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On The Growth Behaviour of NaCl Crystals With and Without Additives

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ABSTRACT

Growth rates of NaCl crystals have been examined in different types of laboratory equipment in order to gain a better understanding of the growth behaviour and the growth kinetics. Effects of growth rate dispersion (GRD) have been studied under conditions also favouring the random fluctuation (RF) model as the constant crystal growth (CCG) model. The experimental units are a fluidized bed (for the crystal collectives) and a microscopic cell (for the single crystals). Effects due to the crystal surface quality have also been examined by means of the above-mentioned equipment.

A number of additives have been introduced to see their effects on the growth rates. This has again been done in both types of equipment in order to check how the growth rates respond with single crystals on the one hand, and on the other with crystals collectives that means as average growth rates. Among the additives are e.g. lead chloride and magnesium chloride as additives with a common ion, and $K_3Fe(CN)_6$ as an additive without a common ion.

The results achieved have been used in a comparison with other crystals growing from aqueous solutions where the same experiments have been executed. Conclusions for growth mechanisms have been compared with those known from the literature.

INTRODUCTION

Considering that sodium chloride is such an interesting and popular material, it is surprising how few papers on the crystallization of this material exist, and hence how few data on the growth behaviour are available. A good summary and evaluation of these data up to 1985 was made by Langer (1985) who listed 14 papers dealing with the subject.

Theories and new methods introduced into crystallization in the last few years, such as growth rate dispersion and the way to prove the dominance of surface integration or diffusion steps in the growth kinetics of crystals by comparing perfect with fragmented crystals, will be applied here. Furthermore, the use of additives will be introduced in the discussion. Therefore results of experiments with additives will be presented.

BACKGROUND

Bearing in mind growth rate dispersion as an explanation of experimental growth rate data, special equipment for the experiments has to be chosen. Before the equipment is described, growth rate dispersion (GRD) (see Ulrich, 1989) as such should be summarized. Crystals of the same size grow at a different rate under the same conditions. The deviation in growth rates is between zero and a maximum value that differs for each substance. If there is no interference in the growth process and the conditions at which crystals grow remain constant, then crystals grow at a constant rate which means that the so-called Constant Crystal Growth (CCG) model holds.

If there are crystal–crystal contacts or are fluctuations in the supersaturation or temperature level, the growth rate of the crystals can change. Then the so-called Random Fluctuation (RF) model has to be applied. The conclusion that can be drawn from this is that there is no reliable crystal growth data from single crystal experiments unless there are such high numbers that there is statistical relevance. For fundamental understanding single crystal experiments are, however, still very valuable.

For all other cases collectives of crystals should be examined. Here this is done in a fluidized bed type equipment. The advantages of the fluidized beds are:

easily adjustable and good recording conditions of temperature level, supersaturation, impurity concentrations, and fluid dynamics in connection with crystal sizes. In this case, the equipment is used in a way that a split in two fluidized bed is always used so that a direct comparison between the growth behaviour of two different pre-prepared crystal collectives can be made. The different preparation of the crystals lies for instance in the use of cured, perfect crystals on the one hand and fragmented, non-perfect crystals on the other hand.

EQUIPMENT

The apparatus for the experiments with collectives of crystals in which crystal–crystal contacts are permitted is the fluidized bed. Such equipment has been introduced before (see e.g. Ulrich et al., 1989; Ulrich, 1989), even having a configuration of the measuring chamber split in two.

In the case of single crystal experiments, small measuring cells are used which can be positioned under a microscope and which have a stagnant solution. Again, this type of equipment has been introduced in detail before (see e.g. Kruse et al., 1990; Ulrich and Kruse, 1990). In these cells, which are controlled concerning temperature and therefore supersaturation, no crystal–crystal contacts are possible.

EXPERIMENTAL RESULTS

As can be seen in Fig. 1, there is no significant difference to be found in the growth rates for the fragmented and the so-called perfect crystals in the fluidized bed experiments. The growth and the dissolution rate as a function of supersaturation and undersaturation, respectively, are plotted in Fig. 1. The additive $PbCl_2$ makes no difference to this aspect as is indicated by similar diagrams (not shown here). However, the increase in concentration of the additive to 0.32, 0.5, 0.75 and 1.0 ppm in weight reduces the growth rates of the NaCl crystals significantly, as can be seen in Fig. 2.

A variation of the difference in velocity of supersaturated solution and the crystals in the range 0.008–0.021 m/s did not lead to any significant difference in the crystal growth rates.

In Fig. 3 it can be seen that NaCl crystals grow according to the CCG-model if they are grown as single crystals in a stagnant solution. The data result from experiments in the microscope cell. The crystals' size over time for one supersaturation is plotted.

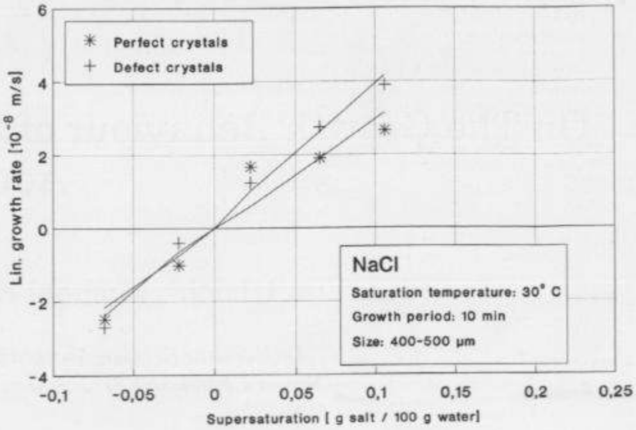

Fig. 1. Growth and dissolution rates of perfect and fragmented NaCl crystals.

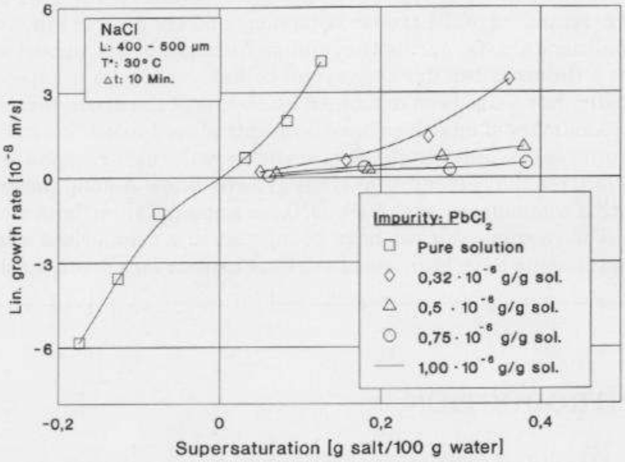

Fig. 2 Growth and dissolution rates of NaCl crystals with the additive $PbCl_2$.

DISCUSSION

From the data presented and the known data from literature the following can be concluded:

1. NaCl crystals grow in accordance with the GRD-theory. In the case of single crystals in stagnant solutions the CCG-model can be used for a description (see Fig. 3).

2. Growing in accordance with the GRD-theory means that there is no more need for an explanation of size dependence in crystal growth. The faster growth of larger crystals can be sufficiently explained on the one hand by better mass transfer due to higher terminal velocities and, on the other hand, by the fact that only fast-growing crystals will populate the large size regions. This special collective of crystals then, of course, grows faster.

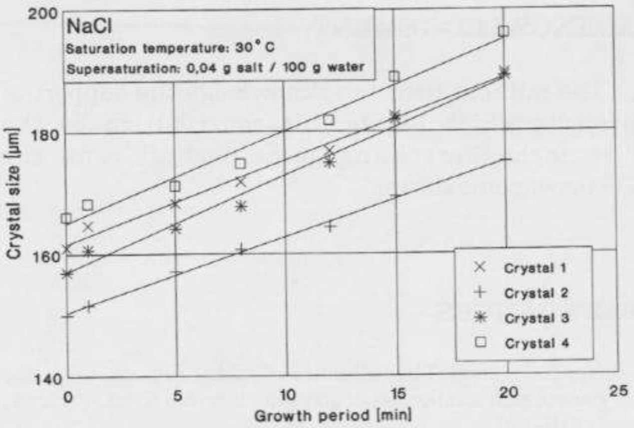

Fig. 3. Change in size with time. NaCl crystals in a microscopic cell in stagnant solution.

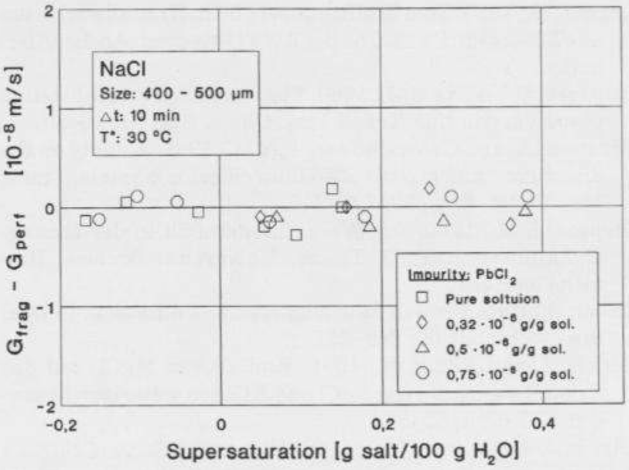

Fig. 4. Differences in growth and dissolution rates for NaCl crystals from pure solution and with additives-contaminated solution over supersaturation and undersaturation, respectively.

3. NaCl crystals grow in temperature ranges around 30°C diffusion controlled. This is proved by the fact that in experiments perfect and fragmented crystals lead to the same growth rates (see Figs. 1 and 4). There is no change in this behaviour in the range of the observed slip velocities from 0.008 to 0.021 m/s. The range of velocities is the range of normally occurring thermal velocities in fluidized beds.

4. The additive $PbCl_2$ suppresses the growth rate of NaCl with increasing concentrations (see Fig. 2 and also Yuan et al., 1990). The additive, however, does not influence the perfect crystals any differently from the fragmented ones as can be seen in Figs. 1 and 4 (Zhang et al., 1990). In Fig. 4 the difference in growth rates of fragmented and perfect crystals is plotted for supersaturation and undersaturation, respectively. The diagram incorporates results from pure solutions as well as solutions with different additive concentrations.

5. As far as the effect of the additives $MgCl_2$ and $K_3Fe(CN)_6$ on the growth of perfect and fragmented crystals is concerned, the results are the same as for $PbCl_2$. The effects of $MgCl_2$ concerning other aspects are, however, very different.

6. The additive $K_3Fe(CN)_6$ acts in the same way as $PbCl_2$. It needs only stronger concentrations (about 10 times) to reach the same effectiveness. In Fig. 5 (Zhang et al., 1990) the growth and dissolution rates of NaCl crystals with different additive concentrations are presented. A higher concentration of the additive leads to a stronger suppressing of the growth rate and the dissolution rate, respectively.

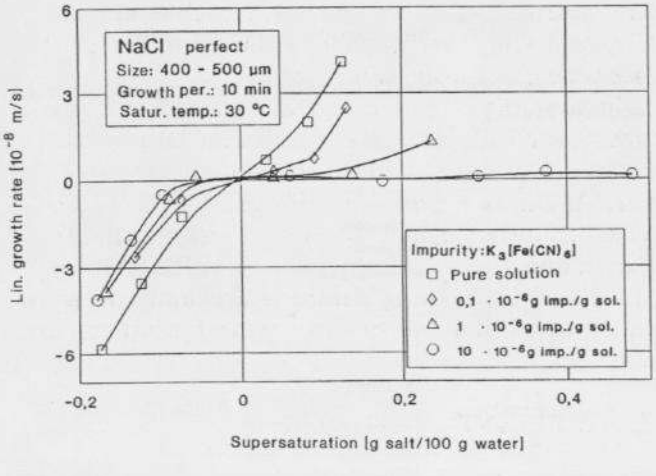

Fig. 5. Growth and dissolution rate of NaCl crystals with the additive $K_3Fe(CN)_6$.

7. The additive $MgCl_2$ creates the initial impression of accelerating the growth rate of NaCl crystals. A more careful scrutiny, however, show that it shifts the saturation point in the concentration ranges (40–500 ppm) in which it was examined (see Fig. 6, Ulrich and König, 1991). With much lower concentration, no effect could be detected.

8. The additives examined which influence the surface of a diffusion-controlling growing crystal by blocking the growth and the dissolution do this in the same manner for both perfect and fragmented crystals. This means that the substance changes in its behaviour to a reaction controlled substance.

9. The strong effect of additives especially on the growth behaviour of NaCl crystals is shown in Fig. 7, giving literature data in a comparison with the authors' own data in the presence or absence of

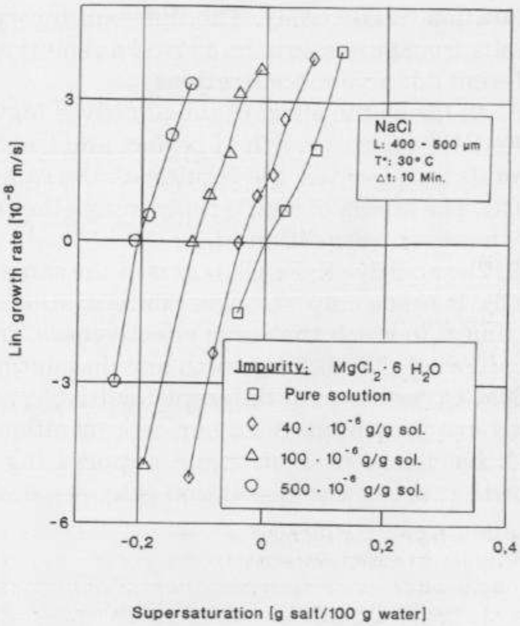

Fig. 6. Growth and dissolution rates of NaCl crystals with the additive $MgCl_2$.

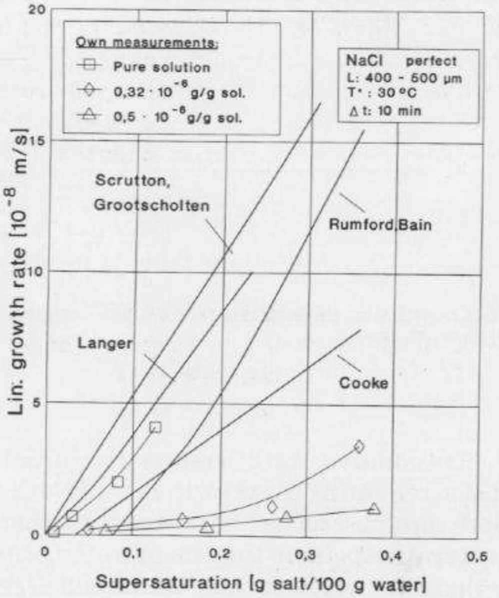

Fig. 7. Growth rates of NaCl — a comparison with the literature.

additives ($PbCl_2$) (see Stepanski, 1990). The growth rate is plotted over the supersaturation. The rather large scatter of the data could easily be explained if the assumption is made that, in one or the other literature data, unknown additives have been present in very small quantities.

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REFERENCES

Cooke, E.G., 1966. The influence of added impurities on the growth and nucleation of sodium chloride. Krist. Technik, 1: 119–126.

Kruse, M., Stepanski, M. and Ulrich J., 1990. On the Growth of small single crystals with and without additives. In: J. Ulrich (Editor), BIWIC 1990 (Bremer International Workshop for Industrial Crystallization), 12./13.9.1990, Proceedings, Bremen/Germany, pp. 90–97.

Langer, H., 1985. Zum Stofftransport beim Kristallwachstum aus Lösungen, Ph.D. Thesis, RWTH-Aachen, Aachen/Germany.

Rumford, F. and Bain, J., 1960. The controlled crystallization of sodium chloride. Trans. Inst. Chem. Eng. 38: 10–20.

Scrutton, A. and Grootscholten, P.A.M., 1981. A study on the dissolution and growth of sodium chloride crystals. Trans. Inst. Chem. Eng., 59: 238–246.

Stepanski, M., 1990. Zur Wachstumskinetik in der Lösungskristallisation. PhD. Thesis, Universität Bremen, Bremen/Germany.

Ulrich, J., 1989. Growth Rate Dispersion — A Review. Crystal Res. Techn., 24 (3): 249–257.

Ulrich, J. and König, A., 1991. Einfluß von $MgCl_2$ auf das Kristallwachstum von NaCl und KCl aus wässrigen Lösungen. CIT 63: 1, 55–56.

Ulrich, J. and Kruse, M., 1990. GRD and Effects of Surface Quality, a Better Explanation than Size-Dependent Growth. In: A. Mersmann (Editor), Proceedings 11th Symposium on Industrial Crystallization 18.–20.9.1990, Garmisch-Partenkirchen, Germany, pp. 361–366.

Ulrich, J., Kruse, M. and Stepanski, M., 1989. The influence of the history of crystals on their growth rates. In: Y. Harano (Editor), International Symposium on Preparation of Functional Materials and Industrial Crystallization '89, Proceedings, Osaka/ Japan, pp. 113–116.

Ulrich, J. and Stepanski, M., 1989. The Effect of Additives on the Growth Behaviour of Reaction and Diffusion Controlled Growing Crystals. In: J. Nyvlt and S. Zacek (Editors), Industrial Crystallization '87. Elsevier, Amsterdam, pp. 253–256.

Yuan, J.J., Stepanski, M. and Ulrich, J., 1990. Fremdstoffeinflüsse auf Kristallwachstumsgeschwindigkeiten bei der Kristallisation aus Lösungen. CIT 62: 8, 645–646.

Zhang, S.B., Stepanski, M., Yuan, J.J. and Ulrich, J., 1990. Investigations of Crystal Growth Rates in the Presence of Different Additives. In: A. Mersmann (Editor), Proceedings 11th Symposium on Industrial Crystallization 18.–20.9.1990, Garmisch-Partenkirchen, Germany, pp. 695–700.