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Long-Time Growth Rate Changes of Sodium Chlorate, Potassium Dihydrogen Phosphate, and Rochelle Salt Crystals Independent of Growth Conditions

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ABSTRACT: Results of investigations of the changes in growth rate inherent to crystals (i.e., independent of macroscopic external conditions) during a 15-h growth period are presented. The results of the investigations regarding the time evolution of the growth rate dispersion are also presented. The majority of the investigations were carried out with sodium chlorate crystals, and several experiments were carried out with potassium dihydrogen phosphate (KDP) and Rochelle salt crystals. It was found that, for the majority of the crystals, the main changes in growth rate occurred in the initial growth stage, which extended to for up 4 h. These growth rates probably slowly decrease toward the end of the growth run. Some of the very high initial growth rates that decreased during the initial growth period were followed by relatively high intermediate growth rates for the next few hours and then subsequently decreased. The growth rates for the majority of crystals probably gradually decreased after 15 h of growth. The results obtained show that these changes, which have not previously been taken into account, should be included in the interpretation of growth rate changes affected by various parameters (supersaturation, temperature, fields, stress, impurities, etc.). The obtained results could improve the current crystal growth theories, which are based on the design of specific growth conditions that result in a target product.

1. INTRODUCTION

Changes with time have been observed in the growth rates of crystals. Lacmann and Tanneberger[1] noticed that, during the first hour of observation, damaged crystals of potassium alum exhibited characteristic healing periods, with growth velocities that were initially very high and subsequently decreased to a constant value. The rapid increase in the growth rate of sodium chlorate crystals in the initial stage stabilizes in about 90 min and then undergoes a gradual decrease, as reported by Matsunaka et al.[2] Flood et al.[3] observed that the initial rate of crystal growth in batch experiments for up to 30 min of growth is significantly higher than subsequent crystal growth of D-fructose from aqueous ethanol. Gibbsite single crystals growing from aqueous sodium aluminate solutions were studied by Sweegers et al.,[4] who reported that, after an initial increase, the growth rate reached a maximum and then decreased slowly. The decrease in the growth rate with time was explained in terms of a decrease in supersaturation in the closed cell system.

Results of systematic studies of the changes in growth rate independent of growth conditions, that is, inherent to crystals, were published recently. The growth rate changes of sodium chlorate crystals during 4 h of growth,[5] as well as the stability of the growth rates of these crystals,[6] were investigated.

The influence of various parameters, such as impurities, stress, ultrasound, and electric and magnetic fields, on the growth rates of crystals grown from aqueous solution has been studied in depth for a long time. The effects of growth rate history on current growth rate were studied through changes in supersaturation[7,8] and crystal dissolution and refacing[9,10] during the growth runs. However, the changes in growth rate inherent to crystals have not attracted particular attention, even though they

might have a significant influence on conclusions concerning the effects of additional parameters on the growth rate.

The growth rate dispersion (GRD) has been studied extensively for a long time,[11−18] but the time evolution of the GRD has been studied only recently.[5] This phenomenon is still not well understood. It can be a consequence of differences in the dislocation structure between equivalent crystallographic faces of the crystal[19,20] or in the degree of crystal lattice strain.[21−26]

Numerous authors have proposed several purely empirical models for size-dependent growth kinetics that anticipated an increase in growth rate with increasing crystal size.[27−32]

Investigations of process modeling and the determination of kinetic data might significantly improve our understanding of crystallization processes and the possibilities designing crystallization processes in which the final product quality and its application are of great importance. Modeling of the product properties depends strongly on the crystal growth kinetics. For that reason, this article presents the results of investigations of the growth rate changes inherent to crystals, and the resulting GRD changes, in prolonged growth experiments (up to 27 h). These investigations follow up on the recent study of the time evolution of the GRD,[5] with the aim of analyzing the growth rate behavior after 4 h of crystal growth. The main investigations were carried out with sodium chlorate crystals. To confirm the similar growth rate behaviors of different substances, the growths of potassium dihydrogen phosphate (KDP) and Rochelle salt crystals were studied as well.

Table 1. Experimental Conditions

| crystal	N (n)	T (°C)	σ (mass %)
SC	132 (12)	28.0 ± 0.1	1.3
KDP	28 (3)	26.0 ± 0.1	10.4
RS	25 (3)	29.0 ± 0.1	8.2

2. EXPERIMENTAL SECTION

The aim of all of the experiments described herein was to investigate the changes in growth rate inherent to sodium chlorate (SC), potassium dihydrogen phosphate (KDP), and Rochelle salt (RS) crystals grown from aqueous solutions. The analar grade of these systems (99% purity) was used. The solutions were prepared by equilibrating an excess of crystals with distilled water for 3 days at a saturation temperature of $T_0 = (31.0 \pm 0.1)$ °C. The solution supersaturation is expressed in terms of mass percentages as $\sigma = (C - C_0)/C_0$, where C and C_0 are the concentration and the saturation concentration, respectively, at the growth temperature. The crystal growth temperatures T and the corresponding relative supersaturations σ for all of the investigated substances are listed in Table 1. Also included are the numbers of growth rates measured, N, along with the number of growth runs performed, n, in parentheses.

Crystals were nucleated in the cell by momentarily stopping the solution flow and introducing air bubbles through a needle into the cell. To avoid uncontrolled changes of growth conditions, the nucleation was performed at the crystal growth temperature. This procedure was repeated several times until small crystals had appeared at the bottom of the cell, sufficiently distant from their closest neighbors to avoid intergrowth during the growth periods.

The crystals were observed under a microscope using transmitted light at a total magnification of 60×, which gave an accuracy of ±5 μm. Between 5 and 12 crystal nuclei were selected for detailed growth observations during each growth run. We measured the changes in crystal length in the chosen direction and calculated the corresponding average linear growth rate in that direction within the observation interval. The measurement time interval varied from 20 min (at the beginning) to 90 min (at the end of the longest experiments).

Many difficulties, such as nucleation and accumulation of small crystals in the interior of the pipes through which the solution flowed and the formation of crystals intergrown inside the crystallization cell, were encountered during the long-term experiments (about 24 h). To enable long growth runs of several crystals, a specially designed experimental setup was used. A schematic drawing of the setup is shown in Figure 1a, and a schematic of the crystallization cell used is shown in Figure 1b. To optimize the growth conditions by minimizing spontaneous crystallization in the entrance (C_1) and the exit (C_2) solution pipes, the diameters and lengths of thermostatically controlled water pipes (C_3–C_5) were changed. The cooled section of pipe C_1 was 120 cm long, whereas the heated section of pipe C_2 was 80 cm long. The solution flow rate was about 0.5 mL/s, which corresponds to solution velocities of 8 and 25 mm/s through the entrance (C_1) and exit (C_2) pipes, respectively. The thermostatically controlled water flow rate was about 10 L/min, which corresponds to water velocities of 0.7 and 1.2 m/s through the entrance (C_3) and exit (C_5) pipes, respectively. This setup configuration ensured the lack of considerable spontaneous nucleation in the cell and pipes for 24 h in approximately one-third of the
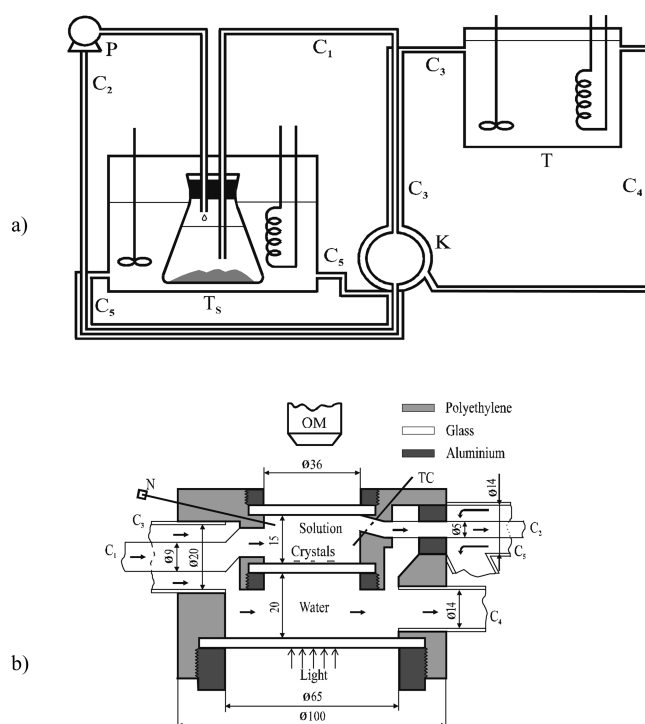

Figure 1. Schematic drawings of the (a) experimental setup and (b) crystallization cell. C_1, pipe for incoming solution; C_2, pipe for outgoing solution; C_3–C_5, thermostatically controlled water pipes; OM, optical microscope; N, needle; TC, thermocouple; K, crystallization cell; T and T_s, thermostats providing growth and saturation temperatures, respectively; and P, peristaltic pump. All dimensions are given in millimeters.

experiments. The capacity of the cell was about 15 mL. The velocities of the solution at the bottom (around the crystals) and at the top of the cell were about 0.05 and 0.5 mm/s, respectively. The temperature of the aqueous solution in the crystallization cell was kept constant to within ±0.02 °C. The typical crystal arrangements in part of the cell at the beginning and end of a growth run are shown in Figure 2 for all substances investigated.

Further analysis excluded complete growth runs with flow rates that decreased or with many intergrown crystals (approximately two-thirds of growth runs). Separate crystals intergrown with neighbors were excluded from the analysis as well (crystals 1–4 in Figure 2). A wide range in the initial growth rates, as well as different growth behaviors of crystals with the same initial growth rates, required the observation of large numbers of crystals. This method, as opposed to measuring only one crystal per growth run investigation, significantly improved the statistics.

The growths of 66 sodium chlorate crystals (132 in the ⟨100⟩ direction), 28 KDP crystals (in both the ⟨100⟩ and [001] directions), and 25 Rochelle salt crystals (in the [001] direction) were observed. In Table 2, the intervals between the crystal sizes at the beginning (l_0) and end (l) of the experiments for the measured growth rate directions are reported.

The growth rate changes inherent to sodium chlorate, KDP, and Rochelle salt crystals are presented in terms of initial, intermediate, and stabilized growth rates. The initial crystal growth rate was calculated using the first two experimental data points, pertaining to the first 20–30 min of growth. The intermediate and stabilized growth rates were

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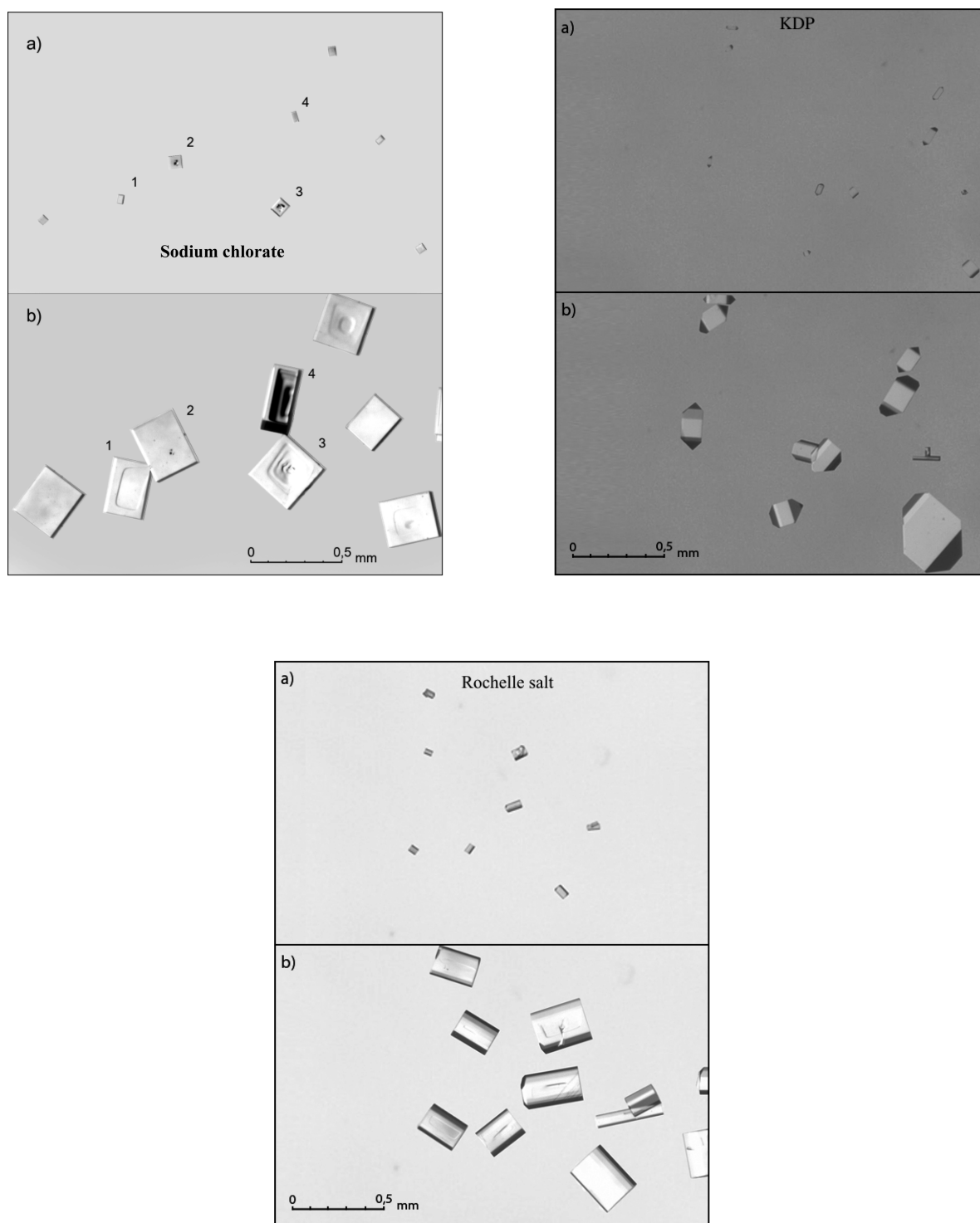
Figure 2. Typical crystal arrangements, in part of the cell, at the (a) beginning and (b) end of the growth run, for all investigated substances.

calculated using three experimental data points measured after 3 and 11 h of growth, respectively. Intermediate growth rates were calculated after 3 h of growth because the first significant changes in growth rate in all investigated substances ended during that period for the majority of the crystals observed. Stabilized growth rates were calculated after 11 h of growth, because four (of the 12) growth runs finished after 15 h, and because after that period, only a few

growth rates changed significantly. Five of the experiments performed ran for more than 24 h.

3. RESULTS

To test the stability of the supersaturation in long-term experiments, the stabilities of the dissolution and refaceting temperatures were tested in introductory experiments. In the

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Table 2. Initial and Final Crystal Size Intervals

crystal	direction	l_0 (mm)	l (mm)
SC	$\langle 100 \rangle$	0.02−0.87	0.18−6.81
KDP	$\langle 100 \rangle$	0.07−1.07	0.75−2.89
	[001]	0.07−0.46	0.87−3.90
RS	[001]	0.08−1.12	0.62−3.26
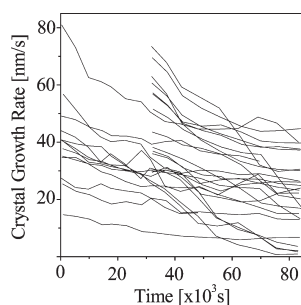
Figure 3. Changes in the growth rate of Rochelle salt crystals in the introductory experiments.

first experiment, crystals were grown for 1 h, and in the second, they were grown for 5 h. In both experiments, after these growth periods, the temperature in the cell first slowly increased (0.05 °C/h) to (30.90 ± 0.02) °C and then gradually increased by 0.02 °C to (31.04 ± 0.02) °C. After that, the temperature gradually decreased in the same steps until crystal refaceting occurred. The solution was held for 45 min at each of these temperatures. The dissolution of crystals was noticed at (31.00 ± 0.02) °C (i.e., at the saturation temperature). Crystal refaceting was noticed at (30.98 ± 0.02) °C. The same results were obtained for crystals grown for 1 or 5 h, for all substances investigated.

Another type of introductory experiment was also performed to test the stability of the macroscopic growth conditions (not just the supersaturation stability). In these experiments, crystals were nucleated and grown at the growth temperature in approximately 24 h. About 10 h after the beginning of crystal growth, additional air bubbles were introduced into the cell, thereby provoking the nucleation of new crystals. In about one-third of the experiments, newly nucleated and already growing crystals had sufficient distances between them to allow for crystal growth without intergrowth with neighbors in the next 11 h. These experiments were performed for all of the substances investigated. In Figure 3, the growth rate changes of Rochelle salt crystals in this type of introductory experiment are presented. Similar changes in growth rate were obtained for the other substances investigated.

For all of the substances investigated, a significant dispersion in growth rate was noticed at all crystal growth stages, even though all of the crystals grew under the same macroscopic external conditions (temperature and supersaturation in the cell).

Most of the growth rates changed significantly during the period of observation. The majority of crystals in all of the investigated substances significantly changed their growth rates in the first few hours of the growth period. The results of eight experiments run for more than 15 h indicated a continuous slow decrease of growth rates, although this decrease was within the measurement error limit for many of the crystals.

3.1. Sodium Chlorate. Figure 4 depicts the time dependence of the crystal size and the changes in the growth rate of sodium
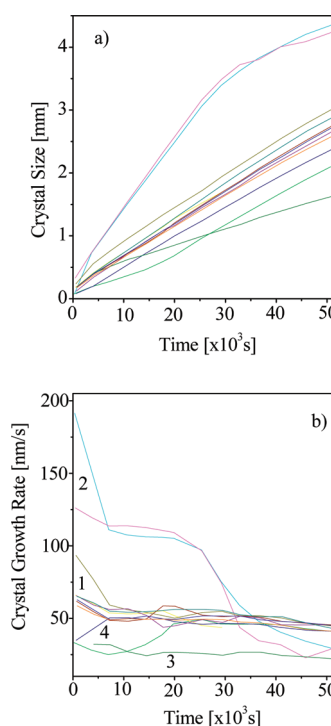
Figure 4. (a) Crystal size and (b) growth rate in the [100] direction as a function of time. In the two plots, each crystal is presented by the same color. The typical growth rate changes listed in the text are denoted 1−4.
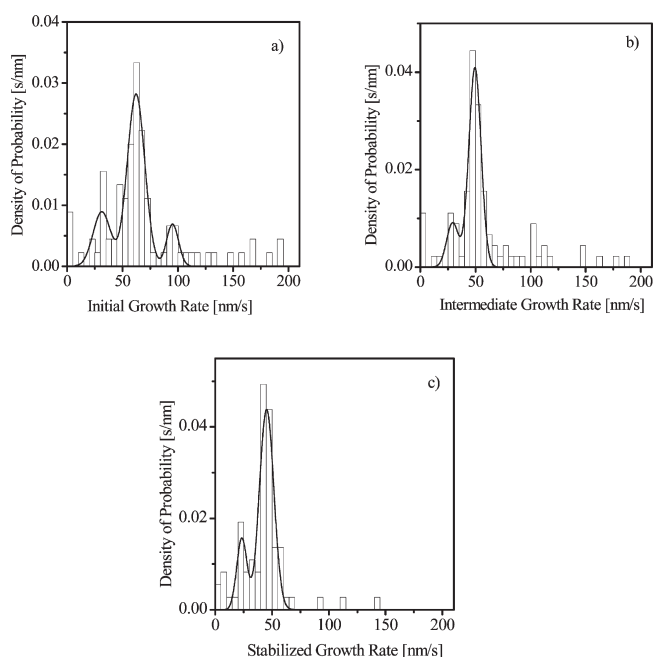
Figure 5. Histograms representing (a) initial, (b) intermediate, and (c) stabilized growth rate dispersions of sodium chlorate crystals.

chlorate crystals in the [100] direction in a typical long-time growth run.

Five types of crystal growth rate changes were noticed in our experiments on sodium chlorate, as follows:

Type 1. The majority of the measured growth rates decreased during the initial period of growth for 2−4 h. This growth rate

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Table 3. Parameters Describing Growth Rate Distributions of Sodium Chlorate Crystals

growth rate	R_1 (nm/s)	R_2 (nm/s)	R_3 (nm/s)
initial	31 ± 2	62.2 ± 0.7	95 ± 3
intermediate	29 ± 2	49.5 ± 0.5	
stabilized	24 ± 2	45.0 ± 0.4	

Table 4. Parameters Describing Growth Rate Changes of Sodium Chlorate, KDP, and Rochelle Salt Crystals

substance	direction	$\overline{R}_1$ (nm/s)	$\overline{R}_2$ (nm/s)	$\overline{R}_3$ (nm/s)
SC	$\langle 100 \rangle$	68 ± 4	59 ± 4	41 ± 2
KDP	$\langle 100 \rangle$	36 ± 2	29 ± 2	26 ± 2
KDP	$[001]$	43 ± 4	36 ± 4	21 ± 3
RS	$[001]$	49 ± 4	41 ± 3	31 ± 3

did not change until the end of the experiments (within the measurement error limits).

Type 2. Eleven very high initial growth rates decreased and then, after 2−4 h, reached relatively high intermediate growth rates that were retained for the following few hours. After that, they reached stabilized growth rates.

Type 3. Seven growth rates did not change during the whole growth run (within the measurement error limits).

Type 4. Five growth rates increased during the first couple of hours of the experiment and reached the values which were retained until the end of the growth.

Type 5. One of the crystals stopped growing in one direction. Three crystals did not grow at all.

Some of these behavior types are illustrated in Figure 4.

The histograms representing growth rate dispersions of sodium chlorate crystals in various growth periods are shown in Figure 5, with the growth rate dispersions of the initial, intermediate, and stabilized growth rates shown in parts a−c, respectively. To describe the growth rate distribution, the fitting of finite mixture normal distributions to the frequency distributions were performed. Details of the fitting procedure were described previously.[10,15,16] It can be seen from the histograms that some of the growth rates at the beginning and end of the distributions did not pertain to any of the maxima. These growth rates were eliminated from the fitting procedure. The distributions obtained are also included in Figure 5. Because of the relatively small number of growth rates analyzed, only three, two, and two maxima of the initial, intermediate, and stabilized growth rate distributions, respectively, are well-defined.

In Table 3, the parameters describing the initial, intermediate, and stabilized growth rate distributions, namely, R_1, R_2, and R_3, the growth rates corresponding to the first, second, and third distribution maxima, respectively, are reported.

In Table 4, the parameters describing the growth rate changes, namely, $\overline{R}_i$, $i = 1$, 2, and 3, the arithmetic means of the initial, intermediate, and stabilized growth rates, respectively, for sodium chlorate, KDP, and Rochelle salt crystals are reported.

To verify similar growth rate changes at lower supersaturations, two additional experiments were performed, in which sodium chlorate crystals were grown at $T = (29.0 \pm 0.1)$ °C in a solution saturated at $T_0 = (31.0 \pm 0.1)$ °C, corresponding to a supersaturation of 0.9%. In the two growth runs, 12 and 15 crystals (23 and 30 growth rates, respectively) were observed.
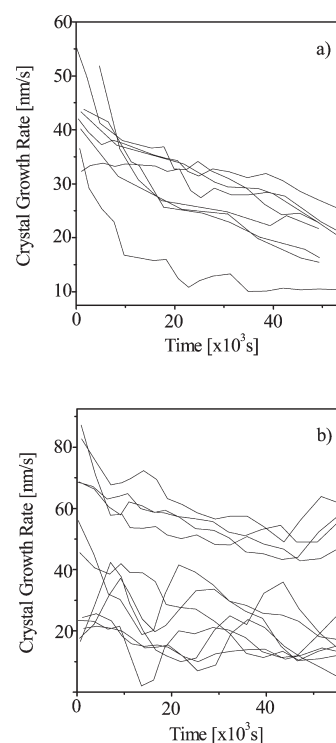
Figure 6. Time dependence of the changes in the growth rate of KDP crystals in the (a) $\langle 100 \rangle$ and (b) $[001]$ directions, in a typical long-time growth run.
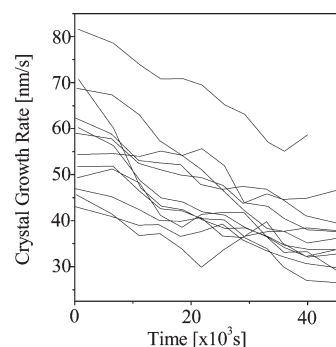
Figure 7. Changes in the growth rate of Rochelle salt crystals in the $[001]$ direction in a typical long-time growth run.

The obtained results show growth rate changes similar to those at a supersaturation of 1.3%. The growth rate decreases in the first stage of the experiments occurred in a shorter time than those at 0.9% supersaturation.

3.2. KDP. Parts a and b of Figure 6 depict the time dependence of the growth rate changes of KDP crystals in the $\langle 100 \rangle$ and $[001]$ directions, respectively, in a typical long-time growth run. Crystal growth rate changes in the $\langle 100 \rangle$ direction of types 1, 3, and 4, described for the growth of sodium chlorate crystals, occurred for KDP crystals, too. Neither crystals that did not grow at all nor crystals that stopped growing were observed. Similarly to the sodium chlorate crystals, type 1 growth rate changes dominated.

3.3. Rochelle Salt. Growth rate changes of Rochelle salt crystals in the $[001]$ direction in the long-time growth run are presented in Figure 7. Types 1−4 changes in growth rate occurred for Rochelle salt crystals as well. Crystals that did not
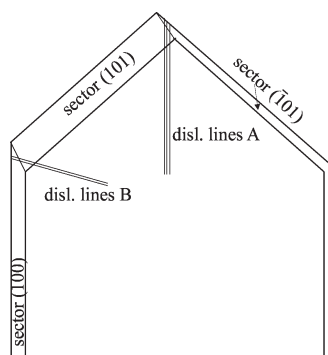
Figure 8. Transition of the dislocation source between KDP growth sectors.

grow or that stopped growing during the growth run were not observed. Similarly to the results for sodium chlorate and KDP crystals, type 1 rate changes in growth dominated.

In addition to the crystal growth rates presented above, a few crystals of sodium chlorate and one crystal of Rochelle salt grew at very high initial rates. These crystals intergrew with their neighbors relatively quickly, so their growth rate changes could not be traced, and the growth run could not be stopped completely. It is possible that these crystals did not retain stabilized growth rates during the 15 h of the experiment.

4. DISCUSSION

From the results presented in the preceding section, one can draw the conclusion that the changes in growth rate, independent of macroscopic growth conditions, of sodium chlorate crystals in the $\langle 100 \rangle$ direction, KDP crystals in the $\langle 100 \rangle$ direction, and Rochelle salt crystals in the $[001]$ direction are very similar. A possible reason for the absence of type 2 changes in the KDP crystal growth rate might be the relatively small number of crystals observed. KDP and Rochelle salt crystals that did not grow or that stopped growing were likely missing for the same reason or because of the relatively high supersaturation. The appearance of crystals that did not grow and crystals that stopped growing under supersaturated solutions was noticed earlier for both KDP[10,15,33] and Rochelle salt[10,22,34,35] crystals.

The growth rates of KDP crystals in the $[001]$ direction changed during the growth run in a very complex way. Although significant fluctuations in growth rates were observed, the tendency for them to decrease and level off with time can be seen in Figure 6b and Table 4. The growth in the $[001]$ direction of KDP evolves through the growth of eight $\{110\}$ faces, four at each opposite side of the crystal. According to BCF (Burton–Cabrera–Frank) growth theory,[19,20] the KDP crystal growth rates in the $[001]$ direction can change as the result of transition of the dominant dislocation source between different $\{110\}$ faces or between the $\{110\}$ and $\{100\}$ faces (Figure 8).

Changes in the eight (110) growth sectors, which determine growth in the $[001]$ direction, can result in significant growth rate fluctuations, which occurred in the experiments described. The fluctuations of the growth rates can also be explained in terms of fluctuations of the dislocation growth sources caused by impurities.[36] The results of the KDP growth rate measurements in the $[001]$ direction were not included in the investigations of the growth rate changes inherent to the crystal.

It can be seen from Figures 4–7 and Tables 2 and 3 that sodium chlorate, KDP, and Rochelle salt crystals change their growth rates during long periods of growth, even under constant experimental conditions. In general, from the growth rate investigations of sodium chlorate in the $\langle 100 \rangle$ direction (at two supersaturations), KDP in the $\langle 100 \rangle$ direction, and Rochelle salt in the $[001]$ direction, the following conclusions can be drawn:

- The majority of the measured growth rates (80–90%) significantly decreased in the initial growth period, because of the growth conditions and the substance investigated. These growth rates probably slowly decreased after the initial growth period, although any changes that occurred were within the measurement error limit.
- About 10% of the particles had very high initial growth rates. These growth rates decreased in the initial growth period and reached relatively high intermediate growth rates, which were retained for the following few hours. After that, the growth rates decreased again.
- Less than 10% of the growth rates increased predominantly in the first stage of the growth run or did not change significantly at all.
- The appearance of unusual changes in growth rates is scarce. Some sodium chlorate growth rates were zero all the time, or decreased to zero, even though the solution was supersaturated and the other neighboring crystals grew, as noticed earlier.[5,6,10,16,37]
- The growth rates of the majority of the crystals probably slowly decreased after 15 h of growth.

A significant decrease, mostly in the initial growth stage, occurred in more than 90% of the growth rates. Possible reasons for this phenomenon, such as a decrease of the solution supersaturation during the long-term experiments, a decrease of the overall mass-transfer coefficient, the presence of impurities, the transition of the dominant dislocation source from one face to a neighboring face, a change in crystal surface stage, and lattice strain effects on the crystal growth, are discussed in the following paragraphs.

Supersaturation. The same dissolution and refacing temperatures of the crystals grown for 1 and 5 h confirm the stability of the macroscopic solution supersaturation, within the measurement error limits. The main characteristic of another type of introductory experiments was that the new crystals introduced into the cell continued to grow similarly to the already-growing crystals, with higher initial growth rates. In addition to the confirmation of supersaturation stability, this also confirms that neighboring crystals did not influence the growth of the observed crystals. That is, the newly nucleated crystals grew similarly to the ones that were already growing, and even the distances between crystals were smaller. Both types of introductory experiments showed that the macroscopic growth conditions in the cell used were stable. On the basis of these results, one can conclude that changes in the macroscopic solution supersaturation cannot induce a significant growth rate decrease in the initial growth stage. Control of the microscopic supersaturation distribution was not possible in the experiments performed. This confirms that the observed growth rate changes are independent of macroscopic experimental conditions, that is, they are inherent to the crystals.

Changes in Mass-Transfer Coefficient. In the volume diffusion model of crystal growth, the overall mass-transfer coefficient decreases during the growth, because it is inversely proportional to the size of the crystals, which can result in a decrease in crystal growth rate.[38] It can be expected that surface-integration-controlled growth occurred for all substances investigated in our

experiments. This was previously confirmed for sodium chlorate,[39] KDP,[40,41] and Rochelle salt[42] crystal growth. The results of our experiments confirm these expectations. Specifically, the coefficients of linear correlation between the initial growth rates and the initial crystal sizes are 0.52 for sodium chlorate, 0.63 for KDP, and 0.32 for the Rochelle salt. Better correlations were established previously (more crystals observed): 0.55 for sodium chlorate[5] and 0.72 for KDP.[33] These small and positive values suggest that growth rates of crystals slowly increase with crystal size, which is in contrast to the volume diffusion model. This conclusion, valid for the correlation between initial crystal sizes and initial growth rates, can be extended to the growth of one crystal. That is, the differences in the initial crystal sizes are 14—43 times (Table 2) greater than the difference between the final and initial crystal sizes of one crystal. Therefore, it can be concluded that the mass-transfer changes are not relevant for the growth rate changes that occurred in our experiments.

Presence of Impurities. Changes in growth rate are usually explained by random perturbations in impurity concentrations near the crystal surface. An increase in impurity concentration leads to a decrease in the crystal growth rate.[43] Growth rate dispersion and zero and negative values of the growth rates of calcium sulfate crystals can also be explained by the effects of impurities.[44,45] Fluctuations of growth rates of the (001) face of potassium nitrate can be induced by fluctuations of the growth sources of dislocations caused by impurities.[46] Changes in impurity concentrations in the initial growth stage can be the cause of the noticed significant changes in crystal growth rate.

Transition of the Dominant Dislocation Source from One Face to the Neighboring One. According to BCF theory,[19,20] the crystal growth rate can change regardless of the growth conditions, as the result of a transition of the dominant dislocation source from one face to a neighboring face (growth sector changed).[47,48] In this process, the possibilities of increasing and decreasing the growth rate are equal. Consequently, the tendency for the growth rates to decrease and level off, as observed in our experiments, cannot be explained by this process.

Surface Stage Changes. Figure 5 shows that crystals grown with very high growth rates (very high activity of the dominant dislocation group) disappeared, as expected, because the dominant dislocation group cannot determine the growth of large crystal faces.[33] In other words, the reason for the high growth rates in the initial period of the growth process might be a high level of imperfection of the surface of the crystals after nucleation.

Effect of Lattice Strain on Crystal Growth. Changes in the growth rate during the initial growth stage could be explained in terms of the effect of lattice strain on crystal growth. It has been shown that the growth rate of a crystal is inversely proportional to its mosaic spread, which represents a measure of the "overall" lattice strain or defects in the structure of the crystal.[21—26] The described change in the crystal growth rate could be a consequence of corresponding changes in the crystal lattice strain. The lack of differences in the physical properties of crystals grown at various rates, because of GRD, could be a result of strain leveling, which unifies the growth rates. Physical properties are usually measured on large crystals. These crystals grow at levelized rates, but only small portions of the crystals grow at different rates during the initial growth stage, which does not make a significant effect on the physical properties of the bulk crystal.

The reason for neglecting the changes in growth rate at the start of the growth period in earlier investigations is the criterion typically applied for the constant crystal growth (CCG) model: the linear coefficient of the correlation between the crystal size

and the time should exceed 0.99.[25,49] Some authors have used rougher criteria for the CCG model (for example, 0.81).[46] A rough criterion was also used in our previous investigation. Such rough criteria can mask the natural changes in the crystal growth rate.[5] Careful observation of the crystal size versus time graphs in many articles (such as those of Shiau[17] and Mitrović[50]) showed that some changes in growth rate (mostly decreasing) occur during the first stage of growth under constant supersaturation. The decrease of the gibbsite single-crystal growth rate observed by Sweegers et al.[4] was explained through the supersaturation, which decreased in the closed-cell system. The described decrease in growth rates within the first 3 h of growth is similar to the results of our experiments. This indicates that these changes are not induced by supersaturation alone. They can be inherent to crystals as well.

The first results of the systematic study of changes in the growth rate inherent to sodium chlorate crystals during 4 h of growth were published recently.[5,6] It was shown that the growth rates of sodium chlorate crystals changed (mostly decreased) during the first 2 h of growth. The tendency of the growth rates to level off with time was detected. As mentioned above, 11 very high initial growth rates of sodium chlorate crystals (of 132) decreased and, after 2—4 h, attained relatively high intermediate growth rates that remained stable for the following few hours and then subsequently decreased again. The existence of these crystals could not be detected in the short-term experiments.[5]

Growth rate dispersion has been noticed for many substances,[11—18] but the time evolution of the GRD was studied only recently.[5] It can be seen in Figure 5a—c that the maxima of the intermediate and stabilized sodium chlorate growth rate distributions shifted to lower values compared to the initial growth rate distribution. Thirteen initial growth rates and only two stabilized growth rates of sodium chlorate crystals were higher than 100 nm/s. About 55% of the initial growth rates and even about 70% of the stabilized growth rates pertain to the second distribution maximum. The presumption that the growth rates would be more evened out after prolonged growth[5] was confirmed by the investigations presented. This result is in accordance with an earlier sodium chlorate growth rate investigation and with the general observation of a decrease in the range of growth rate dispersion with increasing crystal size.[26] It can be concluded that a significant GRD existed during the whole growth run (i.e., in any crystal growth stage observed). The shape of the distribution, which describes the GRD, changed during the growth.

The existence of three (Figure 5a) or two maxima (Figure 5b,c) indicates that growing sodium chlorate crystals pertaining to these maxima have activities of the dominant dislocation groups that accumulate around three or two values,[16,33] respectively. Over the course of time, the crystal growth rates exhibit a tendency of leveling (i.e., the crystals have common face dislocation activities). Figure 5 shows that crystals grown with very high growth rates (very high activities of the dominant dislocation group) disappear, as expected, because the dominant dislocation group cannot determine the growth of large crystal faces.[33]

From our results, one cannot draw any conclusion about a correlation between the inherent changes in crystal growth rate and the crystal size or growth period. Specifically, the observed crystals reached stabilized growth rates over a wide range of growth periods and with different crystal sizes. The size-dependent growth investigations suggest that the growth rate increases with the crystal size.[27—32] These results refer to the observation of many crystals at one time. Our results show that, in most cases, the growth rate of a crystal decreases with its size.

The influence of various parameters, such as impurities, stress, ultrasound, electric and magnetic fields, supersaturation, and dissolution and refaceting, on the growth rate of crystals grown from aqueous solution has been studied intensively for a long time. The majority of these studies were performed under the same temperature and supersaturation, with the additional parameter introduced after a certain period. Most of the experiments were relatively short (no longer than a couple hours). Growth periods with constant growth conditions in these experiments were comparable to the period of growth rate changes inherent to crystals. Accordingly, the growth rate changes inherent to crystals must be included in all conclusions drawn from these investigations.

5. CONCLUSIONS

It was shown in this work that changes in growth rate inherent to crystals (i.e., independent of macroscopic external growth conditions) do, in fact, occur. These changes are dominant in the first few hours of crystal growth. During this period, the growth rates of the majority of the crystals decreased significantly. A slow decrease of the growth rates probably occurs during prolonged crystal growth. Leveling of the crystal growth rates during the long growth period is evident. Crystal growth changes result in adequate changes in the growth rate dispersions. Possible reasons for this phenomenon have been discussed.

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