Brief scientific papers
UDK 544.653.2:546.56
doi: 10.7251/COMEN1702190M

GROWTH MECHANISM OF *KDP* CRYSTALS FROM AQUEOUS SOLUTIONS

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Abstract: The results of the effect of the growth history on Potassium Dihydrogen Phosphate (KDP) crystals growth mechanism are presented in the paper. Crystals were grown in temperature range of $24-28°\mathrm{C}$ from aqueous solutions, saturated at $T_0=(31.0\pm0.1)°\mathrm{C}$. Two types of the experiments were performed. In both types, after the nucleation at $T_\mathrm{n}=(26.0\pm0.1)°\mathrm{C}$ crystals were grown at the same temperature for about 1.5 hour and then dissolved at temperature $T_\mathrm{d}=(34.0\pm0.1)°\mathrm{C}$ for about 15 min. After refaceting, in the first type, the crystal growth started at $24°\mathrm{C}$, followed by the temperature increasing in steps of $\Delta T=1°\mathrm{C}$ to $28°\mathrm{C}$. In the second type, after refaceting the crystal growth started at $28°\mathrm{C}$, followed by the temperature decreasing in steps of $\Delta T=1°\mathrm{C}$ to $24°\mathrm{C}$. Obtained results indicate that KDP crystals growth mechanisms do not depend on growth history. They are discussed in accordance with the current theories.

Keywords: Potassium Dihydrogen Phosphate, growth from solution, growth mechanisms.

1. INTRODUCTION

An analysis of crystal growth rate versus solution supersaturation dependence (R,σ) is widely used to determine mechanisms of crystal growth. A significant number of researchers have studied the crystal growth process from solutions for different substances and several crystal growth mechanisms have been proposed in the literature [1−9]. Growth rate mechanism determination on base (R,σ) dependence is more difficult because of growth rate dispersion (GRD). GRD describes the phenomenon in which crystals of the same material under the same solution conditions grow at different rates. This dispersion might be caused by different configuration of dislocation groups and lattice strain [10−12]. Partial dissolution and refaceting creates new defects in the structure of crystals which probably changes number of dislocations and adds additional strain lattice. Narrowing of GRD after partial dissolution and refaceting is experimentally confirmed [13]. Investigation results for KDP crystals [13, 14] show that the growth history affects growth rates. Pantaraks and Flood [15] have showed that the growth and solution history have influence on roughness of crystal surface and current crystal growth.

Difficulties in determining the crystal growth mechanism from growth rate versus solution supersaturation dependence are discussed in [16]. It is shown that growth mechanism of sodium chlorate from aqueous solutions depend on growth history - different growth mechanism operates if growth temperature is set up by rising or by lowering temperature.

In this paper, results of investigation of the effect of cooling of aqueous solution from 28°C to 24°C and heating solution from 24°C to 28°C after partial dissolution for KDP are presented. Growth mechanism was analyzed by equations which are proposed by theory. Results indicate that crystals growth at constant supersaturation do not depend on growth history.

2. THEORY

Table 1. Equations used to describe different growth models

Equation	
$R=k_1\sigma^{1/2}$ (1)	$R=k_5\dfrac{\sigma^2}{\sigma_\mathrm{c}}$ (5)
$R=k_2\sigma^{5/6}$ (2)	$R=k_6\sigma^n$ (6)
$R=k_3\dfrac{\sigma^2}{\sigma_\mathrm{c}}\tanh\left(\dfrac{\sigma_\mathrm{c}}{\sigma}\right)$ (3)	$\dfrac{\sigma^2}{R}=k_7+k_8\sigma$ (7)
$R=k_4\sigma$ (4)	$R=k_9+k_{10}\sigma$ (8)

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In order to establish the mechanism responsible for the growth of KDP in {100} direction under investigated conditions, growth rate versus solution supersaturation dependence (R,σ) were analyzed. Equations (1−7) which correspond to different crystal growth models are listed in Table 1. Only equation (8) is empirical, σ_c is critical value of solution supersaturation and k_1 - k_{10} are constants [16].

3. EXPERIMENTAL PROCEDURE

The purpose of all experiments was to investigate how supersaturation changes influence the growth mechanism of KDP crystals. Analar grade of this system (99% purity) was used. Crystals grew from aqueous solutions which were prepared by equilibrating an excess of crystals with distilled water for three days at saturation temperature. Crystals were nucleated in the cell spontaneously. Observed crystals' dimensions were measured by digital optical microscope (Nikon SMZ800) supplied with camera (Luminera, Infinity 1) using transmitted light. The complete experimental setup which was used has been described in detail in [17]. Crystals which were sufficiently distant from neighbour crystals in order to avoid intergrowth during the growth, were preselected for growth rate measurements during each growth run.

In order to investigate the growth mechanism of KDP crystals, two types of experiments were performed. The first type of experiments was with supersaturation decrease and the second type of experiments was with supersaturation increase. In all experiments, the solution was saturated at temperature $T_0 = (31.0 \pm 0.1)°\text{C}$. The procedure in the first part and the second part of all experiments was the same for both type of experiments, i.e. crystals grew at temperature $T_n = (26.0 \pm 0.1)°\text{C}$ about 1.5 hours and after that, in the second part of experiments, crystals were dissolved about 10 min and refaceting. The third part of experiments was different and lasted about 7 hours. In the first type of experiments after refaceting, crystal growth was performed at temperature 24°C followed by temperature increase in steps $\Delta T = 1°\text{C}$ to $28°\text{C}$. In the second type of experiments after refaceting, crystal growth was firstly performed at temperature 28°C followed by temperature decrease in steps $\Delta T = 1°\text{C}$ to $24°\text{C}$. Crystals' sizes were measured in different intervals which depended on how fast crystal grew on selected temperature.

The concentrations of solution were calculated on the basis of empirical formula $C = 0.17554 + 0.00102t + 0.0000743\,t^2$ and the relative supersaturation is defined as $\sigma = C - C_o / C_o$, where C and C_o are the actual and saturated solution concentrations, respectively. All experimental data were fitted by equations (1−8) as in [16].

4. EXPERIMENTAL RESULTS AND DISCUSSION

Growth rate dispersions occurred and histograms which represent these dispersions are presented on Figure 1 and Figure 2. These dispersions are described by a simple normal distribution. High growth rates at the end of dispersions are excluded from the fitting procedure, they probably pertain to dominant dislocation group of higher activity [13]. As it can be seen from Figure 1 and Figure 2, growth rates of KDP crystals in {100} direction after dissolution and refaceting pertain to one maximum. Growth and saturation temperatures T and T_0, relative supersaturation σ, the most probable growth rate for experiments with supersaturation decreases $R_{\max D}$ and increases $R_{\max I}$, and number of measured growth rates in these experiments N_D and N_I is presented in Table 2. Figures 3 and 4 depict the most probable growth rate at constant supersaturation versus supersaturation dependence for type I and type II experiments, respectively.

In order to determine the most suitable correlation between the KDP crystal growth rate in {100} direction and supersaturation and to determine crystal growth mechanism in the supersaturation range 6.18 - 14.72%, experimental data were fitted with equation (1-8). Goodness of the fit is tested with Chi-square test. Smaller values of χ^2, for the same data set, correspond to equations which better describe (R,σ) dependence. Values of χ^2 for equations (1−8) are presented in Table 3 and different line style belong to different equation. Also, for equation (6) the value of parameter n is given in parentheses in Table 3. From Figures 1, 2 and Table 2, it can be seen that positions of the distribution maxima slightly differs for experiments in which the solution supersaturation decreases and those in which the solution supersaturation increases.

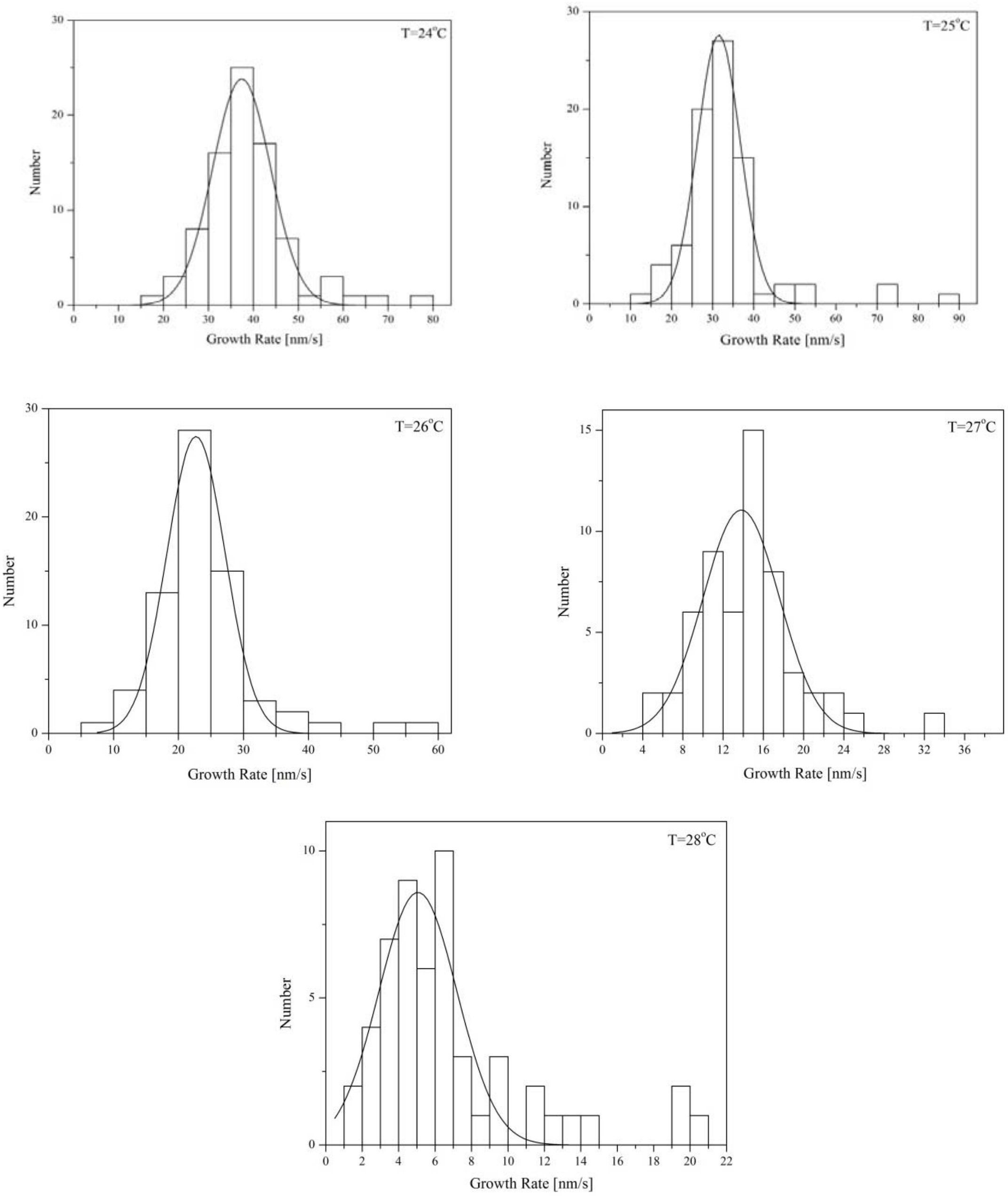

Figure 1. Histograms representing {100} face growth rate dispersion for type 1 experiments with supersaturation decreases

Higher χ^2 values obtained for equations 1 and 2 indicate that two-dimensional crystal growth does not exist in those experiments. Lower values of χ^2 obtained for equations (3) and (5), which correspond to BCF model, and (7) which correspond to Chernov's model, show that in supersaturation range 6.18-14.72%, spiral growth operate. Also relatively low value of χ^2 for equation (5) show that mentioned σ supersaturation range is quite below the critical supersaturation i.e. $\sigma << \sigma_c$. In both types of experiments, it can be noticed that the smallest values of χ^2 is obtained for linear equation with intercept. This equation is empirical and none of the theories for spiral growth mechanism predict this kind of (R,σ) dependence. Power obtained by fitting the data with equation (6) in experiments with supersaturation decreases (n=1.81) and in experiments with supersaturation increases (n=1.86), suggest that high interaction between diffusion fields of growth units between the steps do not exist i.e. diffusion fields do not overlap.

These results show that growth mechanism of KDP crystals in {100} direction is the same if the growth temperature is achieved by rising or by lowering solution temperature, which is in contrast to sodium chlorate growth in {100} direction [16].

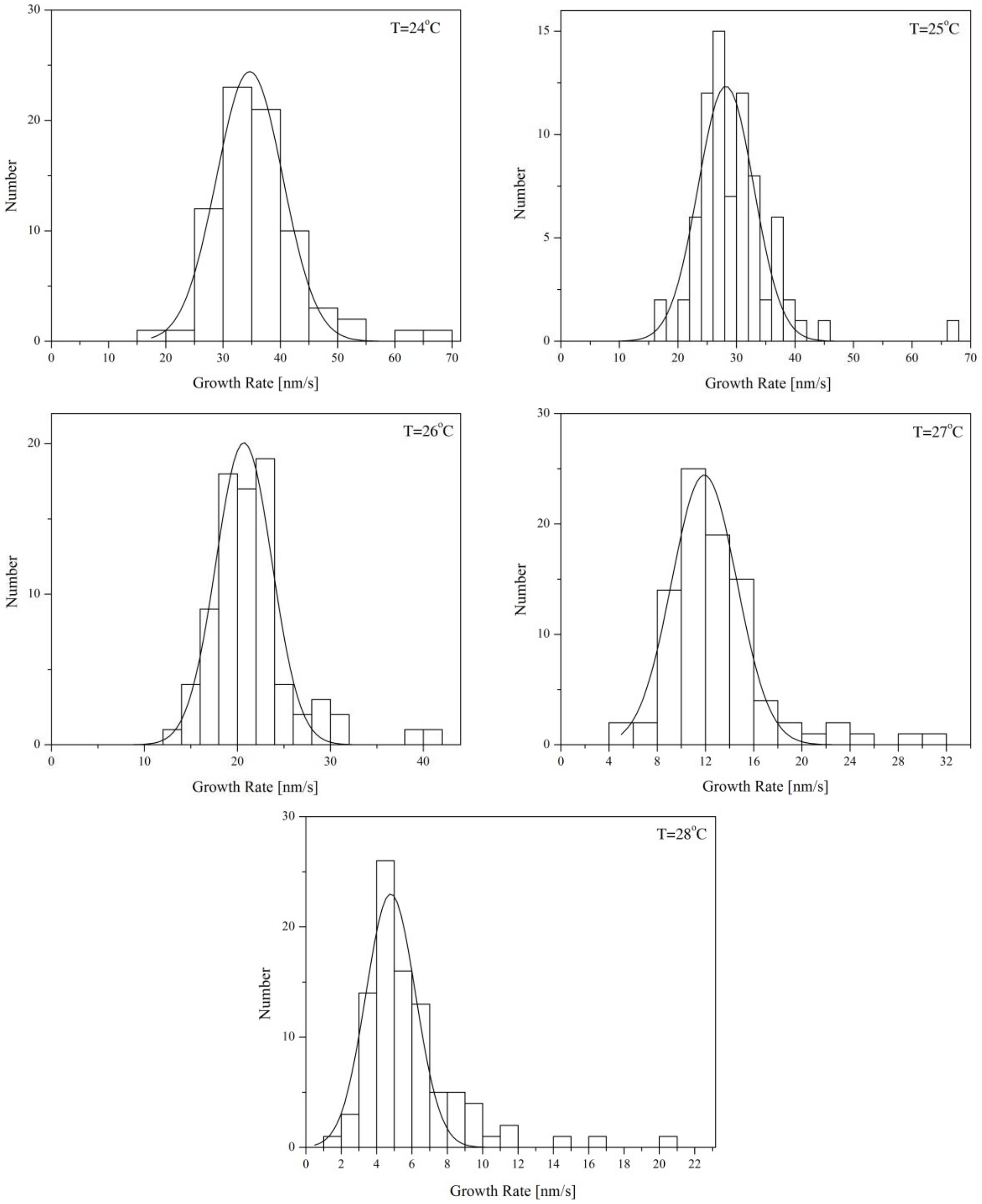

Figure 2. Histograms representing {100} face growth rate dispersion for type 2 experiments with supersaturation increases

Table 2. Experimental conditions and Results

T_0[°C]	T[°C]	σ[%]	N_D	R_{maxD}[nm/s]	N_I	R_{maxI}[nm/s]
31.0	24.0	14.72	84	37.5±0.3	75	34.6±0.3
31.0	25.0	12.56	81	31.5±0.5	77	28.3±0.7
31.0	26.0	10.42	69	22.7±0.3	81	20.7±0.3
31.0	27.0	8.29	59	13.9±0.1	89	11.9±0.3
31.0	28.0	6.18	53	5.1±0.2	93	4.9±0.2

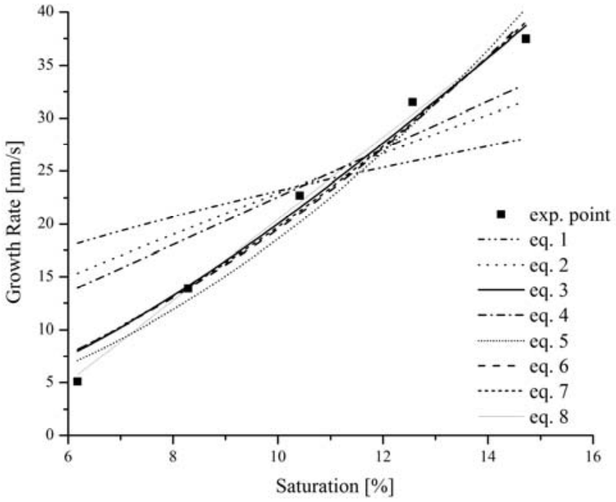

Figure 3. {100} face growth rate vs supersaturation dependence when supersaturation decreases for the most probable growth rate.

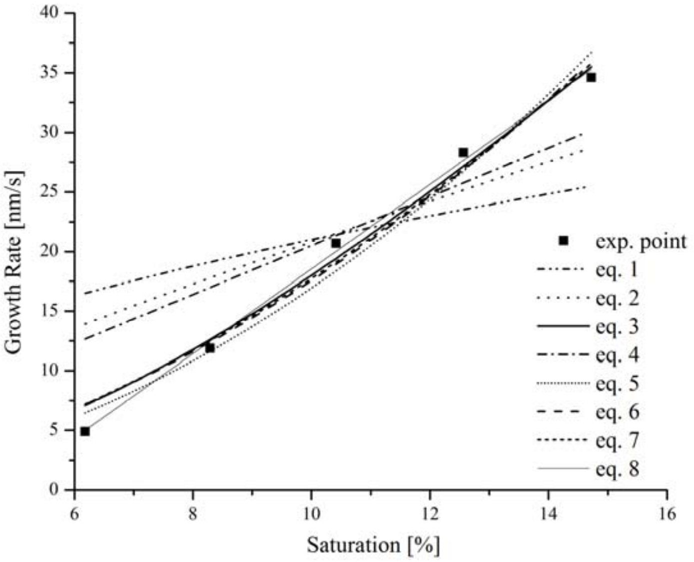

Figure 4. {100} face growth rate vs supersaturation dependence when supersaturation increases for the most probable growth rate.

Table 3. Values of χ^2 for Rmax versus σ Dependence for Type 1 and Type 2 Experiments

	χ_1^2 (Eq. 1)	χ_2^2 (Eq. 2)	χ_3^2 (Eq. 3)	χ_4^2 (Eq. 4)	χ_5^2 (Eq. 5)	χ_6^2 (Eq. 6)	χ_7^2 (Eq. 7)	χ_8^2 (Eq. 8)
Figure 3	85.83	46.83	4.65	32.54	6.04	6.51 (n=1.81)	5.85	1.17
Figure 4	73.31	40.37	3.06	28.17	3.72	4.24 (n=1.86)	3.85	0.58

5. CONCLUSION

In this paper, the results of growth mechanism investigations of KDP crystals in {100} direction from aqueous solution in supersaturation range 6.18 − 14.72%, show that crystals grow according to BCF theory. Mentioned supersaturation range in performed experiments is below the critical i.e. $\sigma << \sigma_c$ and diffusion fields do not overlap (surface diffusion path is much smaller than terrace width). It is shown that growth history of KDP crystals has no influence on mechanism of KDP crystals growth in {100} direction and that the best value of χ^2 is obtained for linear equation with intercept, which is not predicted by current crystal growth theories.

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МЕХАНИЗАМ РАСТА КДП КРИСТАЛА ИЗ ВОДЕНИХ РАСТВОРА

Сажетак: У овом раду су представљени резултати истраживања утицаја историје раста на механизам раста кристала калијум дихидроген фосфата (КДП). Кристали су расли у опсегу температура 24−28°C из водених раствора засићених на $T_0 = (31.0 \pm 0.1)°\mathrm{C}$. Реализована су два типа експеримената. У оба типа, након нуклеације на температури $T_\mathrm{n} = (26.0 \pm 0.1)°\mathrm{C}$ кристали су расли око 1.5 сат на температури нуклеације, а затим су растварани на температури $T_\mathrm{d} = (34.0 \pm 0.1)°\mathrm{C}$ око 15 мин. Након рефацетирања кристали су у првом типу експеримената расли прво на температури $24°\mathrm{C}$, након чега је температура раста повећавана у корацима од $\Delta T = 1°\mathrm{C}$ до $28°\mathrm{C}$. У другом типу експеримената кристали су након рефацетирања расли прво на температури $28°\mathrm{C}$, а потом је температура раста снижавана у корацима од $\Delta T = 1°\mathrm{C}$ до $24°\mathrm{C}$. Резултати указују да механизам раста КДП кристала не зависи од историје раста и дискутовани су у складу са актуелним теоријама.

Кључне ријечи: калијум дихидроген фосфат, раст из раствора, механизми раста.

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