

Nucleation kinetics and technology design for crystal growth from aqueous solution

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Abstract The interrelation into nucleation and thermodynamic parameters of solutions has been established by plotting of various dependencies: the enthalpy of dissolution, solubility product and super-solubility on ionic salt radii and also the extent of deviation from an ideal Debye-Hückel model of electrolyte solution on solubility product. The possible methods of perfect crystal growth from aqueous solution have been found a priori by separating of known set of pair values of solubility and super-solubility into no less than six-nine characteristic and distinctive sub-sets.

Key words Inorganic salt, Solubility, Nucleation, Crystal growth

1. Introduction

The thermodynamic properties of salts and solutions determine essentially the rate of crystal nucleation and growth, and also a quality of the salt crystals. In practice first of all the salts solubility and the stability of supersaturated solutions are the main factors, from which depend the possibility of growth of large perfect crystal from solution [1]. The some properties of salts and solutions can be taken into account at theoretical analysis of the crystallization process: solubility, the heat of dissolution or enthalpy of crystallization - ΔH_c , interface tension - σ_{sc} , salt activity coefficient - γ , diffusion coefficient - D [2, 3]. But now the equation for salt nucleation kinetics in strong electrolytes will be too complicated for analytical examination [3]. Nevertheless, it is possible by the phenomenological analysis of empiric data on interrelation «solution property - peculiarities of crystallization process - crystal quality», or by computer simulation [4]. In this report the system analysis of these interrelations is carried out and the design of crystal growth technology from aqueous solutions is elaborated.

2. The solubility, dissolution enthalpy and super-solubility of salts

The salt solubility can be estimated more exactly by

use of the solubility products (SP) and there is a large spread of these values [5-6]. The theory of solubility is a classical part of physics and physical chemistry of solution, and one is present in many courses of university and polytechnic education [6]. This theory predicts a parabolic, extreme dependence of salt solubility on efficient cationic and anionic radii for the salts, which have the same ionic charges. This classical model is true only for certain electrolytes of simple 1-1 and 2-1 types and one does not conform to a full collection of all experimental data on solubility of electrolyte of other types [4, 7]. The more complete phenomenological analysis has been carried out recently for some group of salts: hydroxides of three-valent cations and 1-1 chloride salts [7]. It was demonstrated that the solubility products change periodically for these and others compounds due to increasing of cation dimensions.

The discrepancy of solubility theory and experimental data is determined by a disregard of phenomena of polymorphism at calculation of energy of crystal lattice (U_{cr}), which predetermined a possibility of periodic change of U_{cr} [5]. The solubility enthalpy (ΔH_s) is small part of lattice energy of crystalline compounds (U_{cr}) and one equal to the difference of large values of U_{cr} and sum of the hydration enthalpy of all ionic components (ΔH_{hi}) [5]. These values (ΔH_s , ΔH_{hi}) change also periodically due to the increasing of ionic radii of salts. In Fig. 1 is plotted the dependence $\Delta H_s = f(R_a)$. The data collect from [8].

The value of ΔH_s and solubility (x_s) determine the surface entropy factor α , which is a measure of the roughness or smoothness of the crystal-medium interface ($\alpha =$

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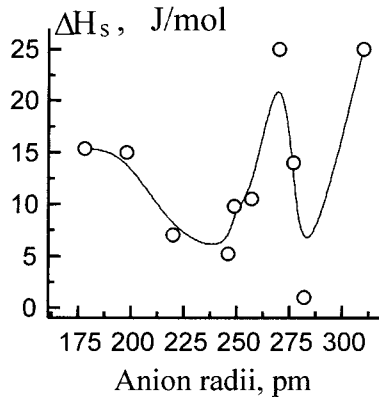


Fig. 1. The dependence of dissolution enthalpy on anion radii of ammonium salts.

$\xi\{(\Delta H_s(T, x)/kT_m) - \ln x_s(T)\}$ [9]. But the dynamic surface roughness α_d is determined also by the deviation extent from the equilibrium state, namely by the supersaturation (concentration of supersaturated solution x_{ss} , limit supersaturation x_{sc}) and by the supercooling of solution [10]. The real activity of salt in solution $a_i = \gamma_i x_i$ must be included in the equation of the nucleation kinetics ($\alpha = \xi\{(\Delta H_s(T, x)/kT_m) - \ln a_s(T)\}$). The low value of these quantities (ΔH_s , α , α_d) is related to the morphological instability of the interface, the impurity incorporations, mother-phase inclusion and the formation of the dislocations and stacking faults [9-10]. Besides, the temperature coefficient of solubility is also determined by ΔH_s and by solution non-ideality [11]. So the variation of interrelation between the thermodynamic properties of solution and their crystallization ability can be exist for various types of electrolyte solutions, which can be also determine by the dimension factors of salts and solvents.

Further it is necessary to analyze the interrelation between solubility and super-solubility and some known crystallization peculiarities of different salt types [4, 7]. The stability of supersaturated solution is estimated by its limit of supersaturation (C_s) or its maximum supercooling (ΔT_m), (width of metastability zone, super-solubility) [1-2, 9]. It is supposed that the dependencies of solubility and super-solubility on solution temperature are similar [12]. But the theoretical and experimental comparison of super-solubility-solubility relationship for various salts is not made up to now in detail [7]. The kinetics of salt nucleation was firstly discussed theoretically by Timan - Reshetnyak for electrolyte solution with the use of the simple equation for an activity coefficient [3]. It is shown that nucleation rate depend on the charges and radii of salt ions. However, this study is not completed

and such approach is possible only for dilute or some ideal electrolytes [4].

3. System analysis of the 1 : 1 salts activity in solution

It is clear that we must also discuss the real activity of the salt in solution. The comparison of thermodynamic characteristics of 1-1 electrolytes and types of salts crystallization is carried out particularly in [4, 7]. Solubility product of salt, having chemical formula $M^+A^- \cdot nH_2O$, is described by the next equation [5]:

$$\lg SP = \sum v_i \cdot \lg c_i \gamma_i + n \lg a_w \quad (1)$$

$$\lg \gamma_{\pm} = -A_d |z^+ z^-| \sqrt{I} / (1 + C\sqrt{I}) + |z^+ z^-| \lg [1 + B(1 + 0.1 I)^q - B] \quad (2)$$

where: A_d , B , C - constants, $B = 0.75 - 0.065q$, $C = 1 + 0.055q \exp(-0.023 \cdot I^3)$, z^+ and z^- - cationic and anionic charge, n_i stoichiometric coefficient of i -component, $a_i = c_i \gamma_i$; a_i , c_i , γ_i - activity, solution concentration and activity coefficient of i -component, a_w - water activity, I - ionic strength ($I = 0.5 \sum c_i z_i^2$), q - sole adjusted coefficient. The Meisner and Kusik equation (2) is true for all values of I , including strong concentrated electrolyte solutions [5]. If $q = 0$, or for weak (dilute) electrolytes ($I \geq 0$, $\gamma_i \leq 1$) we receive the simplest equation for an activity coefficient (the equation by Debye-Hückel):

$$\lg \gamma_{\pm} = -A_d |z^+ z^-| \sqrt{I} / (1 + \sqrt{I}) \quad (3)$$

Therefore the parameter « q » determines an extent of deviation of real electrolyte solution from the ideal Debye-Hückel electrostatic model of solution. The dependencies of q on SP are linear for various 1-1 salts having common ion Fig. 2. These lines form a bundle, a focus of which lies at single point ($q \geq 0$, $SP \geq 0$). Consequently, it is observed both positive and negative values of q -coefficient, and $q = 0$ only for the part of salts (~15-20 %). There are the ideal solutions near this point according to Debye-Hückel theory near this point. The slope of these lines and the lines of other salts increase in the next order: TlA, AgA, KA, CsA, NaA, RbA, LiA, NH_4A . In the same order it is increasing also the mean solubility (S) and solubility product of the 1-1 electrolytes [7].

If $q \neq 0$, than the simple Debye -Hückel equation for an activity coefficient (3) can not be use at analysis of nucleation and crystallization kinetics from many aqueous solutions, including KH_2PO_4 -electrolyte [4-5]. Besides

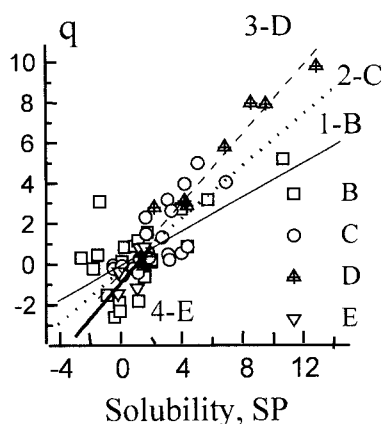


Fig. 2. The dependence of the nonideality extent q for solutions of 1-1 salts on solubility product SP . 1-K-, 2-Na-, 3-Li-, 4- NH_4 -salts.

The coefficient q depend on temperature [5], and this circumstance must be taken into account at analysis of non-isothermal crystallization processes. So, the subsequent development of the nucleation theory from solution is necessary by the use of more correct equation of an activity coefficient for strong supersaturated electrolytes. It is possible, for example, by the introduction into the equation of nucleation theory the most precise equation of Kusik and Meisner for an activity coefficient (equations-1, 2) [5]. But such equation for nucleation kinetics in strong electrolyte will be too complicated for analytical examination. Nevertheless, it is possible by phenomenological analysis, or by computer simulation.

In work [3] the equation (3) was used at theoretical analysis of the nucleation kinetics of KH_2PO_4 crystals from aqueous solution. It is not correct, because for KH_2PO_4 $q = -2.612$. The equation (3) is true for dilute solutions of electrolytes, but the ice crystallize as rule in weak electrolytes. All solutions, in which the crystal growth is possible, have a salt concentration > 5 mass % [1]. Therefore in these case it can be used as rule the equation (2), or some others [5]. Indeed the crystal growth kinetics of the KH_2PO_4 crystals was early considered in detail [13]. Here it was used correctly the more complicated than (3) and more precise equation of an activity coefficient by Pitzer and Mayorga [5, 13]. Nevertheless the equation (3) can be used for discussion of crystal nucleation and growth kinetics of the next inorganic salts, having the values of $q \approx 0$: K_2HPO_4 - $q = 0.099$; Rb_2SO_4 $q = -0.002$; $CsBr$ $q = -0.043$; $CuSO_4$ $q = -0.027$; $NaHCO_3$ $q = -0.039$, and Na_2SO_3 $q = -0.067$; Cs_2SO_4 $q = -0.093$; $NiSO_4$ $q = -0.033$ [5]. In other case we must discuss the nucleation kinetics on the basis of the more complicated equation of an activity coefficient (1, 2).

4. Experimental results on the study of the inorganic salt super-solubility

The system studies of the nucleation kinetics of the next potash and sodium salts was carried out by statistical method of many samples in works [4, 14-17]: $KF \cdot 2H_2O$, KI , KBr , KCl , KNO_3 , KOH , KH_2PO_4 , $K_2C_2O_4$, NaI , $NaBrO_3$, $NaBr$, $NaIO_3$, $NaNO_3$, $NaCOOH$, $NaOH$, and, besides, a limit supercooling is estimated for KNO_2 , $KCOOH$, $KClO_3$, $KCNS$, KCH_3COO , $KBrO_3$, KIO_3 , K_2CO_3 , K_2SO_4 , K_2SO_4 and K_2MoO_4 solutions. The general dependencies of the solubility product (SP) and maximum supercoolings ΔT_m (super-solubility) of ammonium 1-1 electrolytes on anionic radii are presented in Fig. 3. It is evidently that both dependencies are non-monotonic, but ones are not quite similar. The same dependencies of solubility (S in mol%) and solubility product (SP) is more similar.

All discussed dependencies ($q - SP$, $SP - R_a$, $\Delta T_m - R_a$, $q - R_a$, $\Delta H_s - R_a$) are different for 1-1 electrolytes. This circumstance enlarges essentially the variety of salts and their solutions properties, which must be taken into account at a priory search of technology of crystal growth. The known set of the pair $SP - \Delta T$ values for aqueous solution of I-I, II-I and other types of electrolytes is bounded by two direct lines (1-2), Fig. 4.

The certain interrelations between solubility, super-solubility, types of salts crystallisation and possible methods of perfect crystal growth from aqueous solution have been early established [7, 16-17]. At first approximation all salts can be divided into main three parts according to stability of the supersaturated solution:

1) The salts of the first group (I) have the maximum supercoolings of their solutions $\Delta T \sim 81-110^\circ C$. Owing to high stability of the supersaturated solutions the large

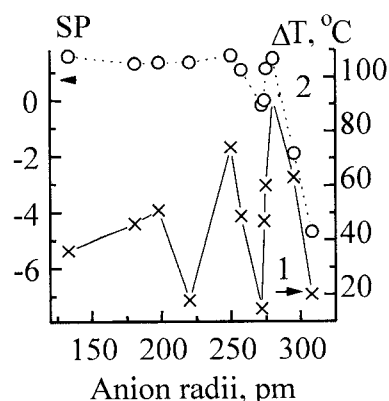


Fig. 3. The dependence of ΔT_m and SP (curve 1-2) for solutions of the ammonium salts on anion radii (R_a).

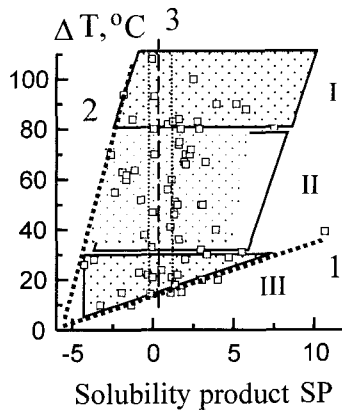


Fig. 4. The indistinct set of the pair values of the SP and ΔT for I-I, I-II and other salt solution.

and perfect crystals of this group of salts can be grown the most easily from pure solutions by different methods, including accelerated ones [1, 16-18].

2) The solutions of the second group (II) have the moderate supercoolings of solution $\Delta T \sim 30\text{--}80^\circ\text{C}$. In pure solution of these salts it is observed usually the growth of imperfect crystals, having many solution inclusions, non-perfect and irregular faces, twins. The perfect crystals of this salts group can be grown only in multinary solutions, which contain certain additive macro- and micro-components [16-17].

3) The solutions of III type have the least values of ΔT ($7\text{--}25^\circ\text{C}$). Owing to low stability of these supersaturated solution it is often observed as rule the rapid growth, the secondary nucleation and the formation of imperfect crystals: twins, sprouts, dendrites, intergrowths, containing the solution inclusions between the crystal interfaces. The perfect crystals of this salts group can be grown only at precise temperature stabilization $\sim 0.01\text{--}0.001^\circ\text{C}$, or also in multinary solutions [16-17].

The line 3 in Fig. 4 is designated the ideal electrolyte solutions according to Debye-Hückel (focus of lines bundle, $q \approx 0$, Fig. 2). The crystals of salts, which form such solutions (the strip along line 3, Fig. 4), can be grown more easily than salts, having the small, or high solubility. Namely the salts, find near line 1 are slight soluble and we must increase a solubility by the addition into solutions certain macro-component. On the contrary we must often decrease a solubility of salt, having too high SP. So, the set of all experimental points in Fig. 4 is separated into no less than six-nine characteristic and distinctive sub-sets, in which the conditions for the perfect crystal growth from aqueous solutions can be predict a priori. In general these results are also confirmed to model of the surface melting [9-10, 16].

More than 10 examples of the choice of the perfect crystal growth technology for the mentioned six-nine sub-set of salts are described in works [16-17]. The crystal growth of the first group of the slight soluble salts is presented with potassium pentaborate tetrahydrate (KB5) [19]. The perfect crystals of KB5 grow from the solutions of nitric acid and magnesium nitrate. The solutions of sulfuric acid have been used at the growth of perfect crystals of iodic acid (I group of high soluble salts) [1]. The crystal growth of I group of moderate soluble salts can be presented with KDP (KH_2PO_4) [18]. The solubility product of KDP equal to -0.44 [5], the solubility is more than $20\text{--}30\text{ mass}\%$ at crystal growth condition [20], and maximum supercooling ΔT_m (super-solubility) is more than $90\text{--}100^\circ\text{C}$ [14-16]. This salt relates to the first group of our classification of salts and the large and perfect crystals of KDP can be easily grown from solution, even by accelerated method [7, 16-17].

The more difficult case of II group of slight soluble salts is the crystal growth of potassium bromate, potassium, ammonium and aluminium iodate [16-17, 21]. The crystal growth of I group of moderate soluble salts is the case of potassium nitrate and urea (carbamide) [17, 22]. The other similar examples can be found by the comparison of results of works [1-2, 14-16]. So, if we can predict, or estimate SP and ΔT for different salt solutions, then we can design of crystal growth technology from aqueous solution for novel materials.

5. Conclusion

The laws of crystal growth from multi-component solutions significantly depend on the individual features of substance and solvent and ones must be taken into account at choice of crystallization condition [4, 7, 14-17, 23]. The knowledge of two predicable solution properties is necessary without fail to estimate a priori an expected efficiency of the crystallization technology: solubility and super-solubility. The investigation results allow predict the crystallization peculiarities of electrolyte solutions, suitable methods and conditions of perfect crystal growth on the basis of known dimensional factors of used salts.

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