallization of aluminium hydroxide,[124] a strong dependence of the agglomeration rate on the size of colliding crystals was obtained, whereas analogous study [95] gaves the opposite result: the agglomeration rate was shown to be independent of the crystal size.

In our opinion, of much greater interest are the models of crystallization based on experimentally substantiated data on its mechanism into which the equation and parameters obtained from other independent sources (experimental or reference data) can be substituted. Such models are of predictive nature and, hence, they can describe more correctly the crystallization process and its mechanism. However, this requires experimental investigations of crystallization stages. It should be noted that although a large body of experimental data has been accumulated and the general form of possible dependences is tentatively clear (they were already used in the aforementioned models), the experimental information on the kinetics of nucleation and aggregation and on the mechanism of crystal intergrowth in aggregates is still scarce and there is a lot of theoretical discrepancies.

V. Mechanisms of aggregation and intergrowth of crystals during crystallization

Unfortunately, there is still no general opinion on how the crystal aggregation and subsequent intergrowth proceed during crystallization and what factors determine the kinetics of these processes. This complicates the development of the theory of mass crystallization and makes it difficult to model the formation of the crystal size distribution upon crystallization of salts from solutions. It is evident that to understand how the crystal aggregation and agglomeration proceed during mass crystallization, the following two problems should be solved:

— the kinetics of aggregation must be elucidated;

— the mechanism of crystal intergrowth must be found.

Based on general considerations, it is clear that the process of crystal aggregation is similar to coagulation of colloids, because in both cases, the binary collisions of solid particles prevail in solutions (see above). With this in mind, it becomes clear that the kinetics of aggregation should be described by the Smoluchowski equation [48] for colloid coagulation the differential form of which is as follows:

$$-\frac{dN}{N^2} = K_a d\tau \qquad (15)$$

It should be admitted that the description of the kinetics of crystal aggregation by formula (15) is not quite accurate. Particularly, it ignores the possible destruction of aggregates formed. The same is true for the description of the kinetics of colloid coagulation by the Smoluchowski equation. However, this equation gives results that are in satisfactory agreement with experimental data, which points to a minor destruction of aggregates of colloid particles under the normal conditions of coagulation. Apparently, under similar conditions of crystallization from solutions with low solid-phase concentration and not very intense stirring, the crystal disintegration and the fragmentation of agglomerates would also be insignificant, the more so because, in contrast to aggregates of colloid particles, which are attached together by weak van der Waals (and like) forces, the crystals in the agglomerates formed during crystallization are bound together by an order of magnitude stronger chemical bonds. The fact that the crystal disintegration and the fragmentation of agglomerates can be neglected to a first approximation follows, in particular, from the results of studies [47, 109–111] in which it was demonstrated that the Smoluchovski equation can roughly describe the kinetics of crystal aggregation during spontaneous crystallization of various salts (see Figs 4 and 5) as well as the crystal size distribution of the final crystalline product (see Fig. 6). It should be added that today the applicability formula (15) for analysis of experimental data on crystal aggregation has been generally recognized.[125–130]

Naturally, it can be assumed that the rate coefficient for crystal aggregation K_a in Eqn (15) can be represented as a product of several multipliers that reflect the probability that crystals with the orientation suitable for their intergrowth collide in solution and the probability that, once collided, the crystals intergrow.[125–128, 131–134] The following expression was proposed for K_a:[112, 132, 134]

$$K_a = K_w P v^{-1} W W_1^* = K_w^* W \qquad (16)$$

where K_w is the hydrodynamic factor dependent on the hydrodynamic conditions of the crystallization and determining the probability of crystal collisions in solution /m^3 s^{-1}; P is the steric factor equal to the probability of crystal orientation suitable for their intergrowth upon collision; W is the probability that the crystals being in contact intergrow upon collision; W_1^* is the probability that the intergrowth bridge (crystallization bridge) formed between the crystals is not destroyed by subsequent collisions; $K_w^* = K_w P v^{-1} W_1^*$ is the proportionality coefficient /s^{-1}. The appearance of the factor v^{-1} in formula (16) is associated with the fact that in expression (15), the total number of crystals (colloid particles) in solution is used in place of their concentration (as in the Smoluchowski equation [48]).

During crystallization, the size of colliding crystals should increase due to their growth and intergrowth; hence, the hydrodynamic coefficient K_w (and, hence, K_a too) should change.[96–98] This was taken into account [135] in the mathematical model of colloid coagulation in stirred solutions by solving numerically the Smoluchowski equation (in its differential form) by the iteration method. The dependences of the total number of particles in solution on the time of coagulation were found. The results of calculations (see curve *1* in Fig. 2 in Ref. 135) were recalculated

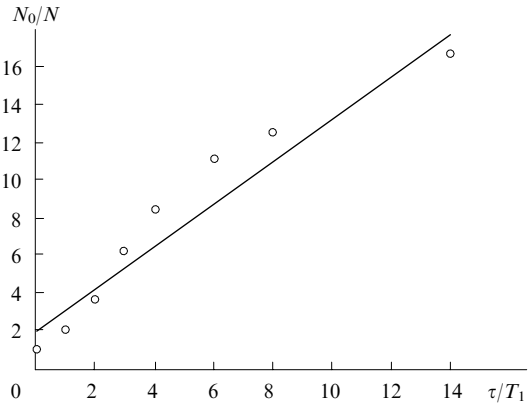


Figure 7. Results of calculations [135] in the coordinates of Eqn (7). Circles are the points of calculated curve *1* (Fig. 2 in Ref. 135); the line is the approximating straight line; T_1 is the coagulation time during which the total number of particles in solution N decreases to $N_0/2$ (recalculated in Ref. 132).

in terms of Eqn (7). Figure 7 shows the results of these calculations in the coordinates of Eqn (7).

It can be seen that the calculated data [135] are adequately approximated by a straight line (correlation factor 0.97). This means that in view of the common error of determination of the number of particles in solution (within 10%), treatment of experimental data according to Eqns (7) or (15) will not elucidate the real non-linear dependence (for coagulation in stirred solutions when coefficient K_a depends on the size of colliding particles) and all experimental points will be approximated by a straight line with reasonable accuracy.

Experimental results support this conclusion. Indeed, for coagulation of colloid particles of silicon [136] and titanium dioxide [117] in stirred solutions, it was found that in both cases, the coagulation kinetics is well described by Eqn (15). Moreover, several studies [95, 123, 125, 126, 130, 137] devoted to kinetics of crystal aggregation during crystallization have shown that the best description of this process in terms of Eqn (15) is achieved if K_a is assumed to be independent of the particle size. Thus, for the use of Eqns (15) and (16) to treat the data on crystal aggregation during spontaneous crystallization (or for modelling of this process), the coefficient K_w can be assumed to be constant and independent of the crystal size during crystallization.

The question of the mechanism of crystal intergrowth is crucial when the aggregation and agglomeration of salt crystals during mass crystallization are studied. In 1980, the first attempt to analyze this mechanism was undertaken.[138] It was assumed that in the first stage, the crystals approach one another due to van der Waals forces and then they stay attached for a certain time. Due to their growth, the nearest faces of crystals come closer and intergrow. The expression for the time needed for crystals to intergrow has been derived. The aggregation process was considered as a flow of crystals from the solution bulk to the agglomerate surface. It was assumed that the turbulence in the crystallizer is uniform and isotropic and the radius of agglomerates is small compared with the inner scale of turbulence. From equations derived in terms of this model, it followed that the increase in solution supersaturation and the decrease in the size of intergrowing crystals shorten the time needed for crystal intergrowth, because the stronger the solution supersaturation, the easiier the formation of agglomerates, and agglomeration of small crystals proceeds more readily as compared with large crystals.

It is evident that the model is in qualitative agreement with experimental data. An analogous model was described $\sim$10 years later.[139] It was assumed that the probability of agglomeration is proportional to the product of two probabilities: the probability of collision of two crystals in solution and the probability of their subsequent intergrowth as a result of formation of a crystallization bridge between them. It was assumed that the probability of crystal intergrowth in solution is directly proportional to the product of concentrations of different classes of colliding crystals [described, in fact, by Eqn (15)], while the crystal intergrowth (the formation of the crystallization bridge between the crystals) proceeds according to the scheme shown in Fig. 8. This scheme virtually coincides with that proposed earlier.[138] However, for some reason this scheme ignores the fact that after approaching one another, the crystals continue to grow; it also assumes that the narrow gap at the site of contact of two crystals is preferentially overgrown to produce the connecting crystallization bridge.

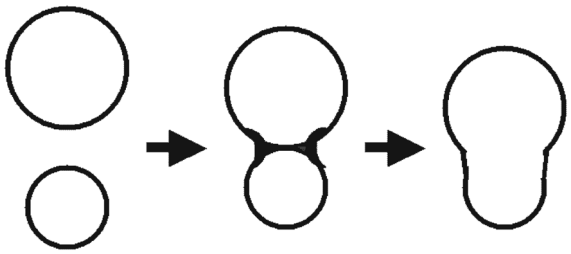


Figure 8. Illustration of the crystal intergrowth during crystallization.[139]

It is more reasonable to consider the process of crystal intergrowth in a different manner, namely, according to the scheme presented in Fig. 9. This scheme demonstrates how the crystal intergrowth should proceed if it really proceeds through the growth of crystal faces. According to this version of intergrowth, it is assumed that once collided, the crystals continue to grow, no preferential overgrowth of the neck between them occurs and, apparently, no crystallization bridge is formed.

In these models, [138, 139] it was postulated that crystals intergrow as a result of the growth of their faces. However,

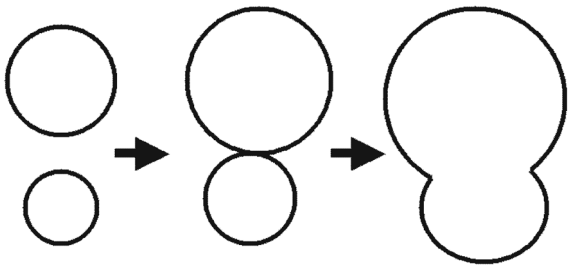


Figure 9. Illustration of the crystal intergrowth without the formation of a crystallization bridge between the crystals.

for this to be true, the crystals should be in contact with one another for a long time sufficient for the gap between them to be filled. According to estimates,[139] this time is from 0.5 to 5000 s, which (as also admitted by the authors) considerably exceeds the true value which, according to some data,[140] amounts to $\sim$0.05 s.

A similar point of view was expressed by Melikhov,[61] who assumed that intergrowth is favoured by the presence of steps and other protrusions on the surface of crystals. Upon sliding in stirred solutions, the crystals may get interlocked by these protrusions and stay in this state for a time sufficient for intergrowth. Naturally, the crystals with atomically smooth faces intergrow with more difficulty. The numerical simulation of the intergrowth for two crystals positioned near one another within a solution has shown that due to deposition of the crystallized substance on the crystal faces, a gradient of concentration of the crystallizing salt appears in the narrow gap between the crystals. The concentration reaches its maximum at the entrance of the gap, and, consequently, protrusions appear in this area, which stick together giving rise to the crystallization bridge.[141]

Hounslow and co-workers [125–128, 130, 131, 142] held the same viewpoint. The agglomeration models considered in their publications represented a somewhat modified version of the models discussed above.[138, 139] In both cases, it was assumed that when two crystals collide in a solution they stay for a certain time near one another (due to adhesion forces) and this time is enough for the formation of a crystallization bridge in the site of contact between the crystals.[125] While studying the isothermal crystallization of calcium oxalate monohydrate, Bramley [142] assumed that the rate of crystallization bridge formation is controlled by the diffusion in the narrow gap between the intergrowing crystals; moreover, in contrast to ideas of Melikhov,[61, 141] the crystal intergrowth was assumed to occur deep in the gap where the crystals contact each other. It is believed that the crystallizing substance is not deposited on the crystal faces inside the gap (the authors did not explain why), so that the growth takes place only in the contact region. Comparison of this model with experimental data on calcium oxalate monohydrate crystallization has shown that the rate of formation of the crystallization bridge is determined by the diffusion rate of the crystallizing salt along the gap between the crystals and the rate coefficient for aggregation correlates best of all with the supersaturation inside the gap as compared with supersaturation in the solution bulk. Furthermore, the process of intergrowth during crystallization from a solution with the non-stoichiometric composition is determined by the concentration of the deficient ion.[142]

Having performed mathematical simulation of crystal intergrowth based on the Bramley model,[142] Hounslow and co-workers [125] arrived at the conclusion that the solution concentration in the gap between crystals should decrease with the approach to the site of crystal intergrowth, which agrees with calculations by Melikhov and co-workers.[141] However, they failed to observe the formation of protrusions at the gap entrance (as opposed to the results of calculations [141]). The reason for this deviation probably lies in the fact that Hounslow and co-workers [125] considered a wide conical gap, whereas Melikhov and co-workers [141] assumed a long narrow gap. Moreover, in contrast to Melikhov and co-workers,[141] Hounslow and co-workers [125] discussed the growth of not only the narrow neck between crystals but also of the crystal faces inside the gap.

Analysis of the innfluence of hydrodynamic conditions on the crystallization in terms of the Hounslow model [125] has shown that increasing the intensity of stirring lowers down the probability of crystal intergrowth. This is in qualitative agreement with the experimental data and with the conclusions drawn in terms of the other models of this process (see above). Furthermore, Hounslow and co-workers [125] theoretically analyzed the effect of mutual orientation of crystals during their intergrowth. It was assumed that the rate of filling of the gap between crystals is directly proportional to the volume concentration of solution, the growth rate of the crystallization bridge surface is proportional to the squared time and the agglomerate remains stable unless it breaks under the action of hydrodynamic forces during crystallization. The possibility of destruction of agglomerates on collisions with one another, crystallizer walls and the stirrer was not discussed. Based on the results of calculations, a diagram of the most stable mutual arrangement of crystals in the agglomerate was plotted.

In a subsequent study,[130] an attempt was undertaken to refine the model of crystal intergrowth. It was postulated that the intergrowth rate is directly proportional to the crystal growth rate which for the calcium oxalate monohydrate is proportional to the squared solution supersaturation. Thus, in the new model, the intergrowth rate was proportional to the squared solution supersaturation rather than to the volume concentration of the salt in the solution. In this case, the solution supersaturation is expressed as the product of concentrations of calcium and oxalate ions and the solubility product of this salt (this is the reason for the appearance of the square of supersaturation while the diffusion control over the growth of crystal faces in the gap between them is retained). Comparing the results found in terms of this model with experimental data demonstrated their satisfactory agreement.

Several years later, Hounslow *et al.*[128] published a paper in which they acknowledged that their earlier calculations of the mass transfer in the gap between intergrowing crystals were incorrect and put forward another model of the intergrowth process. In this model, it was assumed that the crystal aggregation during mass crystallization proceeds according to the Smoluchowski theory of crystal coagulation [48] and that the coefficient of aggregation rate is independent of the size of colliding crystals. While analyzing their own experimental data, the authors [128] concluded that under the crystallization conditions considered (a relatively low speed of solution stirring and a small crystal size), they can neglect the destruction of crystals and agglomerates during crystallization. Furthermore, based on the results of the analysis of microimages of calcite agglomerates, they inferred that the growth rate of crystal faces in the gap between two crystals brought together did not virtually differ from the growth rate of crystals themselves, *i.e.*, no diffusion-induced deceleration of the gap overgrowth occurred. To compare the new model with experimental data, the authors used the experimental results from their earlier publications. The latter were satisfactorily described within the framework of the new model of the process.

Note that almost in all cases, the proposed models were in adequate agreement with experimental data obtained by the same authors. Apparently, this was due to the fact that sufficiently complicated equations with a lot of unknown

factors were used for describing the crystallization process. In comparing the results of calculations with experimental data, the authors adjusted a lot of coefficients by using various versions of the least squares method. Hence, it is not surprising that both their early and later models of the crystal aggregation and intergrowth satisfactorily agreed with experimental data. The same is true for models of other scientists.

In our opinion, the general drawback of the listed models of crystal agglomeration during mass crystallization is that they fundamentally fail to explain how the crystal intergrowth proceeds and are not completely well-posed. For instance, as the crystals approach one another, a thin solution layer always remains between them; this is why during the growth of closely spaced crystal faces, the wedge pressure should arise between them preventing the contact between faces and subsequent intergrowth. It should be recalled that here, we consider not fixed immobile crystals capable of 'squeezing' the solution out of the gap but the crystals that move in solution being suspended in it. Even if crystals come into contact as a result of growth of their faces, this does not mean their intergrowth. On the contact of crystal faces, van der Waals forces arise between them, whereas it is the chemical bonds that are needed for crystal intergrowth. Furthermore, the intergrowth due to converging growth of crystal faces requires that the crystals stay near one another (within an aggregate) for a sufficiently long time. However, according to published data,[140] the time of the contact between the crystals upon their collision in a stirred solution is ~ 0.05 s. It is clear that so short time is insufficient for intergrowth (this especially concerns the crystals of poorly soluble salts with low growth rates of crystal faces).

Meanwhile, another mechanism of crystal intergrowth was proposed by Polak [143] as early as in the 1960s. According to this mechanism, it was assumed that crystals intergrow as a result of the appearance of intergrowth contacts between them in the form of nucleus-bridges. The latter form the chemical bond between the faces of closely spaced crystals (Fig. 10). The formation of these nucleus-bridges was shown to be energy beneficial. The work of formation of a nucleus-bridge (A) is determined by the following equation:[143–145]

$$A = 4h^2\sigma^2\left(h\rho\frac{RT}{M}\ln\frac{C}{C_0} + 2\sigma\right)^{-1} \tag{17}$$

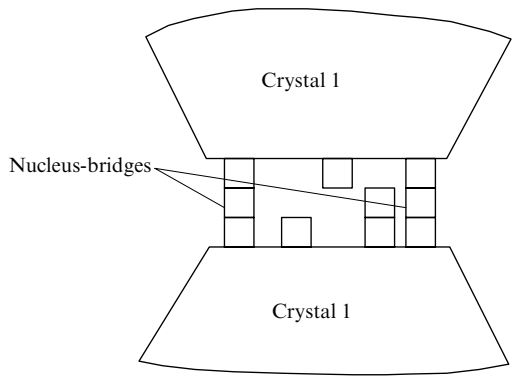


Figure 10. Scheme of intergrowth of two crystals.[144]

where h is the height of the nucleus-bridge that connects intergrowing crystals /m; σ is the specific surface energy (interfacial tension) at the solution/crystal interface /J m^{-2}; M is the salt molar mass /kg mol^{-1}; R is the universal gas constant /J (K mol)$^{-1}$; T is the absolute temperature /K.

This mechanism of intergrowth was later confirmed experimentally in a study of the elementary steps of intergrowth of gypsum crystals under static conditions when the crystals were brought into contact (pressed onto one another by using various forces), fixed in this position and then immersed into a saturated or supersaturated calcium sulfate solution.[144, 145] After the gypsum crystals were kept in this state for a certain period, they were withdrawn from solution and the cohesive force between them was measured by means of a specially developed setup.[146] It was shown that the crystal intergrowth is possible only in supersaturated solutions, whereas in saturated solutions only coagulation contacts can be formed between the crystals (adhesion of crystals due to van der Waals forces). An equation describing the probability of intergrowth of crystals (W) as a function of their contact time and solution supersaturation was derived [144, 145] and can be represented as follows:[132]

$$W = 1 - \exp\left[-D_3\exp\left(-\frac{D_1}{\ln(C/C_0) + D_2}\right)\right] \tag{18}$$

$$D_1 = \frac{4h\sigma^2 N_A M}{\rho(RT)^2} \tag{19}$$

$$D_2 = \frac{2\sigma M}{h\rho RT} \tag{20}$$

$$D_3 = I_0\tau_c \tag{21}$$

where D_1, D_2, D_3, I_0 are constants; τ_c is the contact time of crystals upon collision /s.

The validity of found relationships was confirmed in a study of the intergrowth of crystals and particles of various compounds and salts, including dissimilar crystals.[147–150] It is interesting that $\sim$20 years later, an analogous study with measurement of the cohesive force arising upon crystal intergrowth was carried out at an up-to-date level;[151] however, its results were interpreted in a different manner.[151, 152]

The fact that the Polak theory [143] had been confirmed experimentally [144–150] and the expression describing the probability of crystal intergrowth in supersaturated solutions had been derived, as demonstrated above, was ignored by other scientists who described the formation of the crystal size distribution during crystallization of salts. Apparently, these scientists believed that no conditions like those used in the mentioned studies [144–150] (particularly, the fact that crystals were pressed to one another) can be realized during mass crystallization and, hence, the Polak theory [143] can be only applied to the intergrowth of immobile crystals under static conditions. Furthermore, the possibility of formation of nucleus-bridges between crystals was questioned.

Nonetheless, it was [132] assumed that during mass crystallization, the crystals indeed intergrow according to the Polak mechanism. Since during mass crystallization, the crystals are in permanent motion, colliding with one another, with the stirrer and with crystallizer walls, it was assumed that the pressing condition may be fulfilled also at the instant of collision of crystals in solution. Since the

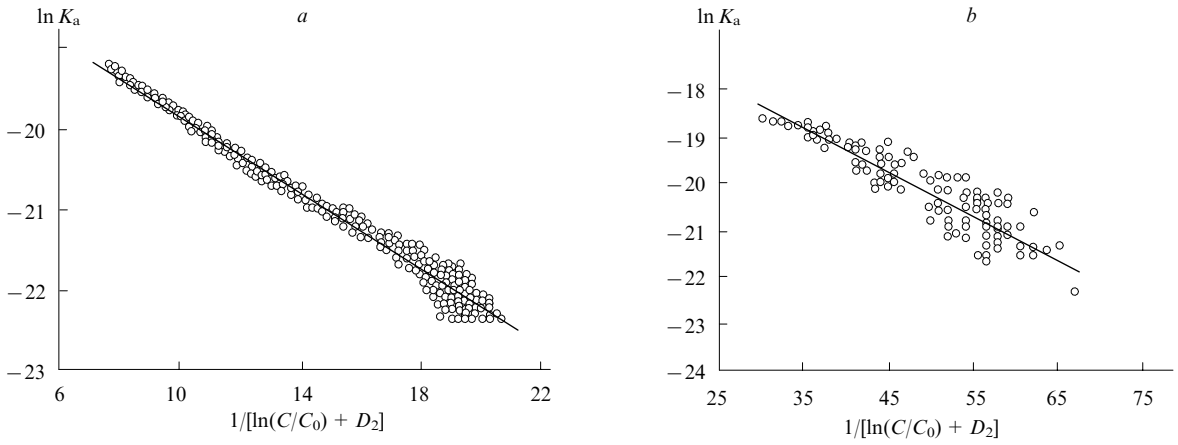


Figure 11. Rate coefficient for aggregation of potassium nitrate crystals *vs.* the degree of solution supersaturation in the coordinates of Eqn (24).[112] Experiment: (*a*) 1; (*b*) 3.

frequency of these collisions is sufficiently high, some of them should be accompanied by the formation of connecting nucleus-bridges between the crystals.

The following equation derived by combining formulas (16) and (18) was proposed[132] for the rate constant for crystal aggregation:

$$K_a = K_w^* W = K_w^* \left\{ 1 - \exp\left[-D_3 \exp\left(\frac{-D_1}{\ln(C/C_0) + D_2} \right) \right] \right\} \quad (22)$$

Equation (22) can be simplified by expanding the exponent into a series and restricting the consideration to the first two terms of this series

$$K_a = K_w^* \left\{ 1 - \exp\left[-D_3 \exp\left(\frac{-D_1}{\ln(C/C_0) + D_2} \right) \right] \right\} \approx \quad (23)$$

$$\approx K_w^* D_3 \exp\left(-\frac{D_1}{\ln(C/C_0) + D_2} \right)$$

After taking logarithm of both sides of Eqn (23), the following formula convenient for further calculations was obtained:

$$\ln K_a = \ln(K_w^* D_3) - \frac{D_1}{\ln(C/C_0) + D_2} \quad (24)$$

For salt crystallization under isothermal conditions, D_1, $D_2 \approx$ const. If the stirring velocity of the solution remains unchanged during crystallization, then we can assume that $\tau_c \approx$ const; hence, D_3 also becomes a constant (more accurately, it varies within a relatively narrow range). If the crystals intergrow exactly by forming nucleus-bridges during crystallization, then the computer treatment of the kinetic data on crystal aggregation (K_a and C) will allow one to select the values of parameters D_1, D_2 and $K_w^* D_3$ that would satisfy relationship (24). These calculations were carried out.[112, 132, 133] Analysis was performed experimental data (including those published before) on the kinetics of crystal aggregation during the spontaneous crystallization from supersaturated aqueous and water–ethanol solutions of the salts with different physicochemical properties: $NaNO_3$, $CaSO_4 \cdot 2H_2O$, KNO_3, NaCl, KCl, $NaNO_2$, K_2SO_4, $Ba(NO_3)_2$. As a result, in each case, the constants D_1, D_2 and $K_w^* D_3$ were selected in such a way that relationship (24) in the $\ln K_a - 1/[\ln(C/C_0) + D_2]$ coordinates was linear. Figures 11 and 12 demonstrate some of these results.

Linnikov[134] analyzed the earlier[126, 130] experimental data on the aggregation of calcium oxalate monohydrate crystals (Fig. 13). It can be seen that these experimental data[126, 130] are also in good agreement with the Polak theory. However, it should be admitted that this agreement could be due to the fact that the unknown parameters in Eqn (24) were well fitted to the particular conditions of the considered experiments. To check this, the specific surface energies of all salts under study were calculated[112, 132–134] using formulas (19) and (20) and the determined values of parameters D_1 and D_2. Note that this calculation is very important because its results can be compared with the specific surface energies found for these and other salts by different authors. A comparison of the results of calcula-

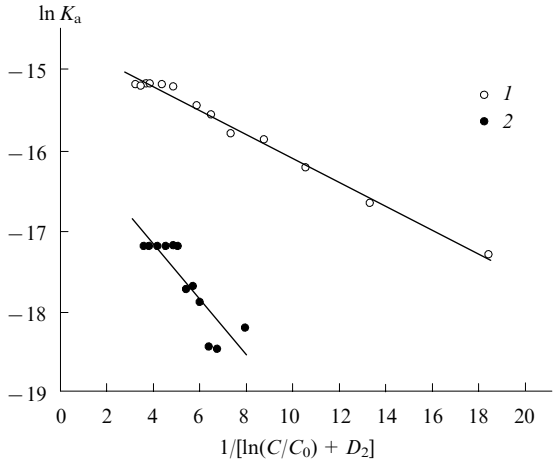


Figure 12. Rate coefficient for aggregation of KNO_3 (*1*) and $Ba(NO_3)_2$ (*2*) crystals *vs.* the degree of solution supersaturation in the coordinates of Eqn (24).[134]
D_2: (*1*) 0.044, (*2*) 0.109

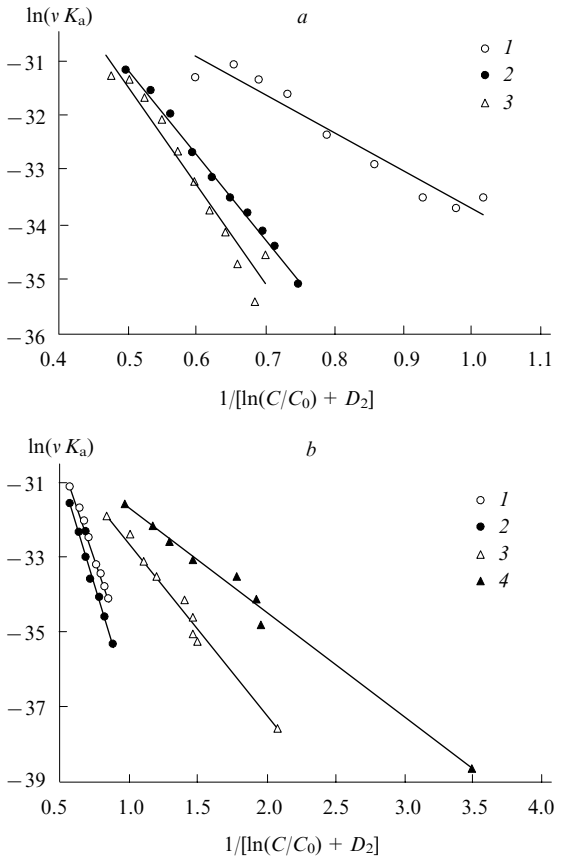


Figure 13. Rate coefficient for aggregation of calcium oxalate monohydrate crystals *vs*. the degree of solution supersaturation in the coordinates of Eqn (24), according to results of Refs 126 (*a*) and 130 (*b*).
Concentration ratio of calcium and oxalate ions: *a*: (*1*) 2; (*2*) 3.33; (*3*) 2.5; *b*: (*1*) 1; (*2*) 0.2; (*3*) 10; (*4*) 5.

tions with the published data could demonstrate whether or not the found parameters D_1 and D_2 were accidental.

The σ values calculated using Eqns (19) and (20) for the salts studied [112, 132 – 134] proved to be reasonable; moreover, they were in satisfactory agreement with experimental data available in the literature for the same salts but found by other scientists, which suggests that the determined values of D_1 and D_2 are not accidental. In addition, the heights of contact nucleus-bridges connecting the intergrowing crystals were calculated. They also were reasonable. Table 1 summarizes the results of these calculations. Note that the accuracy of values found for the specific surface energy and the nucleus-bridge height is not high. However, taking into account that constants D_1, D_2 and $K_w^* D_3$ were assessed by means of non-linear version of the least-squares method and also data of indirect measurements, one can hardly expect better results.

Thus, not only the coincidence of experimental and theoretical dependences but also the calculations of the specific surface energy for salts under study confirm that the Polak mechanism of crystal intergrowth may be realized for crystal intergrowth both under static conditions and under the conditions of mass crystallization in solutions.

It is also interesting to assess the energy benefit of the nucleus-bridge formation over other types of nucleation. Such assessment was carried out.[112] According to the classical theory, among the 'traditional' types of nucleation, the lowest energy barrier is typical of nucleation of crystals on their own substrate. The work of the formation of a two-dimensional nucleus shaped as disk on its own substrate (A_s, J) is described by the equation [153]

$$A_s = \frac{\pi M \sigma^2 a}{\rho RT \ln(C/C_0)} \qquad (25)$$

where a is the lattice parameter /m.

Table 1. Specific surface energy and nucleus-bridge heights for several salts calculated using expressions (19) and (20) and the values of parameters D_1 and D_2 found for the processes of crystal aggregation and intergrowth.[112, 132 – 134]

Salt	C_a (%)	σ /mJ m^{-2}	S_σ /mJ m^{-2}	$h \times 10^9$ /m	S_h /m	n*
KCl	0 – 25.76	0.98	0.703	4.1	0.214	223
NaCl	14.85 – 29.72	0.97	0.402	3.4	0.127	76
KNO_3	0	2.19	2.11	2.46	0.67	4202
	12.8	2.03	–	1.83	–	15
	57.73	0.96	–	2.34	–	11
$NaNO_3$	29.72	1.54	–	1.49	–	7
$CaSO_4 \cdot 2H_2O$	17.83	12.59	–	0.94	–	13
	17.83	10.78	–	1.08	–	7
$NaNO_2$	29.72	0.30	–	4.23	–	5
	32.20	0.44	–	4.40	–	14
K_2SO_4	5.15	1.66	–	2.02	–	17
	10.31	2.80	–	2.31	–	18
$Ba(NO_3)_2$	14.85	3.88	–	1.58	–	17
	5.94	2.58	–	1.57	–	17
$CaC_2O_4 \cdot H_2O$ (see [a])	0	24.3	–	1.09	–	10
	0	26.9	–	1.08	–	11
	0	16.3	–	1.07	–	9
$CaC_2O_4 \cdot H_2O$ (see [b])	0	21.0	–	1.15	–	7
	0	20.1	–	1.15	–	8
	0	8.7	–	1.56	–	7
	0	12.3		1.31		8

Note. C_a is the ethanol volume fraction in the solution; S_σ is the sample standard deviation for σ; S_h is the sample standard deviation for h; n* is the number of points in the calculation. [a, b] The data of Refs 126 and 130, respectively.

Taking into account expression (17), the ratio between the work of nucleus formation on its own substrate and the work of nucleus-bridge formation in the gap between the crystals (A) was found [112]

$$\frac{A_s}{A} = \frac{\pi a}{2h}\left[\frac{1}{2} + \frac{\sigma}{h\rho RT\ln(C/C_0)}\right] \quad (26)$$

It follows from Eqn (26) that the ratio A_s/A increases with a decrease in the solution supersaturation. For example, for $CaSO_4 \cdot 2H_2O$, it was found [134] (see Table 1) that $h \approx 10^{-9}$ m. Hence, for $\sigma = 17 \times 10^{-3}$ J m^{-2}, $\rho = 2330$ kg m^{-3}, $a = 4.75 \times 10^{-10}$ m, $T = 298$ K and $C/C_0 = 3.05$, we obtain that $A_s/A \approx 2.34$.

Thus, the process of formation of the nucleus-bridge in the narrow gap between the intergrowing crystals can even occur in the absence of nucleation on its ownc substrate [112] and it is the nucleation process that requires the least energy.

VI. Forms of crystal intergrowth within agglomerates

In terms of the crystal intergrowth mechanism proposed by Polak,[143] for this process under conditions of mass crystallization, it is assumed that upon collision of crystals in solution, a nucleus-bridge can form between them. Since nucleation is a fluctuation (random) process, the intergrowth itself may be virtually instantaneous (or proceed in a very short period). If the agglomerate formed is not broken in its further collisions with other crystals, the stirrer and crystallizer walls, then after the completion of the process, some irregularly shaped crystals should be found in the crystalline product. Probably, their number is small because the hydrodynamic conditions of crystallization favour the morphological selection of crystal agglomerates and the dominant formation of regular crystal aggregates with low hydrodynamic resistance up to preudo-single crystals (see above). However, the observation of irregular shapes among the aggregates would serve as additional evidence that the Polak mechanism of intergrowth is realized also under conditions of mass crystallization from solutions. Moreover, in our opinion, the discovery of such agglomerates will prove the mentioned mechanism because no other theory can explain their formation (particularly, this concerns agglomerates of large crystals that cannot be held together by van der Waals forces).

This assumption was checked in the following experiments:[112, 154] the potassium nitrate precipitate formed after spontaneous crystallization was thoroughly examined by optical and electron microscopy. Figure 14 shows some of the results. The images were recorded after minor etching of the crystal surface by ultrasonic treatment in 94% ethanol. This procedure made it possible to break pseudo-agglomerates formed through van der Waals forces. While examining the microimages, note the mutual arrangement of crystals in the agglomerates. Thus, the microimage in Fig. 14 *a* shows an agglomerate of two large crystals. Obviously, such an unusual bunch could be formed only for crystals intergrown almost instantaneously on their collision or mutual approach in a stirred solution. Figures 14 *b*–*d* show the microimages of the similar crystal agglomerates.

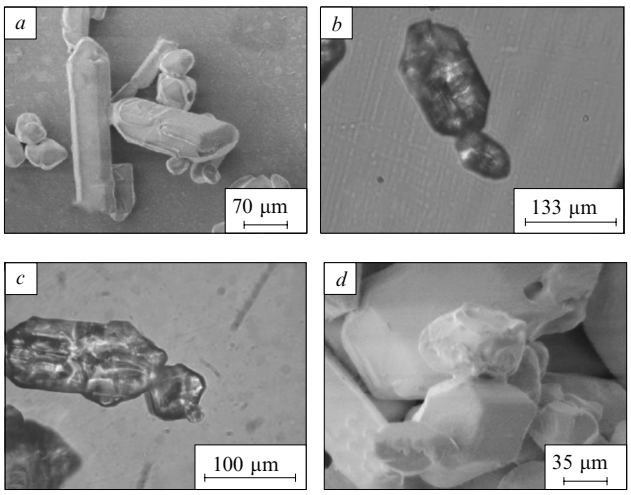


Figure 14. Microimages of irregularly shaped agglomerates of potassium nitrate crystals observed in the precipitate after the completion of crystallization.[154]
For *a*–*d*, see the text.

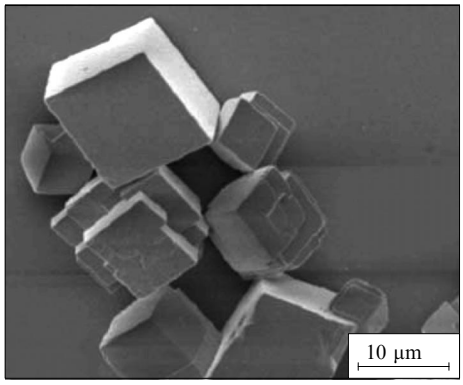


Figure 15. Microimage of an agglomerate of calcium carbonate crystals.[58]

In order to dispel the doubts that the observation of irregular agglomerates was accidental, we analyzed [112, 154] the results of other scientists. The analysis of their data has shown that microimages of irregular crystal agglomerates can be found in many studies. Thus, the images of irregular agglomerates of KNO_3 and $K_4[Fe(CN)_6] \cdot 3H_2O$ crystals,[50] irregular agglomerates of fairly large KCl crystals [51, 52] and odd-shaped agglomerates of KCl crystals [155] were reported.

Indeed, the crystallization of various salts with different physicochemical properties is accompanied by the formation of crystal agglomerates of irregular shape. Such agglomerates are formed from both small and large crystals (Figs 14–17). This is neither accidental nor caused by special conditions of crystallization used in one or another case, being a general phenomenon typical of crystallization of all salts. As was noted above, the formation of such agglomerates can be explained by only instantaneous intergrowth of crystals in solution, which agrees with the Polak theory and contradicts other concepts on the mechanism of crystal intergrowth.

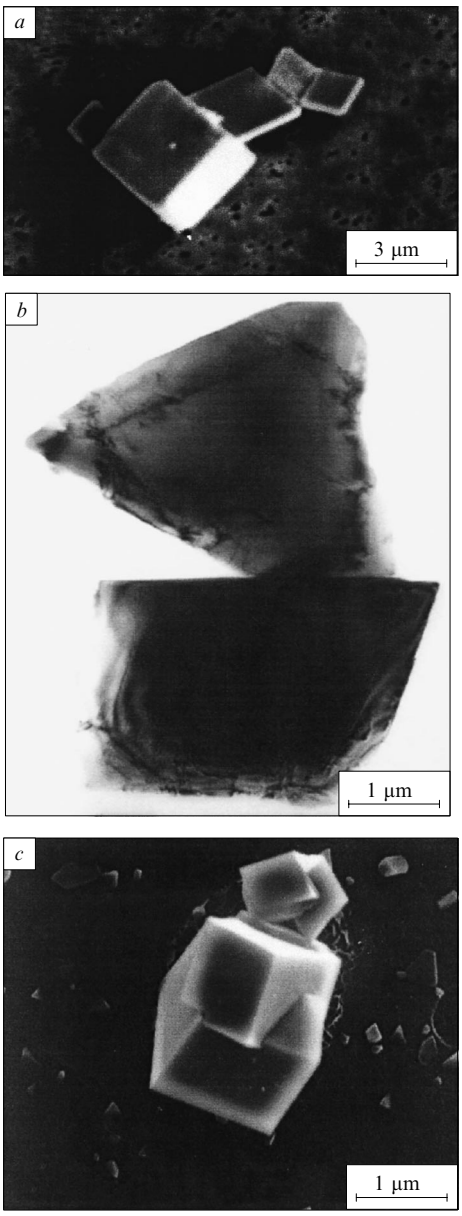


Figure 16. Microimages of agglomerates of calcite (*a*, *b*) and KNO_3 (*c*) crystals.[77]

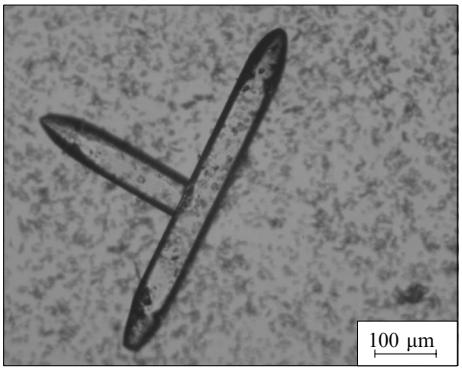


Figure 17. Microimage of an agglomerate of SnC_2O_4 crystals which was observed by V N Krasil'nikov (Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences) during the chemical precipitation of this compound by oxalic acid on boiling in a gently stirred solution.

VII. Mechanism of formation of the crystal size distribution in the crystalline precipitate after completion of crystal nucleation in solution

If the crystal intergrowth during mass crystallization is taken to proceed according to the Polak theory [143] (through the random formation of nucleus-bridges between crystals) and the kinetics of aggregation is described by the Smoluchowski equation [48] of colloid coagulation theory (as evidenced by the above experimental data by various authors), it is possible to construct a new model of crystal precipitation. This attempt was made in a series of studies [112, 156, 157] (the first version of this model was published in Ref. 156; its final version appeared in Ref. 112). In essence, the proposed model is an application of the Smoluchowski theory of colloid coagulation to the spontaneous crystallization from solutions.

The model relies on the following assumptions found experimentally in studies of the isothermal spontaneous crystallization of various salts:[112]

— crystal nucleation at the end of the induction period of crystallization is negligible;

— at the end of the induction period of crystallization, N_0 salt microcrystals are present in solution;

— after the induction period has been completed, the total number of salt microcrystals in solution N decreases due to aggregation;

— the crystal intergrowth during crystallization proceeds *via* the formation of nucleus-bridges between crystals, according to the Polak theory;[143]

— the kinetics of crystal aggregation during crystallization is described by the well-known Smoluchowski equation for coagulation of colloid particles [see Eqn (15)] and the rate constant for the process (the rate constant for crystal aggregation) decreases due to decrease in the solution supersaturation, being described by formula (23).

According to this model, it is assumed that the crystal size distribution during crystallization from aqueous salt solutions is formed as a result of two simultaneous processes:

— growth of crystals in the supersaturated solution;

— aggregation and intergrowth of crystals during crystallization.

The nucleation and its effect on the formation of the crystalline precipitate are beyond the scope of this model. If we assume that the spontaneous crystallization process can be conditionally divided into two successive stages: the nucleation of salt crystals in solution and their further growth and also the aggregation and intergrowth of already formed crystals, then this model considers precisely the second stage of this process when the nucleation has virtually ceased and a certain initial number of microcrystals have been formed (N_0). The growth and aggregation of the latter crystals lead to the formation of the final crystalline product.

Mathematically, the model is described by the system of differential equations which can be solved numerically by the Runge – Kutta method [112]

$$-\frac{dC}{d\tau} = 3.3\,\Psi^{-1}(\pi\rho)^{1/3}n^{1/3}k_g(C_{in}-C)^{2/3}(C-C_0)^z \qquad (27)$$

$$\frac{dn}{d\tau} = -n^2 v\,K_a = -n^2 v\,K_w^*\,D_3\exp\left[-\frac{D_1}{\ln(C/C_0)+D_2}\right] \qquad (28)$$

$$\frac{dn_1}{d\tau} = -2\nu K_a n_1 n \quad (29)$$

$$\frac{dn_2}{d\tau} = 2\nu K_a (0.5 n_1^2 - n_2 n) \quad (30)$$

$$\frac{dn_3}{d\tau} = 2\nu K_a (n_1 n_2 - n_3 n) \quad (31)$$

.....

$$\frac{dn_k}{d\tau} = \nu K_a (n_1 n_{k-1} + n_2 n_{k-2} + n_3 n_{k-3} + \ldots + n_{k-1} n_1) - -2\nu K_a n_k n \quad (32)$$

where Ψ is the coefficient of sphericity of salt crystals that takes into account their deviation from spheres;[158, 159] n is the total concentration of crystal agglomerates in solution /m^{-3}; n_1 is the concentration of primary crystals in solution (the crystals present in solution immediately after the end of the induction period before the beginning of the aggregation process) /m^{-3} ; n_2, n_3, ... n_k are the concentrations of crystals (more exactly, crystal agglomerates) comprising 2, 3, ... k primary crystals, respectively /m^{-3}. Note that immediately after the end of the induction period of crystallization and prior to beginning of the aggregation process, $n_1 = n$.

In the system of equations (27)–(32), the first two equations describe variations in the salt concentration and the total concentration of crystals and crystal agglomerates in solution after the completion of the induction period (or immediately after the beginning of crystal aggregation in solution). The other equations of this system can be used to find the concentrations of crystals (crystal agglomerates) that comprise two, three, four, ... k primary crystals in the course of crystallization. Expression (27) represents the modified equation (2) (after the corresponding substitutions), while Eqns (28)–(32) are the transformed equations of the Smoluchowski theory of colloid coagulation.

The diameters of the resulting crystals (crystal agglomerates) and their mass fraction in the precipitate can be found in the first approximation by using the following formulas:[112, 156, 157]

$$d = d_k = \left[\frac{6k^{2/3}(C_{in} - C)}{\pi\rho \sum_k n_k k^{2/3}}\right]^{1/3} \quad (33)$$

$$Q_k = \frac{100 n_k k^{2/3}}{\sum_k n_k k^{2/3}} \quad (34)$$

$$Q = \sum_k Q_k \quad (35)$$

where d_k is the diameter of a crystal (crystal agglomerate) consisting of k primary crystals /m; Q_k is the mass fraction of such crystals in solution (%); Q is the total mass fraction of all crystals and agglomerates that comprise 1 to k primary crystals in solution (%).

It should be noted that Eqns (33) and (34) represent modified formulas (10) and (11) and differ from the latter as follows: formulas (10) and (11) disregard the mutual overlap of the surfaces of crystals growing within the agglomerate. The agglomerate growth surface represents the sum of surfaces of all constituent crystals; this results in overestimation of the agglomerate mass during crystallization, especially, at the final stage of this process when the number of crystals constituting the agglomerate exceeds 20–40. Equations (33) and (34) represent an attempt to take into account the inner overlap of crystals within the agglomerate. In this case, the agglomerate is considered as a monolithic particle and its growth surface is equal to the surface of a sphere with the same mass. The corresponding calculations have shown that is this case, the overestimation of the agglomerate mass at the end of crystallization is smaller [156, 157] and, correspondingly, the agreement between experimental and theoretical data is better. However, it should be admitted that this method of calculations is also approximate.

Figures 18 and 19 show the typical results of calculations [112, 156, 157] based on Eqns (27)–(35). As can be seen, the experimental data are in rather good agreement with the theoretical curves. Particularly, this concerns the data on

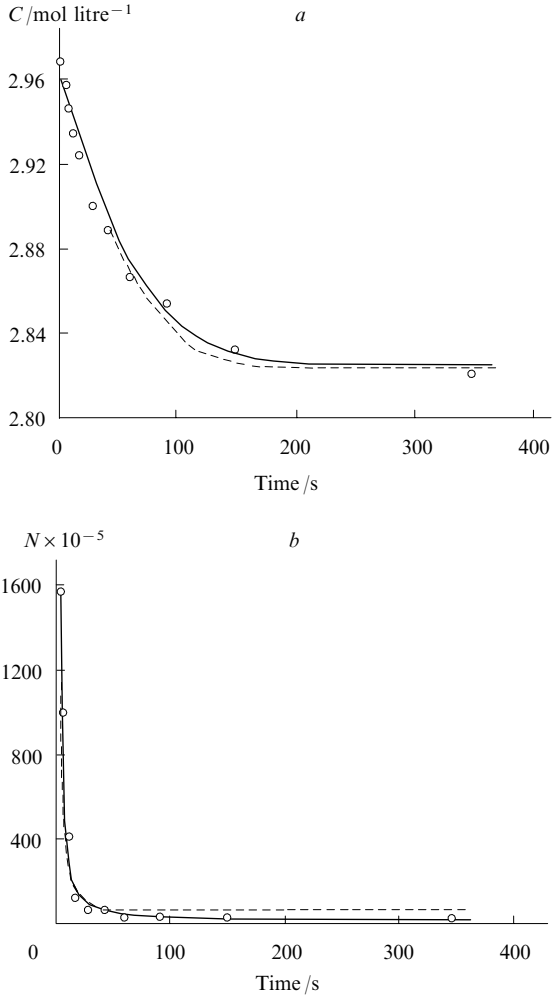


Figure 18. Changes in the salt concentration (*a*) and in the total number of KCl crystals (*b*) in the solution found in an experiment on KCl crystallization from a water–ethanol solution.[156]
Points correspond to the experiment; continuous curves correspond to calculations for $D_1 = 0.69 \times 10^{-2}$, $D_2 = 0.70 \times 10^{-3}$ and $K_w^* D_3 = 0.52 \times 10^{-8}$; the dashed line corresponds to calculations for average values of D_1, D_2 and $K_w^* D_3$; C is the the salt concentration in solution.

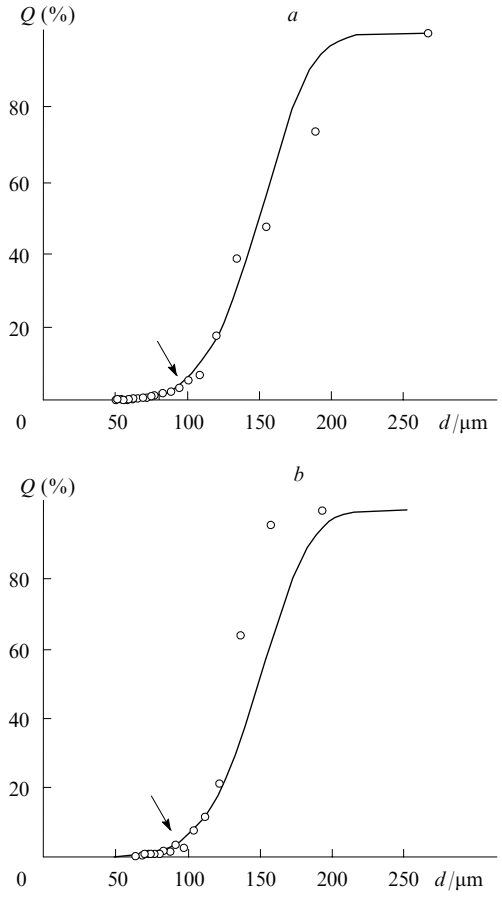


Figure 19. Size distribution of KNO_3 crystals during crystallization from its supersaturated aqueous solution.[112]
(*a*) Experiment 1; (*b*) experiment 4; circles correspond to experimental points; curves are calculations for $D_1 = 0.2358$, $D_2 = 0.0483$, $K_w^* D_3 = 2.5$ (experiment 1) and $D_1 = 0.0455$, $D_2 = 0.0101$, $K_w^* D_3 = 11.608$ (experiment 4).

the decrease in the solution supersaturation (see Fig. 18 *a*) and also on the kinetics of variation of the total number of crystals during crystallization (Fig. 18 *b*). The agreement between the theoretical and experimental data is somewhat poorer as regards estimation of the expected crystal size distribution after the completion of crystallization. Thus, in Fig. 19, the arrows point to the beginning of the theoretical curves describing the crystal size distribution of the crystalline product. Apparently, in the region of small crystal diameters, a certain deviation between the theory and experiment is observed (see Figs 6 and 19), being associated with the approximate nature of calculations based on formulas (33) and (34) and also with the fact that the model proposed does not take into account the processes of secondary nucleation of crystals and their disintegration upon collisions with one another, the stirrer and crystallizer walls. Meanwhile, the good agreement of experimental points with the calculated curves describing the changes in the salt concentration and the total number of crystals during crystallization in solution (see Fig. 18) suggests that the proposed model[112, 156, 157] satisfactorily describes the crystallization process after the end of the induction period and the onset of crystal aggregation.

Note that the theoretical calculations[112, 156, 157] were carried out for both the parameters k_g, D_1, D_2 and $K_w^* D_3$ found experimentally in each particular experiment and their average values calculated based on the corresponding equations. Thus, in the latter case, the value of k_g was calculated by equations found experimentally,[110 – 112] the parameter $K_w^* D_3$ was calculated as the arithmetic mean for all experiments with this salt, and the constants D_1 and D_2 were calculated from Eqns (19) and (20) based on the values of surface energy and nucleus-bridge height found for the given salt (see Table 1).

Thus, the experimental data on crystallization of three salts studied[112, 156, 157] (potassium and sodium chlorides and potassium nitrate) confirmed the proposed crystallization model. A distinctive feature of this model is the fact that almost all parameters involved can be determined in independent experiments or taken from the literature. These parameters include, *e.g.*, the coefficient of crystal growth rate (k_g), the coefficient of sphericity of salt crystals (Ψ), the salt solubility at a given temperature, and the specific surface energy of the salt. Special experiments are required for determination of only three quantities, namely, the nucleus-bridge height (h), the total concentration of salt crystals in solution before the onset of the aggregation process (n) and the product $K_w^* D_3$. Moreover, some of these parameters can be calculated theoretically or estimated based on experimental data for crystallization of other salts. For instance, it follows from the information in Table 1 that for the majority of salts, the nucleus-bridge height is within 1 – 4 nm.

Furthermore, it deserves mention that the earlier testing of the proposed crystallization models solved the inverse problem, namely, the experimental crystal size distribution was compared with the balance equations of the proposed model and the model parameters such that the model best fitted the experimental data were determined by calculations. Since the initial balance equations of the model represented rather sophisticated mathematical expressions with many unknown values, this increased the probability of finding the optimal parameters such that the theoretical and experimental dependences coincided. However, the problem of taking account for the overlap of crystal surfaces within the agglomerate and some other problems have not been solved in any way. That is, in the majority of cases, the mathematical model relied on not fully substantiated theoretical and experimental data. The coincidence of results found in terms of such model with experimental data does not mean at all that the model correctly describes the process modelled. For example, in some published studies, the well-known Erofeev – Avrami – Kolmogorov equation was used for describing the processes to which it is, in principle, inapplicable (multistage chemical reactions, nonisothermal crystallization, *etc.*). Nonetheless, the parameters of this equation that provide coincidence of theoretical and experimental dependences are found. However, when testing the model considered[112, 156, 157] the direct problem was solved, *i.e.*, the parameters preliminarily found by analyzing experimental data on crystallization of salts under study were substituted into this model. After this, calculations were carried out and their results were compared with experimental curves. The satisfactory agreement between the theoretical and experimental dependences confirmed the proposed physical model of this process. Among other things, this serves as an additional proof for the fact

that during the mass crystallization, the crystal intergrowth also proceeds by the mechanism proposed by Polak through the formation of nucleus-bridges between crystals.

The discussed model is incomplete, because it does not reflect the processes of primary and secondary nucleation of crystals and also their possible fragmentation on collisions with one another, the stirrer and crystallizer walls. However, judging from the good agreement between calculated and theoretical curves on the decrease in the solution supersaturation and the change in the total number of crystals during crystallization, the effect of the mentioned processes on the overall kinetics of crystallization is insignificant and can be neglected in the majority of cases. This was pointed out earlier by Hounslow *et al.*[128]

VIII. Conclusion

The analysis of publications devoted to study and modelling of the mass crystallization from solutions provides the concluion that there is no generally accepted model as yet, although the mechanics of this process on the whole is clear.

One of the central problems in describing the formation of the crystalline product during crystallization is to elucidate the mechanism of crystal intergrowth. At present, there are two approaches to this process. According to the first approach, it is assumed that crystals intergrow as a result of simple growth of their faces in a surpersaturated solution; the second approach is based on the Polak theory on the crystal intergrowth as a result of formation of a contact nucleus-bridge between them. It was assumed for a long time that the second mechanism is not realized during mass crystallization from solutions where the crystals are in permanent motion. However, recent studies have demonstrated that this mechanism can be perfectly realized under conditions of mass crystallization. In our opinion, the experimental data unambiguously support this mechanism of intergrowth.

In the description of isothermal spontaneous crystallization, two periods can be distinguished:

— nucleation of crystals in solution during the induction period of crystallization;

— subsequent growth, aggregation and intergrowth of crystals. In several crystallization models, these two periods were combined by a common system of equations. As was demonstrated by analyzing the published experimental data, this is inexpedient as yet. The point is that the mechanism of crystal nucleation in supersaturated salt solutions is still not fully understood (for instance, there is no general opinion on the origin of the crystallization induction period); hence, to describe the nucleation in terms of various crystallization models, different equations are used which, with the proper selection of parameters, give the results satisfactorily consistent with the experimental data. However, as noted above, this does not prove that these equations correspond to the real process. The second stage of crystallization in which a certain number of crystals present in solution after the end of the induction period start to grow further and form aggregates can be described sufficiently accurately within the framework of, *e.g.*, the crystallization model discussed above. We believe that taking this model as the basis, the further studies of mass crystallization from solutions should be focused on investigation and more precise elucidation of the following issues:

— the mechanism of crystal nucleation during isothermal spontaneous crystallization from solutions should be elucidated and the relationships for predicting the concentration of salt crystals formed in solution by the end of the induction period should be derived for different conditions of this process;

— dependences should be derived for theoretical calculation (or at least estimation) of the constant K_w^* under various hydrodynamic conditions of crystallization, as well as for the parameters D_3, P, and W_1^*;

— a more accurate mathematical expression should be found for mass fractions of various agglomerates in the crystalline product during and at the end of the crystallization process, with allowance made for the overlap of crystal surfaces during their growth within the agglomerate.

Solving these problems will make it possible to 'match' the two crystallization stages (nucleation and growth of crystals and agglomeration) and find a plausible model of this process, capable of predicting the operating parameters. Certainly, the range of problems to be solved is not limited to those mentioned above. Thus, more detailed studies and generalizations of experimental data on the mechanism of crystal disintegration during mass crystallization, the secondary nucleation, *etc.* are required. However, the problems included in the above list are of the top priority.

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References

1. O M Todes *Probl. Kinet. Katal.* (7) 91 (1949)
2. S Z Roginskii, O M Todes *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk* 331 (1940)
3. N V Deryabina, K P Mishchenko *Probl. Kinet. Katal.* (7) 122 (1949)
4. R Gindt, R Kern *C.R. Acad. Sci.* **256** 4400 (1963)
5. R Gindt, R Kern *C.R. Acad. Sci.* **258** 5011 (1964)
6. R Gindt, R Kern *Ber. Bunsen-Ges. Phys. Chem.* **69** 124 (1965)
7. V M Kharin *Kolloid. Zh.* **36** 313 (1974) [a]
8. V M Kharin *Zh. Fiz. Khim.* **48** 1724 (1974) [b]
9. V M Kharin *Kolloid. Zh.* **49** 31 (1975) [a]
10. O D Linnikov *Zh. Prikl. Khim.* **68** 186 (1995) [c]
11. O D Linnikov *Zh. Prikl. Khim.* **68** 1166 (1995) [c]
12. O D Linnikov *Desalination* **122** 1 (1999)
13. H Neels *Freiberger Forschungshefte, A* **123** 405 (1958)
14. Yu A Serebryakov, Candidate Thesis in Chemical Sciences, IKhTREMS, Apatity, 1979
15. L B Berliner *Zh. Fiz. Khim.* **48** 592 (1974) [b]
16. J W Gibbs *Collected Works. Thermodynamics* Vol. I (New Haven: Yale University Press, 1948)
17. M Volmer *Kinetic der Phasenbildung* (Leipzig: Steinkopff, 1939)
18. I N Stranskii, R Kaishev *Usp. Fiz. Nauk* **21** 408 (1939)
19. R Becker, W Doring *Ann. Phys. Folg.* **24** 719 (1935)
20. Ya I Frenkel' *Kineticheskaya Teoriya Zhidkostei* (Kinetic Theory of Liquids) (Leningrad: Nauka, 1975)
21. J P Hirth, G M Pound *Condensation and Evaporation* (London: Pergamon Press, 1963)
22. M P Anisimov *Russ. Chem. Rev.* **72** 591 (2003)
23. S Jen-Lei, R Shinnar, S Katz *AIChE J.* **17** 1459 (1971)
24. J Nyvlt, J W Mullin *Chem. Eng. Sci.* **25** 131 (1970)
25. I V Melikhov, L B Berliner *Teor. Osnovy Khim. Tekhnol.* **13** 530 (1979) [d]
26. L B Berliner, I V Melikhov *Teor. Osnovy Khim. Tekhnol.* **19** 24 (1985) [d]

27. V M Fisher *Issledovaniya nad Peresyshchennymi Rastvorami Solei* (Investigations over Supersaturated Salt Solutions) (Riga, 1913)
28. A G Jones, J W Mullin *Trans. Inst. Chem. Eng.* **51** 302 (1973)
29. J Nyvlt, R Rychly, J Gottfried, J Wurzelova *Trans. Inst. Chem. Eng.* **6** 151 (1970)
30. N S Tavare, M R Chivate *Trans. Inst. Chem. Eng.* **57** 35 (1979)
31. M Nakajima, K F Kui, S Hirota, in *World Congress III of Chemical Engineering, Tokyo, 1986* Vol. 2, p. 1016
32. K Toyokura, S Takeuchi, H Sakai, in *World Congress III of Chemical Engineering, Tokyo, 1986* Vol. 2, p. 1020
33. N Teodossiev *Cryst. Res. Technol.* **21** 1167 (1986)
34. V M Berlinkov, B N Driker, S M Prostakov *Zh. Fiz. Khim.* **56** 442 (1982) [b]
35. V M Berlinkov, B N Driker *Zh. Fiz. Khim.* **57** 918 (1983) [b]
36. V M Berlinkov, B N Driker, I A Belyaeva *Zh. Fiz. Khim.* **57** 1277 (1983) [b]
37. M I Sibirev, A I Moshinskii, V D Lunev, Yu V Sharikov, V S Varlamova *Zh. Prikl. Khim.* **56** 794 (1983) [c]
38. A I Moshinskii *Zh. Prikl. Khim.* **60** 1066 (1987) [c]
39. A I Moshinskii *Kolloid. Zh.* **55** 120 (1993) [a]
40. O M Todes, V A Seballo, A D Gol'tsiker *Massovaya Kristallizatsiya iz Rastvorov* (Mass Crystallization from Solutions) (Leningrad: Khimiya, 1984)
41. A D Randolph, M A Larson *AIChE J.* **8** 639 (1962)
42. A D Randolph *Can. J. Chem. Eng.* **42** 280 (1964)
43. A D Randolph, E T White *Chem. Eng. Sci.* **32** 1067 (1977)
44. N S Tavare, J Garside *Chem. Eng. Res. Des.* **64** 109 (1986)
45. A D Randolph, M A Larson *Theory of Particulate Process* (New York: Academic Press, 1988)
46. A Bernardo, M Giulietti *Chem. Eng. Res. Des.* **88** 1356 (2010)
47. E Pozdner *Zh. Fiz. Khim.* **13** 889 (1939) [b]
48. M Smoluchowski *Z. Phys. Chem.* **92** 129 (1917)
49. M L Chepelevetskii *Zh. Fiz. Khim.* **13** 561 (1939) [b]
50. L N Matusevich, K N Shabalin *Zh. Prikl. Khim.* **25** 1157 (1952) [c]
51. S Sarig, A Glasner, J A Epstein, N Eidelman *J. Cryst. Growth* **39** 255 (1977)
52. S Sarig, C L Leci, N Eidelman *J. Cryst. Growth* **47** 365 (1979)
53. N S Tavare, M B Snah, J Garside *Powder Techonol.* **42** 13 (1985)
54. R M Morris *Analyst* **90** 657 (1965)
55. K J Scott *Ind. Eng. Chem. Fundam.* **7** 484 (1968)
56. J Hambersin *Ind. Chim. Belg.* **34** 7 (1969)
57. A Maruscak, C G J Baker, M A Bergougnou *Can. J. Chem. Eng.* **49** 821 (1971)
58. F-W Yan, S-F Zhang, C-Y Guo, X-H Zhang, G-C Chen, F Yan, G-Q Yuan *Cryst. Res. Technol.* **44** 725 (2009)
59. I V Melikhov, A S Kelebeev *Kristallografiya* **24** 410 (1979) [e]
60. A S Kelebeev, I V Melikhov, in *Protsessy v Dispersnykh Sredakh. Mezhvuzovskii Sbornik Nauchnykh Trudov* (Processes in Dispersion Media. Intercollegiate Collection of Scientific Works) (Ivanovo: Ivanovo Institute of Chemistry and Technology , 1986) p. 77
61. I V Melikhov *Fiziko-Khimicheskaya Evolyutsiya Tverdogo Veshchestva* (Physochemical Evolution of Solids) (Moscow: BINOM Laboratoriya Znanii, 2009)
62. I V Melikhov, A S Kelebeev, S Bačič *J. Colloid Interface Sci.* **112** 54 (1986)
63. I V Melikhov, I V Mikheeva, V N Rudin *Teor. Osnovy Khim. Tekhnol.* **19** 742 (1985) [d]
64. I V Melikhov, V E Bozhevolnov *J. Nanopart. Res.* **5** 465 (2003)
65. M El Moussaouiti, R Boistelle, A Bouhaouss, J P Klein *J. Cryst. Growth* **169** 118 (1996)
66. M El Moussaouiti, R Boistelle, A Bouhaouss, J P Klein *Chem. Eng. J.* **68** 123 (1997)
67. F Grases, L Masarova, O Sohnel, A Costabauza *Br. J. Urol.* **70** 240 (1992)
68. A Millan, F Grases, O Sohnel, I Krivankova *Cryst. Res. Technol.* **27** 31 (1992)
69. N S Kozhevnikova (Belova), Author's Thesis in Chemical Sciences, Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, 2004
70. I V Melikhov, B D Dolgonosov *Dokl. Akad. Nauk SSSR* **299** 1175 (1988) [f]
71. I V Melikhov, B D Dolgonosov *Kolloid. Zh.* **51** 911 (1989) [a]
72. I V Melikhov, O V Kuleshova, B M Dolgonosov, M P Moroz *Kolloid. Zh.* **53** 378 (1991) [a]
73. B D Dolgonosov, I V Melikhov *Kolloid. Zh.* **53** 232 (1991) [a]
74. B D Dolgonosov, I V Melikhov *Kolloid. Zh.* **53** 240 (1991) [a]
75. I V Melikhov, S S Berdonosov, I A Kopylova *Kolloid. Zh.* **55** 114 (1993) [a]
76. A V Severin, V F Komarov, V E Bozhevol'nov, I V Melikhov *Zh. Neorg. Khim.* **50** 76 (2005) [g]
77. A P Collier, C J D Hetherington, M J Hounslow *J. Cryst. Growth* **208** 513 (2000)
78. H Cölfen, M Antonietti *Angew. Chem., Int. Ed.* **44** 5576 (2005)
79. V M Yuwono, N D Burrows, J A Soltis, R L Penn *J. Am. Chem. Soc.* **132** 2163 (2010)
80. T X Wang, J Mitchell, H Börner, H Cölfen, M Antonietti *Phys. Chem. Chem. Phys.* **12** 11984 (2010)
81. J H Zhu, S H Yu, A W Xu H Cllfen *Chem. Commun.* **45** 1106 (2009)
82. D Wang, J Li, X Cao, G S Pang, S H Feng *Chem. Commun.* **46** 7718 (2010)
83. R O Da Silva, R H Goncalves, D G Stroppa, A J Ramirez, E R Leite *Nanoscale* **3** 1910 (2010)
84. J F Ye, W Liu, J G Cai, S Chen, X W Zhao, H H Zhou, L M Qi *J. Am. Chem. Soc.* **133** 933 (2011)
85. Z Liu, X D Wen, X L Wu, Y J Gao, H T Chen, J Zhu, P K Chu *J. Am. Chem. Soc.* **131** 9405 (2009)
86. X L Wu, S J Xiong, Z Liu, J Chen, T H Li, P H Wu, P K Chu *Nat. Nanotechnol.* **6** 103 (2011)
87. J Romann, J C Valmalette, V Chevallier, A Merlen *J. Phys. Chem. C* **114** 10677 (2010)
88. C Lausser, H Cölfen, M Antonietti *ACS Nano* **5** 107 (2011)
89. M Guan , G Zhu, T Shang, Z Xu, J Sunm, Q Zhou *Cryst. Eng. Commun.* **14** 6540 (2012)
90. M Niederberger, H Cölfen *Phys. Chem. Chem. Phys.* **8** 3271 (2006)
91. Y Liu, G Zhu, B Ge, H Zhou, A Yuan, X Shen *Cryst. Eng. Commun.* **14** 6264 (2012)
92. I V Melikhov, I E Mikheeva, V N Rudin *Kolloid. Zh.* **50** 885 (1988) [a]
93. I V Melikhov, O V Kuleshova, D G Berdonosova, E V Burlakova *Kolloid. Zh.* **53** 375 (1991) [a]
94. A Halfon, S Kaliaguine *Can. J. Chem. Eng.* **54** 160 (1976)
95. A Halfon, S Kaliaguine *Can. J. Chem. Eng.* **54** 168 (1976)
96. C-J Chin, S Yiacoumi, C Tsourist *J. Colloid Interface Sci.* **206** 532 (1998)
97. F E Kruis, K A Kusters *Chem. Eng. Commun.* **158** 201 (1997)
98. J C Macy, M Cournil *Chem. Eng. Sci.* **46** 693 (1991)
99. L N Matusevich *Kristallizatsiya iz Rastvorov v Khimicheskoi Promyshlennosti* (Crystalization from Solutions in Chemical Industry) (Moscow: Khimiya ,1968)
100. B M Dolgonosov *Kolloid. Zh.* **53** 244 (1991) [a]
101. I V Melikhov, V L Zelenko, Yu N Orlov, V M Podkopov *Kolloid. Zh.* **55** 120 (1993) [a]
102. A G Jones *Crystallization Process Systems* (Oxford: Butterworth-Htinemann, 2002)
103. J-M Kim, S-M Chang, K-S Kim, M-K Chung, W-S Kim *Colloid. Surf., A* **375** 193 (2011)
104. P Sessiecq, F Gruy, M Cournil *J. Cryst. Growth* **208** 555 (2000)
105. S M Prostakov, Author's Thesis in Chemical Sciences, Sverdlovsk, Ural Polytechnic Institute, 1981

106. I V Melikhov, E K Kirkova, M D Djarova *J. Cryst. Growth* **53** 547 (1981)
107. J M Herri, F Gruy, J S Pic, M Cournil, B Cingotti, A Sinquin *Chem. Eng. Sci.* **54** 1849 (1999)
108. E J Ilukkanen, R D Braatz *Sens. Actuators B* **96** 451 (2003)
109. O D Linnikov *Zh. Prikl. Khim.* **74** 1078 (2001) [c]
110. O D Linnikov *Cryst. Res. Technol.* **39** 516 (2004)
111. O D Linnikov *Cryst. Res. Technol.* **41** 10 (2006)
112. O D Linnikov, I V Rodina, I G Grigorov, E V Polyakov *Cryst. Struct. Theor. Appl.* **2** 16 (2013)
113. P A Kouzov *Osnovy Analiza Dispersnogo Sostava Promyshlennykh Pylei i Izmel'chennykh Materialov* (Foundations of Analysis of Dispersion Structure of Industrial Dusts and Ground Materials) (Leningrad; Khimiya, 1987)
114. S M Prostakov, B N Driker, S I Rempel' *Zh. Prikl. Khim.* **55** 2576 (1982) [c]
115. C C Baker, M A Bergougnou *Can. J. Chem. Eng.* **52** 246 (1974)
116. W I Higuchi, R Okada, G Stelter, A P Lamberger *J. Pharm. Sci.* **42** 49 (1963)
117. E F Wahl, C G J Baker *Can. J. Chem. Eng.* **49** 742 (1971)
118. I V Melikhov, M S Merkulova *Sokristallizatsiya* (Cocrystallisation) (Moscow: Khimiya, 1975)
119. C Marsha, E T White *Chem. Eng. Prog. Symp. Ser.* **67** 6 (1971)
120. C Marsha, E T White *J. Cryst. Growth* **8** 172 (1971)
121. O D Linnikov, I V Rodina, V M Kovzel', V M Ronkin *Tsvet. Metall.* 92 (2011) [h]
122. A I Moshinskii *Teor. Osnovy Khim. Tekhnol.* **21** 115 (1987) [d]
123. D Ilievski, E T White *Chem. Eng. Sci.* **49** 3227 (1994)
124. G C Low. Ph.D. Thesis, University of Queensland, Australia, 1975
125. H S Mumtaz, M J Hounslow, N A Seaton, W R Paterson *Trans. Inst. Chem. Eng.* **75** 152 (1997)
126. A S Bramley, M J Hounslow, R L Ryall *Chem. Eng. Sci.* **52** 747 (1997)
127. H S Mumtaz, M J Hounslow *Chem. Eng. Sci.* **55** 5671 (2000)
128. M J Hounslow, H S Mumtaz, A P Collier, J P Barrick, A S Bramley *Chem. Eng. Sci.* **56** 2543 (2001)
129. D Ilievski *J. Cryst. Growth* **233** 846 (2001)
130. M J Hounslow, A S Bramley, W R Paterson *J. Colloid Interface Sci.* **203** 383 (1998)
131. A S Bramley, M J Hounslow, R L Ryall *J. Colloid Interface Sci.* **183** 155 (1996)
132. O D Linnikov *Cryst. Res. Technol.* **39** 529 (2004)
133. O D Linnikov *Cryst. Res. Technol.* **41** 138 (2006)
134. O D Linnikov *Cryst. Res. Technol.* **43** 1268 (2008)
135. G M Fai, R S Gemmel *J. Colloid Sci.* **19** 360 (1964)
136. H H Hahn, W Stumm *J. Colloid Interface Sci.* **28** 134 (1968)
137. P-C Chen, S M Liu, C J Jang, R C Hwang, Y L Yang, J S Lee, J S Jang *J. Cryst. Growth* **257** 333 (2003)
138. B K Tkhai, N S Torocheshnikov *Teor. Osnovy Khim. Tekhnol.* **14** 501 (1980) [d]
139. R David, Ph Marchal, J-P Klein, J Villermaux *Chem. Eng. Sci.* **46** 205 (1991)
140. D Levins, J R Glastonbury *Trans. Inst. Chem. Eng.* **50** 32 (1972)
141. I V Melikhov, A Ya Gorbachevskii, A G Churbanov *Matem. Modelirovanie* **12** 87 (2000)
142. A S Bramley Ph.D. Thesis, University of Adelaide, Australia, 1994
143. A F Polak *Tverdenie Monomineral'nykh Vyazhushchikh Veshchestv* (Hardening Monomineral Binding Materials) (Moscow: Izd. Lit. po Stroitel'stvu, 1966)
144. E D Shchukin, E A Amelina, R K Yusupov, V P Vaganov, P A Rebinder *Dokl. Akad. Nauk SSSR* **213** 155 (1973) [f]
145. V P Vaganov, E A Amelina, R K Yusupov, E D Shchukin, P A Rebinder *Kolloid. Zh.* **36** 436 (1974) [a]
146. E D Shchukin, R K Yusupov, E A Amelina P A Rebinder *Kolloid. Zh.* **31** 913 (1969) [a]
147. S I Kontorovich, Ya I Lankin, V V Amilinskii, E D Shchukin *Kolloid. Zh.* **42** 639 (1980) [a]
148. Ya I Lankin, S I Kontorovich, E A Amelina, E D Shchukin *Kolloid. Zh.* **42** 649 (1980) [a]
149. S I Kontorovich, Ya I Lankin, N I Sporysh, E A Amelina, E D Shchukin *Kolloid. Zh.* **43** 1076 (1981) [a]
150. V P Vaganov, E A Amelina, E D Shchukin *Kolloid. Zh.* **40** 329 (1978) [a]
151. F Pratola, S J R Simons, A G Jones *Chem. Eng. Res. Des.* **80** 441 (2002)
152. M Brunsteiner, A G Jones, F Pratola, S L Price, S J R Simons *Cryst. Growth Des.* **5** 3 (2005)
153. A A Chernov, E I Givargizov, Kh S Bagdasarov, V A Kuznetsov, L N Dem'yanets, A N Lobachev *Sovremennaya Kristallografiya* (Modern Crystallography) (Moscow: Nauka, 1980) Vol. 3
154. O D Linnikov, I G Grigorov, I V Rodina, E V Polyakov *Dokl. Akad. Nauk* **439** 355 (2011) [f]
155. K Schmok *Cryst. Res. Technol.* **23** 967 (1988)
156. O D Linnikov *Cryst. Res. Technol.* **41** 988 (2006)
157. O D Linnikov *Cryst. Res. Technol.* **42** 758 (2007)
158. A N Verigin, I A Shchuplyak, M F Mikhalev *Kristallizatsiya v Dispersnykh Sistemakh* (Crystallisation in Dispersion Systems) (Leningrad: Khimiya, 1986) p. 248
159. S F Kuz'kin, V P Nebera *Sinteticheskie Flokulyanty v Protsessakh Obezvozhivaniya* (Synthetic Flocculating Agents in Dehydration Processes) (Moscow: GOSGORTEKhIZDAT, 1963)

[a] — *Colloid. J. (Engl. Transl.)*
[b] — *Russ. J. Phys. Chem., Ser. A (Engl. Transl.)*
[c] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[d] — *Theor. Found. Chem. Eng. (Engl. Transl.)*
[e] — *Crystallogr. Rep. (Engl. Transl.)*
[f] — *Dokl. Chem. (Engl. Transl.)*
[g] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[h] — *Non-ferrous Metall. Trans. (Engl. Transl.)*