
**MEASUREMENT OF GROWTH RATES FOR SINGLE CRYSTALS
AND PRESSED TABLETS OF $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ON A ROTATING DISC**

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Received December 15, 1988

Accepted March 16, 1989

Dedicated to late Academician Eduard Hála.

Measured growth and dissolution rates of single crystals and tablets were used to calculate the overall linear rates of growth and dissolution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals. The growth rate for the tablet is by 20% higher than that calculated for the single crystal. It has been concluded that this difference is due to a preferred orientation of crystal faces on the tablet surface. Calculated diffusion coefficients and thicknesses of the diffusion and hydrodynamic layers in the vicinity of the growing or dissolving crystal are in good agreement with published values.

Thanks to its well-defined hydrodynamic conditions of measurements, the rotating disc has lately been used also in crystallization, especially for theoretical purposes, i.e., in studies on mass transfer between the solution and the crystal or for comparison of experimental data with growth theories. The rotating disc can be used to measure the growth rate of a chosen well-developed and well-defined single crystal face. In addition, the measurement provides data on diffusional mass transfer in the vicinity of the growing crystal face. For substances that do not form sufficiently large crystals, the rotating disc can be used to measure the growth of a tablet pressed from the polycrystalline material¹. Because of its simplicity and the possibility of use for both single crystals and substances for which the preparation of single crystals is difficult or impracticable, the apparatus with a rotating disc is becoming a universal method for measuring the crystal growth rate. So far it has been used to obtain kinetic data for hexamethylenetetramine², potassium dihydrogenphosphate³, sodium perborate⁴, and saccharose⁵.

Since the crystals on the surface of a tablet are randomly oriented, it is generally assumed that the measurement provides the overall crystal growth rate^{1,2}. However, this has not as yet been experimentally confirmed, and there is uncertainty as to what rate is actually measured in this case. Is it the rate for the most slowly or the most rapidly growing face, or a mean value corresponding to the random distribution of the crystal faces on the surface of the tablet?

The aim of this work was to verify the applicability of tablets for measurements by comparing the linear growth rate for a chosen face of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ single crystal with data obtained under the same conditions for tablets pressed from tiny $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ crystals.

THEORETICAL

The growth rate for i -th single crystal face is given by

$$g_i = \frac{\Delta m}{A_i \Delta t \rho_c}, \quad (1)$$

where Δm is the change in the mass of the measured crystal face, A_i is its size, Δt is the measurement time, and ρ_c is the crystal density. The overall growth rate of a single crystal is defined as

$$G = \frac{k_G \beta}{3\alpha \rho_c} \Delta w^g = k'_G \Delta w^g, \quad (2)$$

where α and β are the geometric factors referred to the characteristic dimension of the crystal, k_G is the growth rate constant, Δw is the supersaturation, and g is the order of growth kinetics.

If the single crystal is embedded in the disc so that the $1\bar{1}0(\bar{1}10)$ face is in contact with the solution, then the growth along the b -axis is measured. By measuring the dimensions of a large number of crystals, one can determine the dimension parameters L_a , L_b , and L_c , and from these the shape factors α_b and β_b referred to the dimension L_b .

$$\alpha_b = \frac{L_a L_b L_c}{L_b^3} = \frac{L_a L_c}{L_b^2} \quad (3)$$

$$\beta_b = \frac{2(L_a L_b + L_a L_c + L_b L_c)}{L_b^2} = 2 \left(\frac{L_a}{L_b} + \frac{L_c}{L_b} + \alpha_b \right). \quad (4)$$

By definition,

$$V = \alpha_b L_b^3, \quad (5)$$

where V is the crystal volume, and

$$A = \beta_b L_b^2, \quad (6)$$

where A is the crystal surface area. The average linear face growth rate, g_M , is de-

defined as

$$g_M = \frac{dV}{dt} \frac{1}{A} = \frac{dm}{A \rho_c dt} \quad (7)$$

From Eq. (5) the change in the volume with time is obtained as

$$\frac{dV}{dt} = 3\alpha_b L_b^2 G_b, \quad (8)$$

where G_b is the rate of crystal growth along the direction L_b . Substitution of Eqs (6) and (8) into (7) gives

$$g_M = \frac{3\alpha_b}{\beta_b} G_b. \quad (9)$$

Using the relationship

$$G_b = 2g_b, \quad (10)$$

where g_b is the growth rate of the crystal face along L_b , we obtain the final equation

$$g_M = \frac{6\alpha_b}{\beta_b} g_b = \frac{6\alpha_b}{\beta_b} \frac{\Delta m}{A_i \Delta t \rho_c}. \quad (11)$$

For a tablet pressed from polycrystalline material, the situation is more complicated in that we do not know which crystal face actually grows. One way to solve this question is to use the measured growth rate g_i , defined by Eq. (1), and the geometric factors $\alpha_a, \beta_a, \alpha_b, \beta_b$, and α_c, β_c to calculate the overall growth rate for the tablet, and to identify the mean linear growth rate that is closest to the rate measured for the single crystal

$$g_{T,a(b,c)} = \frac{6\alpha_{a(b,c)}}{\beta_{a(b,c)}} \frac{\Delta m}{A_i \Delta t \rho_c}. \quad (12)$$

The exponent g can be calculated from measured data by evaluating Eq. (2) in logarithmic form using the least-squares method. The separation of the diffusion and reaction steps for growth is made by using Karpiński's correlation⁶. On the basis of equations for

$$\text{diffusion step} \quad dm/dt = k_D A (w - w_i) \quad (13)$$

$$\text{reaction step} \quad dm/dt = k_i A (w_i - w_{eq})^2 \quad (14)$$

$$\text{overall growth} \quad dm/dt = k_G A \Delta w^g, \quad (15)$$

where dm/dt is the mass rate of crystal growth, k_D is the rate constant of the diffusion step, k_I is the rate constant of the reaction step, and w , w_i and w_{eq} stand for the concentration in the bulk solution, the concentration on the crystal surface, and the equilibrium concentration, respectively, we can write, using Eq. (2),

$$\frac{dm}{dt} \frac{1}{A} = \frac{3\alpha\varrho_c}{\beta} G_M \quad (16)$$

and

$$\frac{3\alpha\varrho_c}{\beta} G_M \frac{1}{k_I} = \left(\Delta w - \frac{3\alpha\varrho_c}{\beta} G_M \frac{1}{k_D} \right)^2. \quad (17)$$

Dividing by $(G_M\varrho_c)^{0.5}$ gives

$$\frac{\Delta w}{(G_M\varrho_c)^{0.5}} = \frac{1}{k_D} \frac{3\alpha}{\beta} (G_M\varrho_c)^{0.5} + \left(\frac{3\alpha}{\beta} \right)^{0.5} \left(\frac{1}{k_I} \right)^{0.5}. \quad (18)$$

Denoting $x = (G_M\varrho_c)^{0.5}$ and $y = (G_M\varrho_c)^{-0.5} \Delta w = \Delta w/x$, we can rewrite Eq. (18) in the linear form

$$y = \frac{1}{k_D} \frac{3\alpha}{\beta} x + \left(\frac{3\alpha}{\beta} \right)^{0.5} k_I^{-0.5}. \quad (19a)$$

Using the least-squares method, we can now evaluate the rate constant k_D of the diffusion step and the rate constant k_I of the reaction step.

For $g = 1$ this separation of the diffusion and the reaction steps cannot be used and it holds

$$k_G = g_M\varrho_c/\Delta w = 6\alpha/\beta g_i\varrho_c/\Delta w \quad (19b)$$

or

$$k'_G = 2g_i/\Delta w \quad (19c)$$

From the equation⁷

$$k_d = \frac{0.6205\varrho_1 D^{2/3} \omega^{1/2}}{\nu^{1/6} f(Sc)} \frac{1}{(1 + w_{eq})^2}, \quad (20)$$

where ϱ_1 is the solution density, ω is the angular speed of disc rotation, D is the diffusion coefficient, ν is the kinematic viscosity, and Sc is the Schmidt number, we can calculate the diffusion coefficient using known values of ν and ϱ_1 . The value of the function

$$f(Sc) = 1 + 0.2980(Sc)^{-1/3} + 0.1451(Sc)^{-2/3} \quad (21)$$

approaches unity. The obtained value for $Sc = v/D$ will then serve as a check on the assumption given by Eq. (21).

Using the relationships⁸

$$\delta_D = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \quad (22)$$

$$\delta_H = 3.6 (\nu/\omega)^{1/2} \quad (23)$$

we can also calculate the thicknesses of the diffusion and hydrodynamic layers in the vicinity of the growing crystal or tablet in the disc.

EXPERIMENTAL

Apparatus

The growth rate was measured using an apparatus differing from those previously used¹⁻⁵ by some changes in design¹⁰. A schematic diagram of the apparatus is shown in Fig. 1. Thorough mixing in measuring vessel 1 containing about 5 litres of solution is achieved by simultaneous rotation of low-speed magnetic stirrer 2 and rotating disc 3. Four plexiglass baffles 4 are symmetrically disposed below the liquid surface. In order to obtain a smooth flow in the region of the rotating disc, a circular plexiglass plate 5 is placed at twice the disc diameter parallel to disc face. The solution in the vessel is kept close to ambient temperature by a combination of infrared lamp 6 and fan 7 operated by controller 8. The disc is driven by control unit 9 maintaining a present constant speed in the range 2 to 25 revolutions per second.

The disc (see Fig. 2) is a Teflon cylinder 70 mm in diameter with a 25 mm diameter circular conical hole bored into the smooth base for fixing a disc insert. The insert is made by casting acrylic resin into a mould so as to embed a crystal or tablet with the surface area to be measured

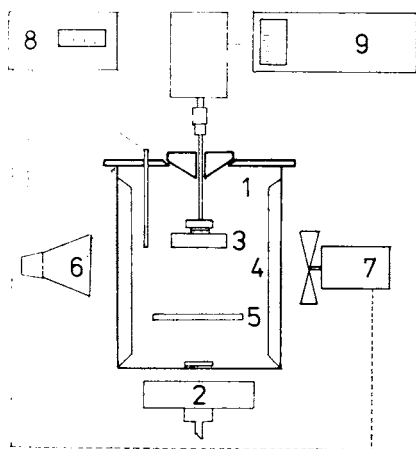


FIG. 1

A schematic diagram of the apparatus

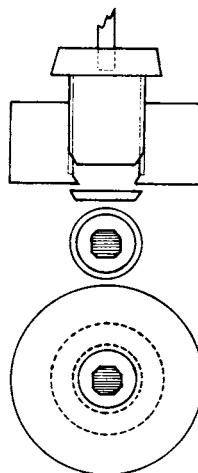


FIG. 2

Combined disc

exposed in the surface plane of the insert. The insert is fixed by tightening a Teflon joint connected to the motor shaft.

Procedure

Single crystals of copper sulphate pentahydrate were grown from crystals produced in a fluidized-bed apparatus and suspended in a well-stirred supersaturated solution. A typical shape of the crystals is shown in Fig. 3.

From measurements of 10 to 20 of so obtained single crystals we determined the parameters L_a , L_b , and L_c , and calculated the coefficients α_a , α_b , α_c , and β_a , β_b , β_c .

i	a	b	c
L_i , mm	6.43	2.29	9.64
α_i	0.53	11.82	0.16
β_i	4.78	37.67	2.13

From the grown single crystals with L_a of about 7 mm, those having well-developed $1\bar{1}0$ faces of sufficient size (several tens of mm^2) were selected. Tablets for measurements were made from a sieve fraction with sizes of 0.1–0.2 mm by compression in a hydraulic press under a pressure of $2 \cdot 10^8$ Pa. The tablets and single crystals were embedded in acrylic resin disc inserts, and the exposed surface areas were exactly determined. Both kinds of disc insert were immersed in a saturated solution of CuSO_4 for 30 min, and their initial masses, m , were determined immediately before measurement by weighing on an analytical balance. After about 30 min of rotation in solution of temperature T at an adjusted speed, the gain or loss, Δm , of the mass of the disc insert, and hence the rate of growth or dissolution, was established. In order to calculate the

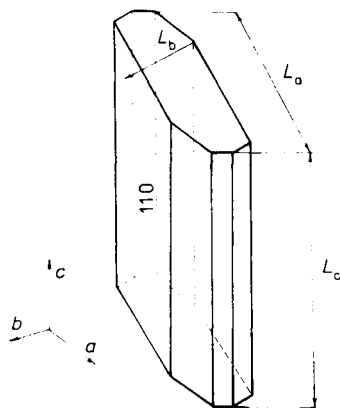


FIG. 3

A typical shape of the measured $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals

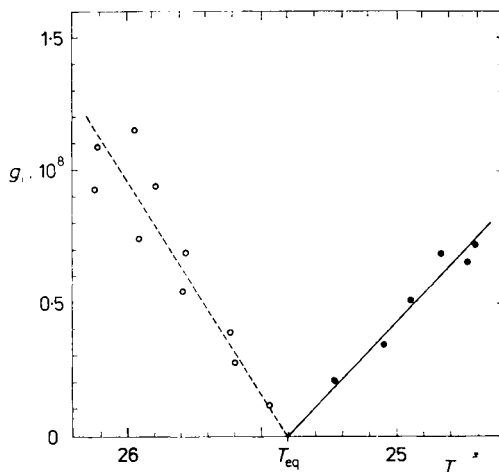


FIG. 4

Determination of the saturation temperature of the working solution. ● —, growth; ○ - - - -, dissolution

supersaturation, Δw , for each measurement, it was necessary to determine the exact saturation temperature, T_{eq} , of the solution. This was obtained by extrapolating a plot of g_i vs T (see Fig. 4) to zero rate of growth or dissolution. The supersaturation of solution in which the measured face of single crystal or tablet grew or dissolved was calculated from the equation

$$\Delta w = \Delta T dw_{\text{eq}}/dT, \quad (24)$$

where dw_{eq}/dT is the temperature coefficient of solubility, whose values were taken from solubility tables⁹. The viscosity of the working solution was measured by a Ubbelohde viscometer, and its density was determined by means of a Paar densimeter.

RESULTS AND DISCUSSION

The above described procedure was used to make a series of measurements of the rate of growth or dissolution of the $1\bar{1}0$ face of single crystals and the surface area of tablets pressed from polycrystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The disc rotation speed was 2.5 rev/s. The measured values were used in Eq. (11) or (12) to calculate the average rate of growth/dissolution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ single crystals along the direction b , i.e., the growth rate of an oriented crystal along the $1\bar{1}0$ direction, or the average growth rate of tablets along the directions a , b , and c for the assumption of microcrystal growth along these directions. The measured data for the dissolution and growth of single crystals and tablets are listed in Table I.

It is seen from the table that the dissolution rate is nearly the same for both the single crystals and the tablets. The small differences in the values are within the limits of experimental error. For growth, however, more significant differences are observed: the tablet grows at a greater rate. For a single crystal from which a well-defined $1\bar{1}0$ face grows along the direction b , g_M can readily be calculated from the shape factors α_b and β_b . The exposed area of the tablet, on the other hand, is composed of various crystal faces. Therefore, the shape factors α_a , β_a , α_b , β_b , and α_c , β_c were used to calculate the average growth rates g_{Ta} , g_{Tb} and g_{Tc} of tablet, and these were compared with g_M .

As seen from Fig. 5, it is g_{Tb} , i.e., the average rate calculated on the basis of growth of the most slowly growing face, that is comparable with g_M for the single crystals. For g_{Ta} and g_{Tc} the differences are too large. Hence it may be concluded that the tablet growth rate is controlled by the growth rate of the largest, i.e., the most slowly growing crystal face, with small contributions from the more rapidly growing faces. These contributions increase the calculated tablet growth rate by about 20%. This indicates that for nonisometric crystals, the orientation of the faces on the surface of a tablet is not random and that the crystals lie predominantly flat.

Compared with data previously reported¹⁰ to illustrate the use of the rotating disc apparatus, the results of the present work are based on a larger number of measurements and therefore are more accurate.

The crystal growth and dissolution on a rotating disc have been studied near the

saturation temperature, where the supersaturation or undersaturation, Δw , of the working solution is not high. As shown recently¹¹, the diffusion coefficient in this region is extremely dependent on the solution concentration, passing through a maximum and decreasing strongly at higher concentrations corresponding to a supersaturated solution. Our calculated diffusion coefficients (for $v = 1.75 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ and $\rho_1 = 1.227 \text{ kgm}^{-3}$) for an undersaturated solution where dissolution takes place are probably those occurring in the region of the maximum in the D - w curve. The growth, on the other hand, has been measured in a supersaturated solution beyond the bend in the curve, where the diffusion coefficient decreases dramatically. The decrease in diffusivity with increasing concentration in the region of small supersaturations is apparently the reason why the diffusion coefficients found by us are

TABLE I

Average^a characteristics determined for dissolution and growth of single crystals and tablets of $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ (for the meaning of the symbols and the units, see List of symbols)

Parameter	Dissolution characteristics		
	single crystals	tablets	
$g_i/\Delta w \cdot 10^6$	3.25	3.39	
$k'_d \cdot 10^6$	6.50	6.78	
$k_d \cdot 10^2$	1.39	1.46	
$D \cdot 10^9$	1.06	1.46	
$\delta_D \cdot 10^5$	4.55	4.66	
$\delta_H \cdot 10^3$	1.20	1.20	
	Growth characteristics		
	single crystals	tablets	
$g_i/\Delta w \cdot 10^6$	1.57	1.94	
		growth in the direction	
		<i>a</i>	<i>b</i>
			<i>c</i>
$k'_G \cdot 10^6$	3.14		3.64
$k_G \cdot 10^3$	6.75	2.95	8.34
$D \cdot 10^9$	0.36		1.38
$\delta_D \cdot 10^5$	0.32		4.97
$\delta_H \cdot 10^3$	1.20		1.23

^a The values are averages of at least 15 measurements, and are given at the 5% confidence level.

higher for dissolution of both the single crystals and tablets than for their growth. The absolute values of the diffusion coefficient may be compared with published data¹², $D = 3.8 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

From known diffusion coefficients the thicknesses of the diffusion and hydrodynamic layers have been calculated by means of Eqs (22) and (23). The thickness of the diffusion layer for dissolution is higher for the tablet than for the single crystal, and is generally larger than that for growth. It ranges between 20 and 30 μm , again in good agreement with published values¹³. The thickness of the hydrodynamic layer was calculated to be 1.2 mm.

CONCLUSION

One of the advantages of the rotating disc, as mentioned in the literature, is the possibility of using it to measure the crystal growth rate for substances difficult to grow into single crystals, because in this case the measurement can be made with polycrystalline material pressed into a tablet. However, the measured growth rates for a single crystal and a tablet prepared from $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$, i.e., from anisotropic crystals, are different (see Table I). The growth rate obtained for the tablet approaches most closely that for the $1\bar{1}0$ face, in our case the largest crystal face, but it is still by 20% higher. The difference is probably due to contributions from the less abundant, smaller crystal faces with greater growth rates. Thus, the measured growth rate depends on the make-up of the tablet surface, i.e., on the orientation individual crystal faces assume in the process of pressing, which is not random for anisotropic crystals.

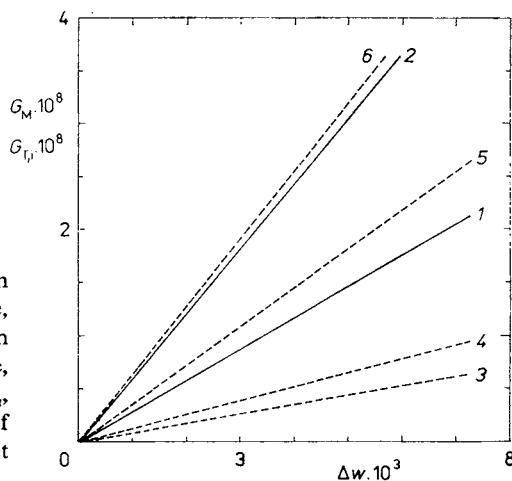


FIG. 5

The overall rates of growth and dissolution of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. 1 Overall growth rate, G_M , of single crystal; 2 overall dissolution rate of single crystal; 3 overall growth rate, G_{Tc} , of tablet; 4 overall growth rate, G_{Ta} , of tablet; 5 overall growth rate, G_{Tb} , of tablet; 6 overall dissolution rate of tablet

The diffusion coefficients and the diffusion layer thickness calculated from the measured growth rates of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ crystals are in good agreement with data obtained by other methods of measurement¹³.

The use of the combined disc described in this paper makes it possible to determine even small changes in the mass occurring during the growth or dissolution of a single crystal or tablet. This is due, above all, to a small mass of the disc insert in which the single crystal or tablet is embedded. In addition, the ease and rapidity with which the insert can be fixed and replaced reduces the total time required to measure the given system.

LIST OF SYMBOLS

A	surface area of crystal, m^2
A_i	surface area of measured face of single crystal or tablet, m^2
D	diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
g	order of growth kinetics
g_i	growth rate of single crystal face or tablet ($i = a, b, c$), m s^{-1}
g_M	average linear face growth rate, ms^{-1}
G_i	growth rate of given crystal dimension ($i = a, b, c$), m s^{-1}
G	overall growth rate of single crystal, m s^{-1}
g_{Ti}	overall growth rate of tablet ($i = a, b, c$), m s^{-1}
k_G	growth rate onstant, $\text{kg m}^{-2} \text{s}^{-1}$
k'_G	growth rate constant defined by Eq. (2), m s^{-1}
k_d	dissolution rate constant, $\text{kg m}^{-2} \text{s}^{-1}$
k'_d	dissolution rate constant defined by analogy of Eq. (2), m s^{-1}
k_D	rate constant of diffusion step, $\text{kg m}^{-2} \text{s}^{-1}$
k_I	rate constant of reaction step, $\text{kg m}^{-2} \text{s}^{-1}$
L_i	linear dimension of crystal ($i = a, b, c$), m
dm/dt	mass rate of crystal growth, kg s^{-1}
m	initial mass of disc insert, kg
Δm	change in disc insert mass, kg
Sc	Schmidt number
T	actual temperature of solution, $^\circ\text{C}$
T_{eq}	saturation temperature, $^\circ\text{C}$
ΔT	difference between actual and saturation temperatures, K
Δt	measurement time, s
V	crystal volume, m^3
w	instantaneous concentration of solution, $\text{kg}(\text{kg of free H}_2\text{O})^{-1}$
w_i	concentration on crystal surface, $\text{kg}(\text{kg of free H}_2\text{O})^{-1}$
w_{eq}	equilibrium concentration of solution, $\text{kg}(\text{kg of free H}_2\text{O})^{-1}$
Δw	supersaturation or undersaturation, $\text{kg}(\text{kg of free H}_2\text{O})^{-1}$
dw_{eq}/dT	temperature coefficient of solubility, $\text{kg}(\text{kg of free H}_2\text{O})^{-1} \text{K}^{-1}$
α_i	volume shape factor ($i = a, b, c$)
β_i	surface shape factor ($i = a, b, c$)
δ_D	diffusion layer thickness, m
δ_H	hydrodynamic layer thickness, m

ω	angular speed of disc rotation, rad s^{-1}
ν	kinematic viscosity of solution, $\text{m}^2 \text{s}^{-1}$
ρ_c	crystal density, kg m^{-3}
ρ_1	solution density, kg m^{-3}

REFERENCES

1. Bourne J. R.: *Ind. Chim. Belg.* 39 (12) 1003 (1974).
2. Bourne J. R., Davey R. J., Gros H., Hungerbuhler K.: *J. Cryst. Growth* 34, 221 (1976).
3. van Rosmalen J. R.: *Thesis*. Delft University of Technology, Delft 1977.
4. Chianese A.: *J. Cryst. Growth* 91, 39 (1988).
5. Webster G., Garside J.: *Proceedings 10th Symposium on Industrial Crystallization, Bechyně, Sept. 21–25, 1987* (J. Nývlt and S. Žáček, Eds), Academia, Prague 1989.
6. Karpínský P.: *Chem. Eng. Sci.* 35, 2321 (1980).
7. Newman J. S. in: *Electrochemical Systems*, p. 309. Prentice Hall, Englewood Cliffs, N. J., 1973.
8. Levich V. G. in: *Physico-Chemical Hydrodynamics*, Ch. II, III. Prentice Hall, Englewood Cliffs, N. J., 1962.
9. Broul M., Nývlt J., Söhnel O.: *Solubility in Inorganic Two-Component Systems*. Academia — Elsevier, Prague 1981.
10. Karel M., Nývlt J.: *Chem. Prum.* 39, 75 (1989).
11. Chang V. C., Myerson A. S.: *Proceedings 9th Symposium on Industrial Crystallization, Hague, Sept. 25–28, 1984* (S. J. Jančič and E. J. de Jong, Eds), p. 27, Elsevier, Amsterdam 1984.
12. *International Critical Tables* (Washburn E. W., Ed.), Vol. V, p. 14, 65, 66. McGraw-Hill, New York 1929.
13. Matuchová M.: *Thesis*. Research Institute of Inorganic Chemistry, Ústí nad Labem 1974.

Translated by M. Škubalová.