Growth and dissolution of NaClO₃ crystal in aqueous solution

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Abstract

Growth and dissolution rates of [100] faces of NaClO₃ crystals of about 0.5 mm across have been measured, along with in-situ observations of both processes, under a wide range of well-controlled super- and under-saturations, 1.1~49%, and 1.6~4.5%, respectively. The experiments were made using a specially designed apparatus, with which both growth and dissolution experiments can be made on the same seed crystal. The growth mechanisms are analysed based on the relation between the bulk supersaturation σ_B and the growth rate R. Physical constants, such as r′/kT, etc. were evaluated.

It is concluded that in the lower supersaturation range than σ_B≈2.5%
BCF mechanism predominates, in moderate supersaturation range 2.5<σ_B<8.0%,
Birth and Spread mechanism of two dimensional nucleation growth is the major growth mechanism, and in much higher supersaturation range, 8.0%>σ_B,
maximum linear law is assumed to be operated. Dissolution mechanism is also briefly discussed, in which the importance of interface kinetics is stressed. The observations on the recovery process from rounded to faceted morphologies and on the occlusion of liquid inclusions are described as well.

Introduction

Growth mechanisms of crystals from aqueous solutions have been studied experimentally under well-controlled conditions by many workers: K-alum (Bennema, 1965; Mullin and Garside, 1967; Botsaris and Denk, 1970; Denk and Botsaris, 1970; Treivus, 1971), sucrose (Smythe, 1967), NaClO₃ (Bennema, 1965; Hosoya and Kitamura, 1978; Hosoya et al., 1978; Simon, 1978), KCl (Klein-Haneveld, 1971), KDP (Mullin and Amatavivadhana, 1967), ADP (Mullin and Gaska, 1969), K₂SO₄ (Bransom et al., 1969), MgSO₄·7H₂O (Troost, 1968), Na₃P₂O₁₀·6H₂O (Troost, 1972). Among these, one of the most important results is the works by

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Bennema (1965) on K-alum and NaClO₃ in which very precise growth rate measurements were made under very low supersaturations. His data of growth vs. supersaturation relations clearly indicate that spiral growth or BCF mechanism (Burton et al., 1951) operates even in aqueous solution growth. Thereafter experimental data have been reported on several compounds which support the BCF mechanism. The effect of number of cooperative screw dislocations on the growth rate is also confirmed on sucrose crystal (Valčić, 1975).

In contrast, the two dimensional nucleation growth mechanism (2DNG mechanism) in aqueous solution growth has not been studied in detail, with exception of a few works. Recently, Hosoya and Kitamura (1978) have measured the growth rates of euhedral NaClO₃ crystals under relatively high supersaturation, and demonstrated that the Birth and Spread mechanism (B & S mechanism) (Ohara and Reid, 1973) among 2DNG mechanisms is operative under the supersaturation range they experimented. They compared their data with those obtained by Bennema (1965), and concluded that as increasing the supersaturation, the growth mechanism of euhedral crystals changes from BCF mechanism to B & S mechanism of 2DNG and that the transitional supersaturation was approximately 2.8%. A similar transition has been demonstrated in the theoretical work by Kuroda et al. (1977).

For the case of K-alum, several discussions based on the results of growth rate measurements have been published (Bennema et al., 1967; Lewis, 1974; Garside et al., 1975), as to the change of predominant growth mechanism due to the increase of supersaturation. The published data show that under very low supersaturation a linear relation is expected, under moderate supersaturation a parabolic relation, and under relatively high supersaturation a linear relation is again expected. The slight deviation of the linear relation under very low supersaturation was inferred to the Mono-nuclear mechanism (Ohara and Reid, 1973) among 2DNG mechanisms (Bennema et al., 1967). However, Lewis (1974) considered that the linear relation, the parabolic relation and the latter linear relation are due to the second linear law (Bennema, 1967), the parabolic law (Bennema, 1967), and the maximum linear law (Bennema, 1967), respectively. The second linear law is expected for the BCF mechanism when a large number of co-operative screw dislocations are outcropped, while the parabolic law for a small number of screw dislocations. This suggests that the seed crystal used in Bennema's work contained a large number of co-operative screw dislocations than the seeds used in other experiments.

The problem inevitably involved in these arguments is that the discussions are based on the compiled data obtained by different workers whose experiments were made under different growth conditions using different apparatuses. It is
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therefore absolutely necessary to carry out growth rate measurements under a wide range of supersaturation, which may cover the regions for BCF to volume diffusion, through 2DNG mechanisms, using the same apparatus and the same seed crystal. This is one of the main purposes of the present study.

The problem of dissolution kinetics in aqueous solution has been studied by some workers on K-alum (Garside and Mullin, 1968), KCl (Klein-Haneveld, 1971), ADP (Alexandru, 1971), NaClO₃ (Simon, 1978), and so on. All the previous works except for the work on NaClO₃ by Simon (1978) have been made using the weighing method. Although the work by Simon (1978) was in-situ observation, he used a capillary vessel which is filled with a single crystal, thus the effect of surface tension being avoidable. It is therefore necessary to use a specially designed cell, which enables to carry out both growth and dissolution experiments on one and the same seed crystal, and further to avoid the effect of surface tension.

With such purpose, a newly designed apparatus, a modification of the apparatus reported by Hosoya and Kitamura (1978), has been constructed in the present work. Using this apparatus, NaClO₃ crystals are studied, since the crystals are bounded mainly by (100) and thus easy to make precise rate measurement, and also because the published data in low and relatively high supersaturation ranges can be used to compare with the obtained data.

**Design of apparatus**

The experimental system consists of two apparatuses, one for preparation of a saturated solution and the other for in-situ observation and measurement. The former apparatus is similar as that reported by Hosoya and Kitamura (1978). Saturated solution of NaClO₃ is prepared in a vessel or in a two-necked flask (500 ml) immersed in a water bath regulated at a constant temperature. The temperature control units are designed by combining the on-off and the continuous regulators with which temperature may be controlled with a precision of ±0.01°C. The water in the bath (91) is continuously stirred by the flow of water. A heater is placed at the bottom of the water-bath. A contact thermoregulator and a thermister are placed in the middle of the water bath. The temperature of the solution is watched by a mercury thermometer readable to 0.005°C. Purified nutrient of NaClO₃ is entirely dissolved in the vessel. When the temperature of the vessel drops, excess amount of dissolved NaClO₃ precipitates. When precipitation occurs, the solution is stirred by the Teflon-coated rotator, while the temperature is kept constant by the control unit. After few days, the solution and the precipitates coexist together in equilibrium, and the solution is assumed
to reach the saturated condition at a constant temperature, $T_s$. A part of the saturated solution is transferred from the vessel into solution reservoir, where temperature is kept higher than $T_s$ to prevent undesired precipitation.

The cell for in-situ observation is constructed with upper and lower chambers as shown in Fig. 1, a similar design as that reported by Hosoya and Kitamura (1978). The frame of the cell and the windows are made of glass, so that in-situ observation can be made on the stage of an optical microscope. The upper chamber of 1 mm in thickness and 20 mm across is filled with the solution and the temperature is controlled by the flow of thermostated water running in the lower chamber. The thermostated water is generated in a copper tube placed in the middle way to the chamber. This copper tube has a shape of coil in whose middle space a heater is installed as shown in Fig. 2. This modification is necessary to carry out the experiment for a wide range of super- and undersaturation. Temperature of the running water is measured by a chromel-alumel thermocouple placed in contact with the glass plate at the lower side of the upper chamber. At the same place, thermistor is also placed for controlling

Fig. 1. Diagram of the cell for in-situ observation. A: thermocouple, B: thermistor, C: seed, S: solution.

Fig. 2. Block diagram to show the set-up of the apparatus.
the temperature of water through the control unit, where the continuous control using a silister is operated. The temperature of the cell is regarded as the growth temperature, $T_g$, after recalibration is made using the growth and dissolution rates, which will be described in a later section. Due to thermal inertia, it takes about a few minutes to settle the temperature of the chamber at a constant value within a fluctuation of $\pm 0.1^\circ\text{C}$ after commencing to circulate new thermostated water.

Although in the present experiment, the temperature fluctuates more as compared to the apparatus in Hosoya and Kitamura (1978) in which the temperature was controlled within a fluctuation of $\pm 0.01^\circ\text{C}$, it has an advantage in that super- or undersaturation can be controlled much widely and more easily by changing the setting of register of the control unit. As will be described later, the data obtained using this apparatus had enough precision to be used for discussion of the growth and dissolution mechanisms. A similar apparatus is also used to study the nucleation and growth of NaClO$_3$ crystal from the aqueous solution (Oohira, 1979), which will be reported separately.

**Actual measurement**

Before a saturated solution is supplied, a seed crystal is placed at the center of the bottom surface of the upper chamber, whose temperature is maintained at a higher temperature than $T_s$. Seed crystals are prepared in another sealed beaker by spontaneous nucleation process. The saturated solution prepared in the apparatus is then poured from the reservoir into the upper chamber, followed by sealing the chamber with molten paraffin. Since the solution is undersaturated, no nucleation takes place at this stage, and the seed crystal will start to dissolve to some extent. The whole cell is fixed on the microscope stage. After the seed crystal dissolves to a sufficiently small size, the temperature of the water in the lower chamber is changed to $T_g$, and in-situ observation is initiated. After the seed crystal is recovered to the initial size, the growth and dissolution processes are alternatively observed by changing the temperature of the water in the lower chamber. In this experimental system, the temperature of the saturated solution, $T_s$, is fixed, while the temperatures of growth and dissolution are changed in a wide range. Both growth and dissolution experiments are made on one and the same seed crystal in one experimental run. An example of actual temperature programme is shown in Fig. 3. Since the solution may be boiled if a very high supersaturation as corresponding to $T_s-T_g = 40^\circ\text{C}$ is aimed, which will certainly reduce the precision, we have fixed the $T_s$ around 40°C.
Although any microscopic techniques may be applied, the dark field and inclined illumination techniques have been used to take a series of photographs. Under dark field illumination, the crystal surface parallel to the optical axis, i.e., perpendicular to the chamber surface, appears as a bright sharp line. Inclined illumination technique is powerful to observe shapes of the crystal and the inclusions.

The solubility curve for NaClO₃ is assumed to be linear against concentrations. The line calculated by the least squares method using the published data of solubilities by Bennema (1965) is used similarly as in the previous work (Hosoya et al., 1978). The solubility data by Bennema cover the range from 20°C to 50°C, in which region the curve may be regarded as a straight line. For lower temperature range than 20°C, the data by Linke (1965) were used in the present study, after calibration, since the curve in this region deviates slightly from the extrapolated line of the Bennema’s curve.

Results

Recovery process

The seed crystal is at first dissolved and takes a rounded form. Starting from this rounded morphology, the seed changes its morphology to a faceted one as growth proceeds, and eventually becomes a cube bounded by {100}. This process is called the recovery process (Hosoya and Kitamura, 1978). During this process, it is seen that several different faces appear but eventually only one stable form remains, that liquid inclusions are trapped, and that kinematic wave layers advance inward from the edges of the crystal.

Although the actual recovery processes are slightly different in different runs, it is noticed as a general tendency that several higher index faces such as {120}, {140} appear at first, together with {100} and {110}, but the formers
eventually disappear, resulting in a faceted morphology bounded by (100) alone or with small (110). An example of the process may be seen in a series of photographs shown in Fig. 4. Fig. 5 shows the enlarged photographs of the corners. Essentially similar tendency has been reported by Hosoya and Kitamura (1978). The supersaturation of the final stage, when the faceted morphology is stabilized, is about 1.5%. The supersaturation during the initial stage of the recovery process should have been much higher than 1.5%, since the solution near the interfaces becomes thick due to the preceding dissolution of the seed. Normal growth rates were measured from these photographs, which indicate the order of \((120) > (140) > (110) > (100)\) as seen from the solid line in Fig. 6.

A series of in-situ observations of the recovery process also indicates that inclusions of mother liquid are formed during the recovery process particulary along the edges of a faceted crystal, where transformation from curved surfaces to flat faces occur. Fig. 4 serves to demonstrate the process. This transformation occurs essentially due to the changes of kinematic waves.

It was also observed in some runs that kinematic waves (thick growth layers) originate from the edge and spread to the centre of the face. The advancing rates of such layers were measured from the photographs, which indicate that the layers advance rapidly but soon the rate slows down with time.
Fig. 5. High magnification photographs of corners, showing the recovery process in Fig. 4. Every frame at 1 minute interval.

Fig. 6. Plot of growth rates (solid circles and line) and attachment energies (open circles and dotted line) of different faces, showing growth rate anisotropy.

**Inclusion trap**

Fig. 7a and b are transmission photomicrographs of the crystal obtained in the experiment with the temperature fluctuation shown in Fig. 3. The crystal was grown in 3 hours, within which there are four stages of growth, below $T_s$. 
and the initial and the following two stages of dissolution, above $T_s$. Figure a is a photomicrograph taken with a bright field illumination, and b a set of photomicrographs taken from three different sides with a dark field illumination. In Fig. 7a, points 1 and 4 correspond to the points immediately after a sharp increase of growth rates, whereas points 2 and 3 to the points immediately after the transition from dissolution to growth (see also Fig. 3 where the corresponding points are also indicated).

Both photomicrographs demonstrate that liquid inclusions are trapped, parallel to the interfaces, at all points 1 to 4, corresponding to the places where drastic changes occur and not at other places except corners. As to inclusion traps at corners of crystals, description is already given in the earlier section. The drastic changes occur either by sharp change in growth rates, or by transition from dissolution to growth. No essential difference in the morphologies and densities of liquid inclusions is noted between the two cases.

**Growth and dissolution forms**

Principally two different types of combination of faces are observed on the final faceted morphology depending on the supersaturation; cubic form bounded by well developed {100} and smaller {110} appears under lower supersaturation than about 2%, whereas simple cube with only {100} faces appears under higher supersaturation, though small {110} faces may occasionally associate in the latter.
Fig. 8. Representative photographs showing the change of morphology as increasing supersaturation. The crystal is bounded by (a) flat \{100\} and \{110\} faces, (b) flat \{100\} faces only, and (c) concave \{100\} faces.

Under much higher supersaturation, say higher than about 20\%, \{100\} faces transform to concaved surfaces, resulting in a hopper type morphology (Fig. 8).

In the dissolution process, crystals exhibit a variable morphology depending upon the state of inclusions, though they take essentially rounded morphology bounded by curved surfaces.

Growth and dissolution rates

Growth rate measurements were made on \{100\} faces, which are the most stable face. The dissolution rates were also measured on \{100\} faces at the points where the tangent of the face is parallel to \langle100\rangle. The whole measurements were performed throughout a run in which temperatures are alternatively changed several times below and above \(T_s\). Therefore, in one run, both growth and dissolution rates are measured. Several different runs were made using

Fig. 9. Plot of growth rate \((\times 10^{-6}\text{cm}\cdot\text{sec}^{-1})\) vs. super- and undersaturations.
different seed crystals. Photographs were taken at every minute. Measurements were initiated immediately after the temperature of the cell was stabilized, which was in general a few minutes after the on-set. The supersaturations were recalculated for the point where the growth and dissolution rates can be regarded as zero. The measurements were made in six different runs and for the supersaturation range, 1.1~49%, and for the undersaturation range 1.6~4.5%. The obtained data are given in Table 1a and b and plotted in Fig. 9, where the normal growth and dissolution rates are plotted against the super- and undersaturations. As can be seen, the data smoothly change with the super- and undersaturations, and there is no systematic variation due to different seed crystals.

**Table 1.** Data of bulk supersaturation \( (\sigma_B, \%) \), growth rates \( (R, \times 10^{-4}\text{cm/sec}) \) and growth temperature \( (T_g, ^\circ\text{C}) \) (a), and similar data for dissolution (b).

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Discussion

Growth rate anisotropy

As already described, the seed crystal is at first dissolved to take a rounded form, thereafter the recovery process is initiated. It follows from this that the concentration around the crystal during the initial period of the recovery process is much higher than the bulk. Due to this high supersaturation and to the rounded surface of the seed, the expected growth mechanism during the recovery process is that for rough interface or for high supersaturation, i.e. growth is controlled by volume diffusion. This is evidenced by the fact that some interfaces are concaved, as can be seen in Fig. 4. Similar tendency is noted in the observations by Hosoya and Kitamura (1978).

The growth rate anisotropy obtained in this work may be correlated with the anisotropy of the crystal structure. Assuming that the interfaces are flat even for higher index faces, the attachment energies defined by Hartman (1973) are calculated by Miyata, which gave the following values; \{100\} 6.22 kcal/mol, \{110\} 14.04 kcal/mol, \{140\} 22.71 kcal/mol, \{120\} 26.13 kcal/mol. The ratios of the attachment energies to that of \{100\} are plotted in Fig. 6, by a dotted line. As is clearly seen in this figure, both the dotted line showing the attachment energies and the solid line representing the growth rate anisotropy exhibit a similar tendency. Since it is generally assumed that the attachment energies are related with the normal growth rates (Bennema, 1969), the observed growth rate anisotropy is in good accordance with the calculated attachment energies on the order of magnitude.

Growth and dissolution forms

Dissolution forms are strongly dependent on both the overall morphology of the original crystal and the heterogeneous distribution of defects, i.e. strains on the surface. Corners of a crystal is dissolved much faster than the face centre. Among surface defects, the outcrops of liquid inclusions seem to play the most important role as preferential sites for dissolution.

As to the growth forms in the lower supersaturation range, appearance of \{110\} faces is worth to pay a special attention (Fig. 8). Bennema (1965) reported that in a very low supersaturation range, \{110\} faces appear occasionally truncating the cube edges, and regarded the form bounded by \{100\} and small \{110\} as a growth form which is expected near the equilibrium condition. In the observations reported by Hosoya and Kitamura (1978), which were made under higher supersaturation range than Bennema’s experiment, \{110\} faces was not observed as a stable growth face. These observations suggest that the morphology
of NaClO₃ changes depending on the supersaturation. In the present experiment, \{100\} appears under higher supersaturation range, whereas \{110\} may sometime occur in lower supersaturation range. Since the present experimental condition where \{110\} appears is inbetween the conditions of Bennema’s experiments and Hosoya and Kitamura’s experiment, the occasional occurrence of \{110\} may be inferred to minute fluctuations in either solute or heat flows.

As to the transformation from flat to concave surfaces seen in the higher supersaturation range, we shall discuss in the next section.

**Growth and dissolution mechanisms**

Both the present data and the data obtained in our laboratory using essentially similar apparatuses (Hosoya and Kitamura, 1978a, 1978b; Hosoya et al., 1978; Matsunaka et al., 1980) are plotted against bulk supersaturation in Fig. 10a. In Fig. 10b, both data by our laboratory and by Bennema (open circles) are plotted. There is no systematic deviation of data depending on different seed crystals, nor on different experiments. Thus, it is assumed that nearly equal situations are realized as to the defect distributions in the seed crystals. We shall therefore use all the data plotted in Fig. 10a to discuss the growth and dissolution mechanisms.

As shown in Fig. 10a and b, the interpolated line of the growth rates has two kinks and the whole region can be divided into three; region (A), \(\sim 0.0\% \sim 2.5\%\), region (B) \(\sim 2.5\% \sim 8.0\%\) and region (C) \(\sim 8.0\% \sim 50.0\%\) in bulk supersaturation, \(\sigma_B\). The interpolated line for the region (A) is drawn, taking the data by Bennema into consideration. The interpolated lines of region (A), (B) and (C) have gradients of nearly 1, 3 and 0.5, respectively. The transitional supersaturation from the region (A) to (B) is similar to the values reported in Hosoya et al. (1978), i.e. \(\sim 2.8\%\). We shall discuss the predominant growth mechanism in each region, because there is no theory that can give a unique explanation for the whole data.

Since our data of supersaturation are on the bulk supersaturation \(\sigma_B\), and actual growth is determined not by \(\sigma_B\) but by the interface supersaturation \(\sigma_S\), we have at first to investigate how \(\sigma_S\) is related to \(\sigma_B\). The relation between \(\sigma_B\) and \(\sigma_S\) is not simple, since \(\sigma_B\)'s may vary considerably from position to position on the surface of a euhedral crystal. Follenius (1959) applied François method to estimate \(\sigma_S\) and \(\sigma_B\) around a growing euhedral crystal of NaClO₃. Her data are graphically represented in Fig. 11. In this figure, \(\sigma_S\) corresponds to the interface supersaturation at the central position of a (100) face, \(\sigma_{S(c)}\). As is well known (Berg, 1938), the supersaturation at the edge of a face, \(\sigma_{S(e)}\), is larger than \(\sigma_{S(c)}\). \(\sigma_{S(c)} < \sigma_{S(e)} < \sigma_B\). As can be seen in Fig. 11, \(\sigma_{S(c)}\) has in
Fig. 10. Log plot of growth rate ($\times 10^{-6}$ cm•sec$^{-1}$) vs. $\sigma_B$. (a) Present data plus the data obtained in our laboratory. (b) Plus Bennema's data. ●...present data ○...Bennema's data (1965).
general a linear relation with $\sigma_B$, though in the lower supersaturation region, $\sigma_S(c)$ becomes larger than the interpolated line, suggesting the change along the dashed line. This increase is similar to the increase in computer simulation of Kuroda et al. (1977) up to $\sigma_B$ 10%. Although no data have so far been published for the supersaturation at the edge of the crystal, $\sigma_S(e)$, it can be estimated from the figures in Follenius’s paper that $\sigma_S(e)$ is somewhat around 1.3 times of $\sigma_S(c)$ in high supersaturation region. We shall therefore discuss our data, using the above estimations on $\sigma_B$ vs. $\sigma_S$ relation.

Region A. In the supersaturation region below $\sigma_B < 2.5\%$, the line has a gradient of nearly 1 (Fig. 10), which may well correspond to the relation in the Bennema's data at higher supersaturation region within his experimental range (see open circles in Fig. 10b). On the other hand, the interpolated line in the lower region of Bennema's data has a gradient of nearly 2. Both lines with gradient 2 and 1 were interpreted to correspond to BCF mechanism by Bennema (1967), who estimated from the lines $\sigma_1$ to be very small as $6 \times 10^{-3}$, and C as $1.6 \times 10^{-4}$ cm·sec$^{-1}$ in the following BCF formula,

$$ R = C \cdot \frac{\sigma_S^3}{\sigma_1} \tanh \frac{\sigma_1}{\sigma_S}. \quad (1) $$

According to Bennema, the line with gradient 2 corresponds to the parabolic law, and the line with gradient 1 to the second linear law of BCF mechanism.

The relative shift of the present line in the region A from the Bennema’s line with gradient 1 (Fig. 10b) comes from the difference between the two experimental systems. He used the system with stirring, while no in the present system. If the $C$ value in our data is adjusted to that of the Bennema’s estimation, $\sigma_S(c)$ becomes $\sim 0.8 \sigma_B$, which satisfies the Follenius’s data (Fig. 11).
leads us to conclude that in region A, the BCF mechanism by the screw dislocation near the center of a crystal surface also operate in the present experiment.

**Region B.** In the region B, the line in Fig. 10a has a gradient nearly equal to 3. The growth mechanism corresponding to this region was investigated in detail in our previous paper (Hosoya et al., 1978), which lead to the conclusion that B & S model of 2DNG mechanism was the most appropriate mechanism. We shall re-investigate the validity of our previous conclusion, using all the data and the relation of $\sigma_S$ and $\sigma_B$.

Because the growth by B & S model can be assumed to be more predominant at the edge than at the center of a face, we should investigate $R(\sigma_B)$ relation, using the relation between $\sigma_S(e)$ and $\sigma_B$. Here, a simple relation of $\sigma_S(e) = 1.3(\sigma_B + \sigma_S)$ is assumed for this region as a first order approximation. The constants in the linear relation are obtainable from the range of $\sigma_S(c)$ in this region and two lines for the region A and region C in Fig. 11. Using these constants, we shall investigate the data using the following equation for B & S model (Ohara and Reid, 1973):

$$R = \left( \frac{2\pi C_0}{3} \right)^{1/3} \cdot \frac{2\lambda_3}{a} \cdot C \cdot \sigma_S^{3/4} \cdot \ln(1 + \sigma_S)^{1/6} \cdot \exp \left[ -\frac{\pi}{3} \left( \frac{\gamma}{K_T} \right)^2 / \ln(1 + \sigma_S) \right]. \quad (2)$$

The data are plotted using the following expression, and assuming C as constant in different temperatures within this region:

$$\ln \frac{R}{\sigma_S^{3/4} \ln(1 + \sigma_S)^{1/6}} = -\frac{B_{B \& S}}{T_k^2 \ln(1 + \sigma_S)} + \ln A_{B \& S} \quad (3)$$

![Graph](image)

**Fig. 12.** $\ln \left[ \frac{R}{\sigma_S^{3/4} \ln(1 + \sigma_S)^{1/6}} \right]$ vs. $10^3 T_k^2 \ln(1 + \sigma_S)$ plot.
This plot (Fig. 12) indicates that B & S model is again assumed to be the most suitable mechanism. The values, $A$ and $B$ in eq. (3), are calculated from the line fitting, which gave $A \approx 3.4 \times 10^{-4}$ cm·sec$^{-1}$ and $B \approx 0.3 \times 10^{4}$. The X-ray topographic study by Matsunaka et al. (1980) on NaClO$_4$ crystals grown in our laboratory, using a similar method, also supports substantially this conclusion for the region (B).

Region C. In the region (C), the gradient of the interpolated line (Fig. 10) is less than 1, which gives some problems, since there is no theory in which such gradient is expected for interface kinetics. If growth is principally controlled by volume diffusion, we should expect a gradient of 1. Therefore neither volume diffusion mechanism nor interface kinetics mechanism gives appropriate explanation for the observed gradient. Although more data may be required to investigate in detail the growth mechanism in this region, we may suggest the following two possibilities to account for the observed gradient. Firstly, if both volume diffusion and interface kinetics processes co-operate, the gradient can be different from theoretically expected gradient. However, in this case, a gradient less than 1 can not be expected. Secondly, the deviation in gradient from theoretically expected one may be due to the lack of temperature correction. All the experiments in the present study have been performed using a saturated solution at a constant temperature. Thus a correction for the growth temperature is necessary. For the region (A), this correction is not required since the temperature differences among the data are negligibly small. For the region (B), this was already taken into consideration as discussed above. But for the region (C), where the gradient of the interpolated line is less than 1, the effect of growth temperature should be taken into consideration. Due to this effect, a gradient can become smaller than 1. We therefore assume that the linear law may well correspond to the "maximum linear law", and due to temperature effect, the gradient became smaller than 1.

We may therefore conclude that

1. BCF mechanism followed by the second linear law is operating in the region (A), i.e. $\sigma_{B}$ 0.0~2.5%

2. Birth and Spread model of 2DNG mechanism is applicable for the region (B), i.e. $\sigma_{B}$ 2.5~8.0%, and

3. the maximum linear law may be applied for the region (C), i.e. $\sigma_{B}$ 8.0~50.0%.

It should be added here that these conclusions are applicable for the crystals with sizes around 0.5 mm across. For crystals much smaller or larger than this size, some modifications may be required.

For the mechanism of dissolution process, no detailed theory taking the
interface kinetics into consideration has been put forward. The present data of NaClO₃ show that there is a significant deviation from the linear relation between the bulk undersaturation and the dissolution rates. This deviation should be taken as indicating the effect of interface kinetics. Further investigation is required along this line.

As a final comment, we should mention the difference between our experiment and the experiments by the weighing method, like Bennema’s experiment. In the weighing method, σ_B can be measured more precisely than in our method, since a much larger volume of solution is used. In our method, σ_B measurement is less accurate, since it is estimated from the temperature of a solution of a much smaller volume, although the method has a big advantage in that the growth process can be observed in situ, whereas in the weighing method this is not possible. In spite of the difference between the two methods, both data exhibit a similar tendency on R vs. σ_B plot (see Fig. 10b). Thus, it is reasonable to make a theoretical analysis of our data, although our data may be less accurate than those obtained by the weighing method.

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