

# Growth Kinetics and Behavior of NaCl Single Crystals in Supersaturated Solutions

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## ABSTRACT

The growth rate of NaCl single crystals placed in supersaturated aqueous solutions was measured over a range of experimental conditions to investigate the behavior of crystal growth specific to sodium chloride. It was found that the growth rate at a fixed level of agitation was proportional to the square root of the solution supersaturation. Very high growth rates were observed when micro-crystals were present in the solution, indicating that the micro-crystals contributed to the growth rates. Together with the observation that the crystal surfaces were rough under such conditions, this suggests that attachment of fine crystals might occur in addition to the incorporation of micro-crystals as macro-growth units.

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## INTRODUCTION

Detailed studies of crystal growth kinetics have usually been carried out using a single crystal. Measured growth rates are compared with theoretical models and thus the growth mechanisms can be deduced (Garside et al., 1991). On the other hand, when studying industrial crystallization the growth kinetics are always discussed for multi-particle systems and it is the average growth rates that are of significance in designing crystallizers (Special Issue of Bull. Soc. Sea Water Sci., 1990) and understanding their growth behavior. In the latter case phenomena specific to multi-particle systems such as nucleation, crystal breakage and agglomeration may be involved in the growth kinetics (Jancic and Grootscholten, 1984). This is true for the study of crystal growth of sodium chloride. Most studies carried out for sodium chloride crystallization phenomena have been done using multi-particles, whereas few studies have been reported on the detailed kinetics and phenomena of single crystal growth for the salt.

In the present study growth of sodium chloride crystals from supersaturated solutions is investigated experimentally under a wide range of conditions including solution supersaturation, degree of agitation, crystallization temperature and the presence or absence of micro-crystals in the solution. The influences of these variables on the growth kinetics and associated phenomena are discussed in detail.

## EXPERIMENTAL

### Materials and seed crystals

Commercial table salt containing more than 99% sodium chloride was used after purification by washing with ethanol and subsequent recrystallization from aqueous solutions to eliminate possible impurities like magnesium sulphate and magnesium chloride. Seed crystals of sodium chloride were taken from naturally grown nuclei prepared as follows: in an aqueous solution with a supersaturation of 2 or 3 °K at 313°K droplets of a solution saturated at about 333°K were added where upon primary nucleation was observed. The nuclei were allowed to grow in the solution. Resulting well defined crystals about 1.5 mm in dimensions were selected as the seed crystals. They were drilled on one face and glued to a platinum wire of 0.3 mm diameter.

### Apparatus

Growth experiments were carried out in a small stirred tank crystallizer as shown in Fig. 1. The tank was made of glass and was fitted with a jacket. The inner diameter of the inner vessel was 40 mm and its depth was 100 mm. The bottom glasses of the inner and the outer tanks were made from optically distortion-free glass plates. Water from a thermostat bath flowing through the jacket maintained the solution in the tank at the crystallization temperature. A paddle type stainless steel impeller with two blades

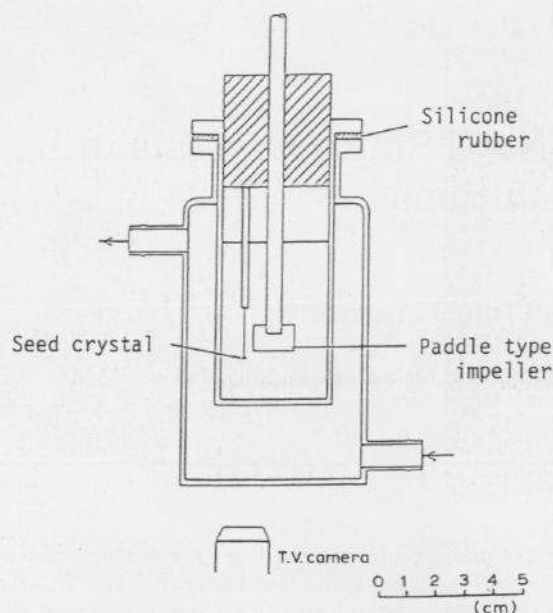


Fig. 1. Set up of the stirred tank crystallizer.

was used. The seed crystal at the tip of the platinum wire was placed close to but slightly below the impeller. The growing crystal was observed with a TV camera having a microscope lens located beneath the tank bottom. The linear growth rate of the seed crystal was determined from the displacement of the crystal on the monitor screen divided by the growth period. The magnification on the screen was approximately 30 or 70 times.

#### Experimental procedure

Seventy ml of aqueous solution, its supersaturation having been carefully adjusted, was placed in the crystallizer and the seed crystal was immersed in the solution. After confirming that the crystal on the monitor screen was square and placed horizontally, recording was started ( $\theta = 0$ ).

The combinations of the experimental variables used in the experiments are summarised in Table 1. The experiments were classified as Group I and Group II depending on the respective objectives: Group I was carried out to provide growth kinetics of single crystals at different temperatures and supersaturations, while Group II was aimed at studying the influences of agitation speeds and micro-crystals on the crystal growth kinetics.

#### Generation of micro-crystals

Since supersaturated aqueous solutions of sodium chloride are rather unstable, primary nucleation is often induced. For the experiments of Group I, only growth without nucleation was recorded, while in

TABLE 1

Combinations and ranges of experimental conditions

Group of run	Crystn. temp. T [°K]	Supercooling $\Delta T$ [°K]	Agitation N [Hz]	Micro-crystal
I	303	2.0-7.0	0.83	Absent
	313			
	323			
II	313	3.0	0-25	Present or absent

Group II growth with and without such nucleation was measured. In a few Group II runs ground powder or commercial granular particles of NaCl was added to cause secondary nucleation and thus provide micro-crystals.

## EXPERIMENTAL RESULTS

#### Observation of crystal surface morphologies

For crystals grown from clear solutions without micro-crystals, surface morphologies varied with the agitated speed in such a way that the surface became rough as the agitation speed increased. With increasing agitation speeds, the surface first began to lose smoothness, then some rough structures appeared, and finally the surface became covered with many projecting structures as if surface nucleation had occurred. Figure 2a illustrates the surface morphology of the crystal grown under the conditions of supersaturation = 2°K, T = 313°K and N = 0.83 Hz.

For crystals growing in solutions with micro-crystals (Group II), the surfaces were rougher compared with those without micro-crystals. More detailed study showed that for agitation speeds up to 1.5 Hz (100 rpm), surfaces were on average smooth with only small rough sites (Fig. 2b). Observed tiny crystals in the solution all settled down to the bottom of the vessel within 20 min.

For agitation speeds of 2-8 Hz (120-500 rpm) the tiny crystals were suspended in the solution and the surface were rough.

Above 8 Hz the surface was very rough and attachment of tiny crystals was clearly observed as shown in Fig. 2c.

#### Effects of supersaturation and temperature on growth rates

From the experimental results of Group I, the average linear growth rate  $\bar{G}$  was correlated as a function of the solution supersaturation and the

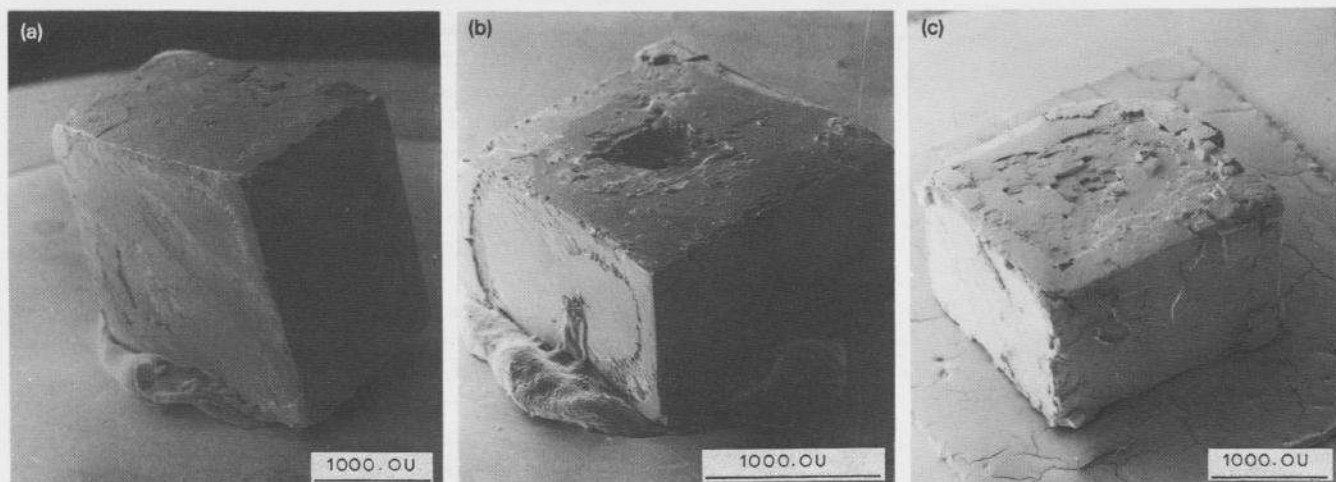


Fig. 2. SEM photomicrographs of NaCl crystal surfaces. (a)  $T = 2$ ,  $T = 313^\circ\text{K}$ ,  $N = 0.83$  Hz in the absence of micro-crystals. (b)  $T = 3$ ,  $T = 313^\circ\text{K}$ ,  $N = 1.7$  Hz in the presence of micro-crystals. (c)  $T = 3$ ,  $T = 313^\circ\text{K}$ ,  $N = 12$  Hz in the presence of micro-crystals.

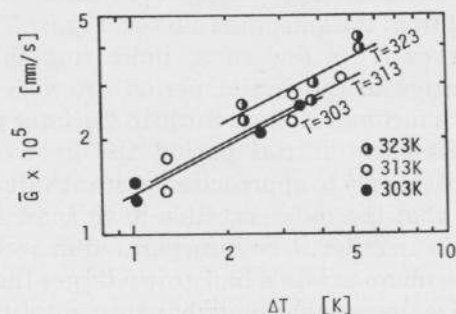


Fig. 3. Growth rates vs. supersaturations for Group I.

temperature of the solution (Fig. 3) assuming a power equation of the form  $\bar{G} = k\sigma^n$  as at:

$$\begin{aligned} 323^\circ\text{K} \quad \bar{G} &= 7.50 \times 10^{-4} \sigma^{0.57} & (\bar{G} &= 5.12 \times 10^{-4} \sigma^{0.5}) \\ 313^\circ\text{K} \quad \bar{G} &= 5.63 \times 10^{-4} \sigma^{0.54} & (\bar{G} &= 4.40 \times 10^{-4} \sigma^{0.5}) \\ 303^\circ\text{K} \quad \bar{G} &= 3.92 \times 10^{-4} \sigma^{0.49} & (\bar{G} &= 4.25 \times 10^{-4} \sigma^{0.5}) \end{aligned}$$

where the average linear growth rate was calculated from the crystal face displacement over one hour and  $\sigma$  was defined as the ratio of the concentration driving force divided by the saturated concentration. The relations in the parentheses represent those when the growth rates are assumed to be proportional to the square root of the supersaturation. The following solubility correlation (Scrutton and Grootsholten, 1981) was adopted and was confirmed to hold experimentally:

$$w = 0.26281 + 1.66243 \times 10^{-5} t + 2.04113 \times 10^{-6} t^2 - 3.4166 \times 10^{-9} t^3$$

where  $w$  [mass fraction] and  $t$  [ $^\circ\text{C}$ ] =  $T - 273.15$ .

The activation energy of growth was found to be

7.5 kJ/mol from the Arrhenius plots of the growth rate coefficients  $k$  when the growth rate is assumed to be proportional to the square root of the supersaturation. It was observed that when the crystals grew faster than about 0.075 mm/h the surfaces were rough and at supersaturations greater than 0.0035 one of the corners grew abnormally fast.

#### Effects of agitation speed and micro-crystals

The growth rates in Group II experiments are shown in Fig. 4. The data points could be clearly classified into two groups; those with micro-crystals present and those with them absent. Although the data have a considerable scattering, the average linear growth rates were about twice as large for the crystals growing in the presence of micro-crystals. In addition the growth rates increased as agitation speed increased for  $N < 7$  Hz (400 rpm), while above this agitation level the growth rates seem to have approached constant values. This observation coincided with that of a previous study in which organic crystals were grown in a very similar experimental

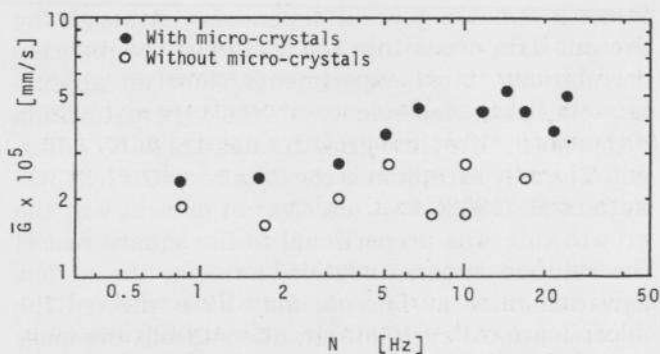


Fig. 4. Effects of micro-crystals on growth rates for Group II.

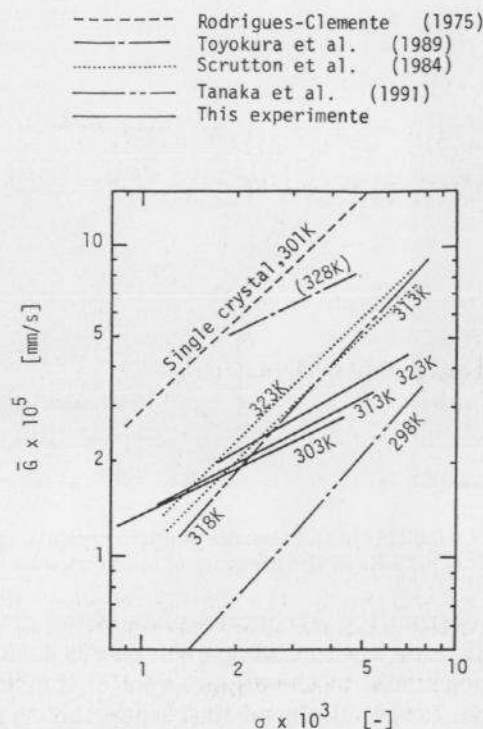


Fig. 5. Comparison of the present growth rates with literature data. All the data except those of Rodrigues-Clemente (1975) are for multi-crystals.

assembly and showed constant growth rate above 12 Hz (700 rpm) (Matsuoka et al., 1985). The difference in the critical agitation speed is due to the difference in physical properties such as diffusivity and kinematic viscosity.

## DISCUSSION

### Dependence on supersaturation

All the linear growth rates at 0.83 Hz (50 rpm) without micro-crystals were roughly proportional to the square root of the solution supersaturation. When this result is compared with previous data for growth rates as shown in Fig. 5, it is found that this is not a common general dependence although the present data are within the scatter of the reported correlations. Most experiments show an approximately linear dependence on the supersaturation although the absolute growth rates are fairly different. The only exception is the data reported by Toyokura et al. (1989). It is not clear at present why the growth rate was proportional to the square root of the solution supersaturation, however the as low agitation rates as 50 rpm may have affected the dependence. At such low agitation speeds the mass transfer resistance cannot be neglected and the rate of mass transfer strongly depends on the Reynolds

number. Since the kinematic viscosity is lower in the lower supersaturation solutions the mass transfer rate in the low supersaturation solution might be higher and hence the overall crystal growth rates are higher to some extent. However this explanation may not be sufficient for the enhancement of growth rates in the low supersaturation region. Further studies are needed to analyze the phenomena.

### Transient growth rate

In order to see how fast the crystal grows at any moment in a batch crystallization when in the presence of micro-crystals, the crystal dimensions were measured every ten minutes in a few runs. Figure 6 shows the increase of the crystal length as a function of the growth period. It is very clear that the crystals increased their dimensions faster in the presence of the micro-crystals than in their absence. By graphical differentiation transient growth rates were determined from the smoothed curves; Figure 7 shows such curves for a few runs, indicating that the growth rates in the initial period are very much faster by a factor of 20 than those in the later period. After this short initial period the growth rate decreased sharply to approach a constant value. This suggests that the micro-crystals have some limitation in size in order to be incorporated in seed crystals. Once micro-crystals had grown larger than this critical size they cannot contribute to crystal growth.

This critical size can be estimated from the average growth rate at a given supersaturation and the period over which they are effective at influencing growth, this being estimated from Fig. 7 to be not longer than 10 min. Over this period the transient growth rate decreased by a factor of 10. For example

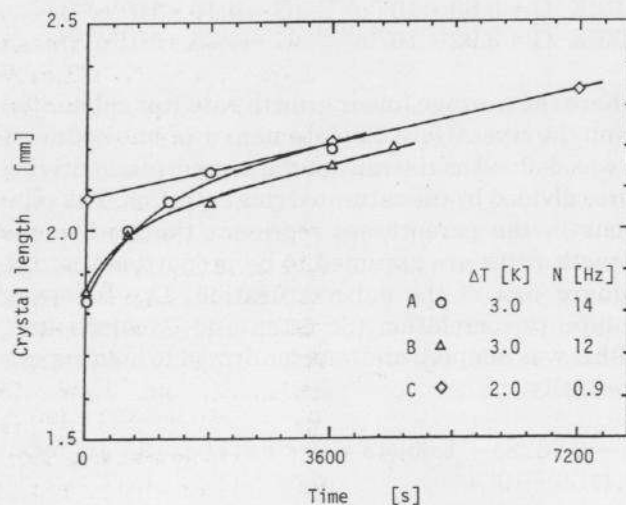


Fig. 6. Changes in crystal size during growth with and without micro-crystals.

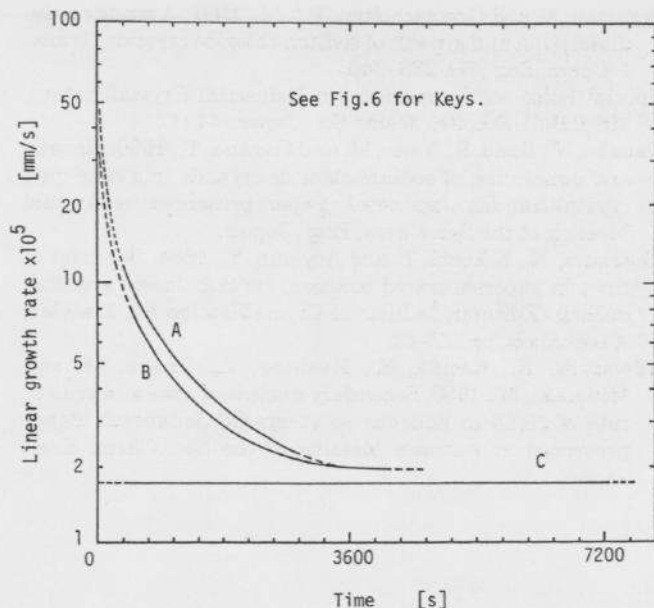


Fig. 7. Transient growth rates of crystals.

crystals A and B in Fig. 6 might have grown in the solution of under-cooling  $3.0^{\circ}\text{K}$  at  $313^{\circ}\text{K}$  at a rate of  $0.08\text{ mm/h}$  (from Fig. 4). If the initial newly born micro-crystals are assumed to be of zero size, the critical radius will be given, by multiplying the effective growth period and the growth rate, as  $13\text{ microns}$ . This may be much larger than any likely new born micro-crystals, hence the assumption of initial size may not have a significant effect on this estimated critical size.

When the ground crystals were added to the solution the growth rates did not increase, rather they became even lower soon after the addition. Since the added powder had a size distribution ranging from  $50$  to  $100\text{ microns}$  and this is clearly larger than the critical size, they did not contribute to either the growth or generation of secondary nuclei: they simply grew to consume the supersaturation.

#### Growth mechanism

When crystals are growing in a solution containing micro-crystals and other crystalline particles the growth kinetics are influenced by them. It is reasonable to assume that the micro-crystals are incorporated into the crystal lattice during crystal growth as macro-growth units. This phenomenon is different to the agglomeration of crystal particles since it results in single crystals. Even though the crystal surfaces are rough, the crystals can be single crystals as reported by Davey et al. (1991). Since considerable differences were found in the average growth rates between growth with and without micro-crys-

tals and that clusters may exist in any supersaturated solutions with or without the presence of micro-crystals, the differences in growth rate were attributed to the existence of the micro-crystals not to the clusters. Clusters may be stable or unstable in supersaturated solutions but they are defined as being smaller than some critical size; they are thus smaller than nuclei. The micro-crystals discussed here are larger than such nuclei but may be smaller than so-called fine crystals visible in the solution. Fines may contribute to crystal growth, and result in the production of rough agglomerated crystals. On the other hand micro-crystals can act as macro-growth units and therefore their existence enhances growth kinetics.

#### CONCLUSIONS

The growth of NaCl single crystals was measured under a wide range of conditions including solution supersaturations, temperature, agitation speed and the presence of micro-crystals. The average growth rates over a one hour growth period in the absence of micro-crystals are correlated as a function of the supersaturation and temperature of the solution. It was found that the average growth rate is increased by the presence of micro-crystals by a factor of up to 2. From the transient growth behavior the contribution of micro-crystals to the growth kinetics was discussed and a growth mechanism whereby the micro-crystals are likely to be incorporated into the crystal as macro-growth units was suggested.

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#### NOMENCLATURE

$\underline{G}$	transient linear growth rate [m/s]
$\bar{G}$	average linear growth rate [m/s]
$k$	overall growth rate coefficient [m/s]
$N$	agitation speed [Hz]
$T$	temperature [ $^{\circ}\text{K}$ ]
$t$	temperature [ $^{\circ}\text{C}$ ]
$w$	concentration in mass fraction [-]
$\theta$	time (growth period) [s]
$\sigma$	supersaturation ratio [-]

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