THE METASTABLE ZONE WIDTH
OF AMMONIUM ALUMINIUM SULPHATE AND MECHANISMS
OF SECONDARY NUCLEATION

Jaroslav NÝVLT

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

The metastable zone width of aqueous solution of ammonium aluminium sulphate was measured as a function of the cooling rate. The measurements were carried out *a)* in the absence of seed crystal, *b)* with one seed crystal at a fixed position in the flowing solution, and *c)* with one seed crystal moving freely on the bottom of the measuring vessel. The results obtained distinctly differ for the three measurements, providing evidence that primary nucleation took place in the first case, secondary nucleation induced by the surface-layer mechanism combined with fluid shear occurred in the second case, and the contact mechanism of secondary nucleation operated in the third case.

Mechanisms of nucleation induced by crystals present in supersaturated solution are collectively termed the secondary nucleation. In the last decade, this phenomenon has received increased attention because of the key role it plays in the generation of crystals in industrial crystallizers. The secondary nucleation may occur by several completely different mechanisms which can be divided into three groups[1-3]:

I. Apparent secondary nucleation: *a)* seeding by crystal dust adhering to the solid phase (dust breeding)[4], *b)* degradation of polycrystals (polycrystalline breeding)[5], and *c)* macro-attrition[6]. This group includes simple mechanisms of no theoretical significance and little practical interest.

II. True secondary nucleation: *a)* the formation of a nucleus directly from a seed crystal[7], *e.g.* by the detachment of dendrites, *b)* the birth of a nucleus from the dissolved substance in the immediate vicinity of the crystal surface; this may occur as a result of changes in the structure of the solution close to the solid phase surface[8,9], or due to the development of a concentration gradient of impurities hindering the nucleation[10], or finally by an adsorption mechanism[11,12].

III. Nucleation induced by contact with other crystal[9] or with some other material[13-15].

Mechanisms *II* and *III* are of fundamental importance in industrial crystallization, but they are not easy to distinguish in practice. The measurement of the width of metastable zone at various cooling rates is one of the methods used to follow indirectly the nucleation kinetics[16-19]. The measurement is carried out either in clear solution or in the presence of crystalline solid phase[12]. The solid phase is usually present in the form of several large crystals which move freely in the solution, slide

along the bottom and impinge on the stirrer[12]. Measurements with a crystal mounted on a stationary holder and washed by the flowing liquid are only sporadic[20]. These two methods, however, may involve different mechanisms of secondary nucleation. The aim of this work was to establish to what extent the difference in the two manners of solid phase positioning is significant.

THEORETICAL

The following relations have been derived[18,19] for the evaluation of the dependence of the metastable zone width, represented by supercooling, ΔT_{max}, on the cooling rate of solution, $-\dot{T}$:

$$\log \Delta T_{max} = A + (1/n) \log (-\dot{T}) \qquad (1)$$

$$\log k_N = (1 - n) \log (dw_{eq}/dT) - An , \qquad (2)$$

where k_N and n are the nucleation rate constant and the apparent order of nucleation, respectively, corresponding to the simple power-law model for nucleation kinetics

$$\dot{m}_N = k_N \Delta w^n . \qquad (3)$$

These relations have been applied successfully to measurements carried out both in the absence and in the presence of a solid phase in the system. The values of n found in the two cases were, as a rule, so close to each other that they could be replaced by a common average value[12,21]. This would seem to indicate that in the systems concerned the secondary nucleation occurred by some of the mechanisms of true secondary nucleation *II*, for in the case of the contact mechanism *III* a lower value[22,23] of the apparent order of nucleation, n, would have been expected. The lowering of n in the case of collision nucleation may be expressed[23] formally in terms of the secondary nucleation coefficient, σ:

$$n_A = (1 - \sigma) n \qquad (4)$$

or

$$\sigma = 1 - n_A/n . \qquad (5)$$

In the first case, *i.e.* for the same values of the apparent nucleation order, $n_A = n$, the dependence according to Eq. (*1*) will be graphically represented by parallel straight lines[19] while concurrent lines with slopes of $1/n$ and $1/n_A$ are expected for the collision nucleation.

EXPERIMENTAL

The metastable zone width of solutions of $NH_4Al(SO_4)_2.12 H_2O$ (analytical grade. Lachema Brno) saturated at 34·1 to 45·5°C was measured on an apparatus described earlier[12,16]. The apparatus was equipped with a digital-controlled thermoregulator[24]. The saturation temperature was periodically checked by the last-crystal-dissolving method. The temperature at which first crystals appeared was followed visually.

TABLE I

Results of metastable zone width measurements for $NH_4Al(SO_4)_2.12 H_2O$

Value	Series		
	1	*2*	*3*
n	2·90	2·90	2·73
σ	—	0	0·06
A	1·5303	1·4200	1·3744
ΔT_{max} (K) for			
$-\dot{T}$ (K/h) = 2	2·55	1·98	1·52
5	3·50	2·71	2·13
20	5·64	4·38	3·54
k_N	0·280	0·585	0·610
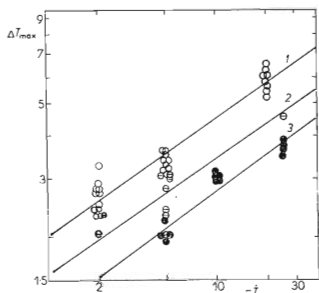
FIG. 1

The metastable zone width for $NH_4Al(SO_4)_2$.
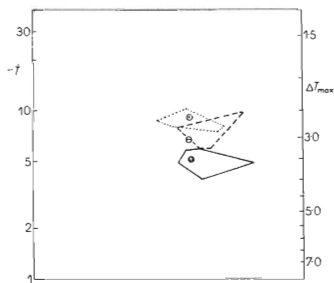.12 H_2O. The numbers denote Series *1—3*
of measurements

FIG. 2

Nomographic representation of the results
of measurements. For identification of points
see Fig. 1

The measurements were carried out in three series of measurements: Series *1* in the absence of solid phase. Series *2* with a single $NH_4Al(SO_4)_2.12\,H_2O$ crystal of 3 to 5 mm in size, mounted on a stationary holder immersed in the stirred solution. Series *3* with the same crystal moving freely on the bottom of the vessel fitted with a magnetic stirrer with a speed of about 200 rpm. A total of 27, 10, and 15 runs were performed in Series *1*, *2*, and *3*, respectively. The results are depicted in Fig. 1. The straight lines shown are least-squares fits to the experimental points, with parallel lines[19] for Series *1* and *2*, and a line of slightly different slope for Series *3*. The evaluation results are summarized in Table I. Also included in Table I are values for the effective nucleation constants calculated from Eq. (2) with the use of temperature coefficients of solubility (dw_{eq}/dT) taken from the literature[25].

DISCUSSION

It is evident from Table I and Fig. 1 that the results differ for the three series of measurements. Even though the difference between Series *1* (in the absence of solid phase) and the other two measurements (in the presence of solid phase) is larger than that between Series *2* and *3*, there are nevertheless distinct differences in results for the two series with the solid phase present. This becomes even more clear-cut on a nomograph (Fig. 2). If $\log(-\dot{T})$ and $\log(\Delta T_{max})$ are plotted along the opposite axes of a nomograph in the reverse direction to each other, each system will be characterized by a single point[21] which lies at the intersection of lines connecting the points representing the corresponding values of $-\dot{T}$ and ΔT_{max}. On drawing the lines connecting the corresponding points for all the measurements, and the envelope of their intersections, we obtain a polygon that characterizes the maximum scatter of the individual measurements. Fig. 2 clearly shows that while the area representing Series *1* of measurements lies outside the other two regions, the sets of data points for Series *2* and *3* form an intersection. It is seen, however, that the points characterizing each separate series of measurements and obtained by least-squares treatment of the experimental data lie clearly outside the domain of intersection. Thus, it may be concluded from the foregoing that the measurement of the metastable zone width for the given system permitted us to characterize the heterogeneous nucleation (Series *1*), the true secondary nucleation occurring by the adsorption-layer mechanism (Series *2*), and even the contact or collision nucleation (Series *3*). That Series *2* and *3* differ little from each other is also seen from the low values of the coefficient of secondary nucleation, σ (Table I). Although the results for Series *2* and *3* partially overlap, they provide evidence that the mode of the solid phase positioning has an influence on the results of metastable zone width measurement.

LIST OF SYMBOLS

A	constant
k_N	nucleation rate constant $(kg\,m^{-2}\,s^{-1})$
$\dot{m}_N$	mass nucleation rate (s^{-1})

n	apparent nucleation order
n_A	apparent order of contact (collision) nucleation
T	temperature (K)
ΔT_{max}	maximum supercooling (K)
$-\dot{T}$	cooling rate (K/h, K/s)
w_{eq}	solubility (kg of hydrate/kg of free water)
σ	secondary nucleation coefficient defined by Eq. (5)

REFERENCES

1. Botsaris G. D., Denk E. G.: Ann. Rev. Ind. Eng. Chem. *1*, 337 (1970).
2. Nývlt J.: Chem. Prům. *23*, 417 (1973).
3. Nývlt J.: *Industrial Crystallisation — The Present State of the Art.* Verlag Chemie, Weinheim 1978.
4. Cise M. D., Randolph A. D.: Chem. Eng. Progr., Symp. Ser. *118* (1972).
5. Strickland-Constable R. F.: AIChE Symp. Ser. *68*, No 121, 1 (1972).
6. Fasoli U., Conti R.: Crystal Breakage in a Mixed Suspension Crystallization, 5-th Symposium on Industr. Cryst., Prague 1972.
7. Strickland-Constable R. F.: *Kinetics and Mechanism of Crystalisation.* Acad. Press, London 1968.
8. Denk E. G., Botsaris G. D.: Fundamental Studies in Secondary Nucleation from Solution. ICCG-3, Marseille 1971.
9. Clontz N. A., McCabe W. L.: Chem. Eng. Progr., Symp. Ser *67*, No 110, 6 (1971).
10. Botsaris G. D., Mason E. A., Reid R. C.: J. Chem. Phys. *45*, 1893 (1966).
11. Powers H. E. C.: Nature (London) *178*, No 4525, 139 (1956).
12. Nývlt J., Gottfried J.: This Journal *32*, 3459 (1967).
13. Lal D. P., Mason R. E. A., Strickland-Constable R. F.: J. Cryst. Growth *5*, 1 (1969).
14. Garabedian H., Strickland-Constable R. F.: Collision Breeding of Crystal Nuclei. ICCG-3, Marseille 1971; J. Cryst. Growth *13*, *14*, 506 (1972).
15. Garside J., Larson M. A.: J. Cryst. Growth *43*, 694 (1978).
16. Nývlt J.: J. Cryst. Growth *3*, *4*, 377 (1968).
17. Nývlt J.: This Journal *37*, 3155 (1972).
18. Söhnel O., Nývlt J.: This Journal *40*, 511 (1975).
19. Nývlt J.: Krist. Tech. *15*, 777 (1980).
20. Nývlt J.: Chem. Prům. *31*, 118 (1981).
21. Nývlt J., Wurzelová J.: Chem. Prům. *22*, 222 (1972).
22. Nývlt J., Wurzelová J., Čípová H.: This Journal *41*, 29 (1976).
23. Nývlt J.: This Journal *46*, 79 (1981).
24. Písařík S.: Report, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague 1980.
25. Broul M., Nývlt J., Söhnel O.: *Tabulky rozpustnosti anorganických látek ve vodě.* Academia, Prague 1979. *Solubility in Inorganic Two-Component Systems.* Academia — Prague + + Elsevier — Amsterdam 1981.

Translated by M. Škubalová.