CRYSTALLIZATION KINETICS FOR THE SYSTEM CuSO$_4$–ZnSO$_4$–H$_2$O FORMING SOLID SOLUTIONS

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The three-component system CuSO$_4$–ZnSO$_4$–H$_2$O forms three types of solid solution. Metastable zone widths measured for selected solution compositions at two cooling rates were used to calculate the kinetic parameters of nucleation. The rate of crystal growth was measured by the fluidized bed method. The results show that the addition of Zn^{2+} to a solution of CuSO$_4$ increases both the nucleation and crystal growth rates, whereas Cu^{2+} added to a solution of ZnSO$_4$ retards the nucleation rate and slightly increases the rate of crystal growth. The nucleation rate (the metastable zone width) is substantially more sensitive to the addition of a second component than is the rate of crystal growth. The crystal growth rate is controlled by a diffusion mechanism.

As shown by an analysis of data on phase equilibria in the system CuSO$_4$–ZnSO$_4$––H$_2$O, this system forms three types of solid solution[1]: triclinic CuSO$_4$.5 H$_2$O with an isomorphous admixture of ZnSO$_4$ (further designated as Cu/Zn) which crystallizes from solutions rich in CuSO$_4$; rhombic ZnSO$_4$ isomorphously contaminated by CuSO$_4$ (Zn/Cu system) which crystallizes in the region of high ZnSO$_4$ concentrations; and zinc sulphate ZnSO$_4$.7 H$_2$O with a substantial admixture of CuSO$_4$ causing a change to the monoclinic type of lattice (ZnCu/Cu system), this solid solution being the equilibrium solid phase in the intermediate concentration range.

The aim of the present work was to investigate the effect of the formation of solid solutions on the nucleation and crystal growth kinetics.

In describing the nucleation kinetics, we use the conventional power law

$$\dot{N}_{N} = k_{N}\,\Delta w^{n}\,. \tag{1}$$

The kinetic measurements consist of measuring the metastable zone width as a function of the cooling rate[2]. The calculation is made using the equations

$$\log \Delta T_{max} = A + \frac{1}{n}\log\left(-\dot{T}\right) \tag{2}$$

and

$$\log k_{N} = (1 - n)\log\left(\mathrm{d}w_{eq}/\mathrm{d}T\right) - An\,. \tag{3}$$

The measurement of the crystal growth rate,

$$\dot{m}_G = k_G A_c \, \Delta w^g , \qquad (4)$$

by the fluidized bed method is based on following the mass gain of crystals[3,4] fluidized by an upward stream of solution having a known supersaturation,

$$\dot{L} = \left(m_f^{1/3} - m_0^{1/3} \right) / t \left(\alpha \varrho_c N_c \right)^{1/3} . \qquad (5)$$

The order of the crystal growth rate, g, is obtained from the linear equation

$$\log \dot{L} = \log \dot{L}_0 + g \log \Delta w , \qquad (6)$$

and the rate constant can be calculated as

$$k_G = 3 \alpha \varrho_c \dot{L} / \beta \, \Delta w^g . \qquad (7)$$

EXPERIMENTAL

Solutions of $CuSO_4.5\,H_2O$ (analytical grade; Lachema) and $ZnSO_4.7\,H_2O$ (analytical grade; Lachema) were made up in distilled water. The solution compositions were checked analytically (by complexometric titration for Zn and iodometric titration for Cu). The equilibrium saturation temperatures were determined by the last-crystal-dissolving method[5]. The solutions prepared are indicated on the phase diagram in Fig. 1, and their compositions are given in Table I.
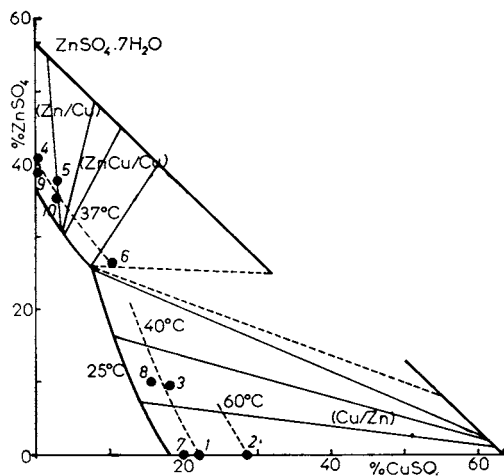

Fig. 1

Phase diagram of the system $CuSO_4$–$ZnSO_4$–H_2O with indication of solution compositions used for measurements

The metastable zone width was measured by a method described in the literature[2,6]: a solution saturated at temperature T_{eq} was placed in a magnetically stirred Erlenmayer flask together with one or two large crystals of pure $CuSO_4.5\,H_2O$ or $ZnSO_4.7\,H_2O$ and cooled at a constant rate $(-\dot{T})$ until the first crystals of the newly precipitated phase appeared. The solution was subsequently heated slowly until the crystals dissolved. The difference between the two temperatures gives the maximum undercooling ΔT_{max}. The temperature was measured with a Pt resistance

TABLE I

Solution compositions

Solution No	mass % $CuSO_4$	mass % $ZnSO_4$	Solution No	mass % $CuSO_4$	mass % $ZnSO_4$
1	22·2	0	6	9·8	25·7
2	28·8	0	7	20·0	0
3	18·3	9·9	8	15·5	10·0
4	0	40·5	9	0	39·0
5	3·0	38·0	10	3·0	35·5

TABLE II

Metastable zone widths for the system $CuSO_4$–$ZnSO_4$–H_2O

System No	T_{eq} °C	$-\dot{T}$ K h^{-1}	Number of runs	ΔT_{max} exper.[a]	n[a]	A	ΔT_{max} calc.
1	40	2	15	4·3 ± 0·4	3·29 ± 0·7	1·619	4·26
		20	20	8·6 ± 0·6			8·58
2	60	2	6	1·9 ± 0·1	2·84 ± 0·4	1·429	1·92
		20	6	4·3 ± 0·3			4·31
3	40	2	12	2·9 ± 0·2	2·51 ± 0·3	1·755	2·87
		20	13	7·2 ± 0·4			7·19
4	37	2	34	1·1 ± 0·1	2·97 ± 0·6	1·139	1·10
		20	20	2·4 ± 0·2			2·40
5	37	2	6	1·4 ± 0·04	2·19 ± 0·2	1·624	1·37
		6	2	2·25 ± 0·07			
		20	28	4·0 ± 0·04			3·93
6	37	2	14	1·9 ± 0·1	2·43 ± 0·25	1·628	1·94
		20	18	5·0 ± 0·2			5·01

[a] Supplemented with the standard deviation.

thermometer which simultaneously controlled a thermoregulator with digital adjustment of the cooling rate. Results of the measurements are summarized in Table II.

The crystal growth kinetics were measured using an apparatus shown in Fig. 2. A slightly undersaturated solution was pumped through a cooler **4**, where the required supersaturation was produced, into a measuring tube **6** with a fluidized layer of growing crystals. On passing through the layer, it returned via a flowmeter **11** back to the storage reservoir **1**. A known number of crystals, N_c, of known initial mass, m_0, was allowed to grow for a time period, t, in a solution of known supersaturation

$$\Delta w = (T_{eq} - T)(dw_{eq}/dT). \tag{8}$$

As the saturation temperature, T_{eq}, was difficult to determine rapidly and with sufficient accuracy, it was obtained by extrapolation of data for the crystal growth rate, $\dot{L}$, as a function of temperature, T, to zero $\dot{L}$. The accuracy of the linear extrapolation was verified in one case by an experiment in which the crystals were dissolved in an undersaturated solution. The saturation temperatures ranged between 27 and 33°C. The crystal shape factors[7] were as follows: $CuSO_4$. $.5 H_2O - \alpha = 0.288$, $\beta = 3.01$; $ZnSO_4 . 7 H_2O - \alpha = 2.714$, $\beta = 12.86$. The measurements were always performed at a minimum of two flow rates of solution, v. A survey of the measurements is given in Table III and in Figs 3—6.
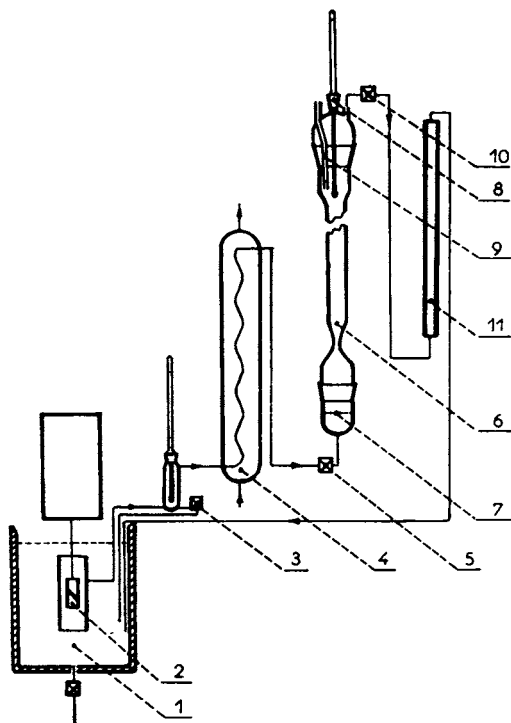

FIG. 2

Apparatus for fluidized-bed measurement of crystal growth rate. **1** stock solution; **2** pump; **3, 5, 10** valves; **4** cooler; **6** measuring tube; **7** fritted glass; **8** thermometer; **9** crystal input tube; **11** flowmeter

DISCUSSION AND CONCLUSIONS

The solution compositions indicated in Fig. 1 were chosen so as to make it possible to assess to what extent and in what sense the addition of a second component
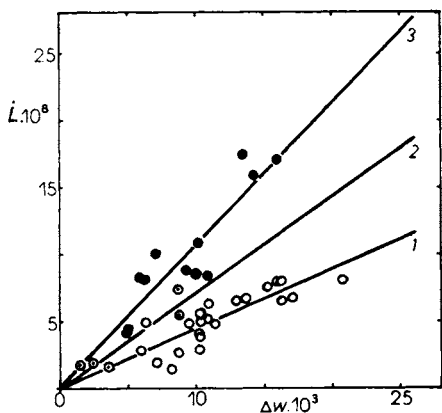

FIG. 3

Linear crystallization rate for $CuSO_4$ (System No 7). 1 $v = 2\cdot6$ cm s^{-1}; 2 $v = 4$ cm s^{-1}; 3 $v = 5$ cm s^{-1}
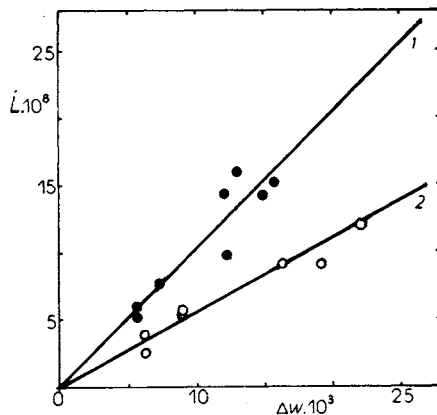
FIG. 4

Linear crystallization rate for $CuSO_4$ with an admixture of $ZnSO_4$ (System No 8). 1 $v = 5$ cm s^{-1}; 2 $v = 2\cdot6$ cm s^{-1}
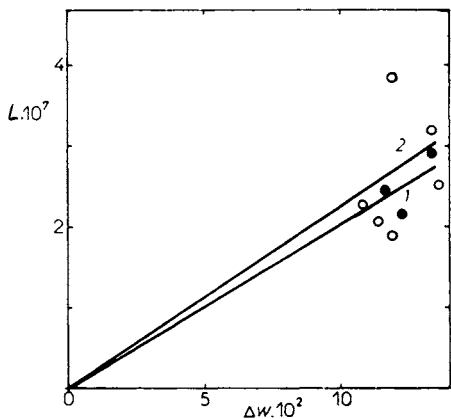
FIG. 5

Linear crystallization rate for $ZnSO_4$ (System No 9). 1 $v = 1\cdot8$ cm s^{-1}; 2 $v = 2\cdot8$ cm s^{-1}
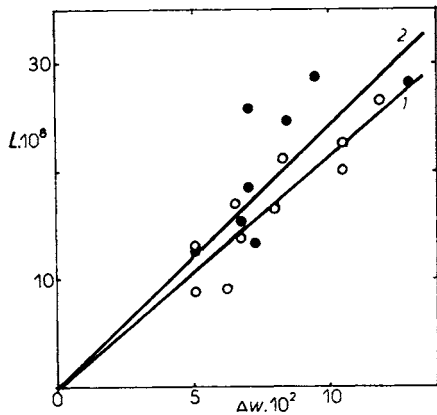
FIG. 6

Linear crystallization rate for $ZnSO_4$ with an admixture of $CuSO_4$ (System No 10). 1 $v = 1\cdot8$ cm s^{-1}; 2 $v = 2\cdot8$ cm s^{-1}

affects the crystallization behaviour of the main component. As indicated by the data listed in Table II, the addition of $ZnSO_4$ to $CuSO_4$ as the major component decreases the metastable zone width whereas the addition of $CuSO_4$ to $ZnSO_4$ has the opposite effect. A quantitative comparison of the data is however difficult to make because the nucleation exponents, n, for the systems somewhat differ. On closer examination, however, it turns out that the nucleation exponents for systems 1 to 3, and similarly for systems 4 to 6, may be regarded as identical within the scatter considered, and hence the data on the metastable zones for systems with $CuSO_4$ or $ZnSO_4$ as the major component may be treated as a system of parallel lines[2]. Results of this treatment are summarized in Table IV, where it is clearly seen that the addition of $ZnSO_4$ accelerates the nucleation of $CuSO_4$ (*cf.* systems 1 to 3) whereas the addition of $CuSO_4$ retards the nucleation of $ZnSO_4$ (*cf.* systems 4 to 6).

The effect of the formation of a solid solution on the rate of crystal growth is far less pronounced. The values of k_G listed in Table III suggest that the crystals of both types of solid solution probably grow somewhat more rapidly than do the pure components, but the experimental data are too scattered to permit the difference to be determined with any certainty. There is a distinct effect of the solution flow rate, suggesting that the crystal growth is controlled by diffusion in the surface layer. The effect of the solution flow rate on the crystal growth rate is usually described by the Frössling equation[8]

TABLE III

Crystal growth rates

System No	v cm s^{-1}	Number of runs	$10^6 L/\Delta w$	Fig. No	$10^3 k_G{}^a$
7	2·6	22	4·43	3	2·9 ± 0·65
	4·0	5	7·28	3	4·8 ± 1·3
	5·0	12	10·76	3	7·1 ± 1·3
8	2·6	7	5·5	4	3·67 ± 0·66
	5·0	8	10·1	4	6·6 ± 1·0
9	1·8	3	2·03	5	2·52 ± 0·25
	2·8	6	2·15	5	2·66 ± 0·61
10	1·8	10	2·14	6	2·65 ± 0·37
	2·8	9	2·43	6	3·01 ± 0·62

a Supplemented with the standard deviavion.

$$\frac{k_G L}{D} = c \left(\frac{v \varrho_1 L}{\eta}\right)^a \left(\frac{\eta}{\varrho_1 D}\right)^{1/3} \tag{9}$$

which, for our purposes, may be simplified to

$$\log k_G = \text{constant} + a \log v . \tag{10}$$

As can be seen from Fig. 7, a straight line of slope $a = 0.92$ can be drawn through the experimental points. The slope usually quoted in the literature is $a = 0.6$, and the corresponding straight lines are drawn in Fig. 7 as dashed lines.

TABLE IV

Metastable zone widths at constant n

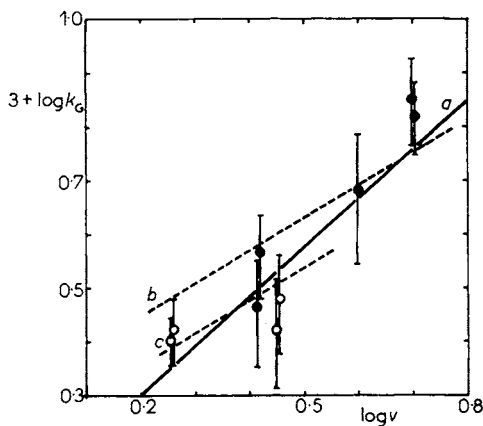| System No	n	A	ΔT_{max}			$k_N \cdot 10^2$	$k_N^{1/n}$
			$-\dot{T} = 2$	5	20		
1	2·90	1·7303	4·05	5·55	8·95	4·98	0·355
(2	2·90	1·4090	1·93	2·65	4·27	16·08	0·532)
3	2·90	1·6089	3·06	4·20	6·77	11·16	0·469
4	2·61	1·2728	1·06	1·51	2·56	2·81	0·255
5	2·61	1·4462	1·58	2·24	3·82	0·99	0·171
6	2·61	1·5514	2·01	2·86	4·86	0·53	0·134

FIG. 7

The crystal growth rate as a function of the solution flow rate, v. a $a = 0.92$; b $a = 0.6$ for $CuSO_4 . 5\,H_2O$; c $a = 0.6$ for $ZnSO_4$. $.7\,H_2O$; ○ $ZnSO_4 . 7\,H_2O$; ● $CuSO_4 . 5\,H_2O$. The bars represent maximum scatter of experimental data

In conclusion it may be summarized that the addition of Zn^{2+} to a solution of $CuSO_4$ increases both the nucleation and crystal growth rates, whereas the addition of Cu^{2+} to a solution of $ZnSO_4$ retards the nucleation rate and slightly increases the rate of crystal growth.

LIST OF SYMBOLS

A	constant in Eq. (2)
A_c	crystal surface area
a	exponent in Eq. (5)
c	constant
D	diffusion coefficient
g	growth order
k_G	growth rate constant
k_N	nucleation rate constant
L	crystal size
$\dot{L}$	linear crystallization rate
$\dot{m}_G$	crystal growth rate
m_0	initial crystal mass
m_f	final crystal mass
$\dot{N}_N$	nucleation rate
N_c	number of crystals
n	nucleation order
T	temperature
T_{eq}	temperature at which a solution is just saturated
$-\dot{T}$	cooling rate
ΔT_{max}	maximum undercooling
t	time period of measurement
v	upward flow rate of solution
w_{eq}	solubility
Δw	supersaturation
α	volume shape factor
β	surface shape factor
ϱ_c	crystal density
ϱ_l	solution density
η	viscosity

REFERENCES

1. Nývlt J., Šnoblová V.: Chem. Prům. *36*, 297 (1986).
2. Nývlt J.: Cryst. Res. Technol. *15* (7) 777 (1980).
3. Kočová H., Nývlt J., Kočí J.: Chem. Prům. *17*, 477 (1967).
4. Nývlt J.: Cryst. Res. Technol. *18* (12) 1461 (1983).
5. Nývlt J.: *Solid–Liquid Phase Equilibria*. Elsevier Amsterdam and Academia Praha 1977.
6. Nývlt J.: This Journal *47*, 1184 (1982).
7. Nývlt J.: Chem. Prům. *31*, 172 (1981).
8. Mullin J. W.: *Crystallisation*. Butterworths, London 1971.

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