EFFECT OF THE RATE OF STIRRING ON CRYSTAL SIZE IN PRECIPITATING OR SALTING-OUT SYSTEMS

Jaroslav NÝVLT and Stanislav ŽÁČEK

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

A simple model is proposed to express the dependence of the mean crystal size on the rate of stirring in precipitating or salting-out systems. The nucleation rate is taken to be proportional to the "interfacial" area of segregated regions. This area is a function of the dissipated energy. The derived relations are applied to results of a series of experiments in which aluminium-potassium sulphate was salted out by the addition of aqueous solutions of methyl alcohol.

Although precipitation is a very common operation in the chemical and related industries, published data for the effect of stirring on the precipitation kinetics or the product particle size are very limited. One of the first workers to point to the importance of stirring in precipitation crystallization was Matz[1]. From a comparison of data published by various authors[2,3] he concluded that the effect of stirring is more pronounced the more concentrated are the component solutions being mixed; an increase in the rate of stirring results in a reduction of the product particle size. Studies on precipitation of aluminium-potassium sulphate by various alcohols[4,5] have shown that the product crystal size is largely affected by the physical properties of alcohols, particularly by the viscosity, which influences the micromixing process.

The first attempt at a theoretical treatment of the effect of micromixing on the quality of the product of precipitation was published by Pohorecki and Baldyga[6,7]. They started from a combination of the diffusion model of micromixing[8] and the crystallization kinetics, treating the micromixing as a continuous mass transfer between an arbitrary point and its environment,

$$-dc_i/dt = k_m(c_i - \bar{c}_i) + R_i ,\qquad(1)$$

where the micromixing coefficient k_m is defined as a complex function of a number of parameters characterizing the hydrodynamics of the system and the diffusivity. According to this model, the mean crystal size increases with increasing rate of stirring, a result not substantiated by experiment. The theory of micromixing has been worked out in further detail in connection with chemical reactors[9-11], and the concepts have also been used by Tavare and Garside[12] to develop two models of

precipitation for the limiting conditions of maximum mixing and/or complete segregation of components. In the latter model, the elementary volumes of the added phase are envisaged as wandering about the crystallizer, each behaving like a small batch reactor with the reaction occurring until a supersaturated solution is produced, followed by nucleation and growth. The mean crystal size decreases slightly with increasing rate of stirring and also with the concentration of the added component. These results are qualitatively as expected, but the model involves simultaneous numerical solution of eleven differential equations.

The aim of the present work was to develop a simple model able to account for experimental data on the effect of stirring on the crystal size in precipitation or salting-out on mixing two components.

THEORETICAL

In the turbulent regime, the mixing occurs in several stages[10,11,13]:

a) The added component (A) is distributed into large eddies rich in A, so that a macroscopically non-uniform mixture is obtained. In this stage, called the distributive mixing, no reaction is assumed to occur at the phase boundary.

b) At the stage of dispersive mixing, large regions A split into smaller ones as a result of the turbulence, but on the molecular scale the segregation is still high. The reaction begins to occur at the boundary of the regions. The stages *a*) and *b*) are collectively called the macromixing.

c) In the region of diffusive mixing, the size of the elementary eddies decreases, according to the Kolmogoroff theory of turbulence, to

$$\delta_0 \sim \lambda_K \sim \left(v^3/\varepsilon\right)^{1/4} , \tag{2}$$

and diffusion starts to mix the components on the molecular scale, resulting in an extensive reaction at the interface. It is assumed that the rate of micromixing in similar systems is the same for the same dissipated energy[9].

d) By shearing forces the size of the Kolmogoroff eddies is further reduced[11],

$$\delta_0/\delta = \left[1 + 0{\cdot}25(\varepsilon/v)\, t^2\right]^{1/2} , \tag{3}$$

but this effect, whose detailed treatment is known as the lamelar model[14], will not be considered here.

Thus, when a salting-out agent A is mixed with the bulk solution of a crystallizing substance, the highest supersaturation is produced at the "interface" between the two components. Hence, the nucleation rate will be proportional to the "interfacial"

area,

$$A_r \sim \delta_0^{-1} \sim \left(\varepsilon/\nu^3\right)^{1/4} \qquad (4)$$

and to a power of the maximum accessible supersaturation at the "interface". Expressing the solubility of crystallizing component 1 over a narrow concentration range corresponding to the metastable zone width by the equation[15,16]

$$w_{1eq} = w_{10} - K_{12}w_A, \qquad (5)$$

where w_{10} is the solubility in water, and w_A is the concentration of salting-out component A in the system, we can write

$$\Delta w = w_{10} - w_{1eq} = K_{12}w_A. \qquad (6)$$

The material balance[16] gives

$$w_A = \frac{m_A(1 + w_{10})(1 - w_{0A})}{m_{10} + m_A w_{0A}(1 + w_{10})}, \qquad (7)$$

where m_A is the mass of component A, m_{10} is the mass of the aqueous solution of crystallizing component 1, and w_{0A} is the mass fraction of water in component A. For a relatively narrow metastable zone, $m_{10} \gg m_A w_{0A}(1 + w_{10})$, so that we get, as a rough approximation,

$$\Delta w = (m_A/m_{10})(1 + w_{10})(1 - w_{0A})K_{12}. \qquad (8)$$

Hence, the nucleation rate will be

$$\dot{N}_N = k_N[(m_A/m_{10})(1 + w_{10})K_{12}(1 - w_{0A})]^n (\varepsilon/\nu^3)^{1/4}. \qquad (9)$$

For nucleation at the "interface", we can assume that $m_A/m_{10} = $ constant. The dissipated energy is proportional to the power input to the stirrer,

$$\varepsilon \sim n_m^3 d_m^5, \qquad (10)$$

so that the nucleation rate is given by

$$\dot{N}_N = K_N n_m^{3/4}(1 - w_{0A})^n, \qquad (11)$$

where K_N is a constant incorporating all constant quantities. The mean crystal size is given by[17]

$$\bar{L}^{1 + 3g/n} = 3B_N m_c^{1 - cg/n} \dot{m}_c^{g/n - 1} \qquad (12)$$

for continuous crystallizers, and by

$$L^{1+3s/n} = 3B_N m_c^{(1-c)s/n}(t_c/3)^{1-s/n} \qquad (13)$$

for batch crystallizers, where

$$B_N = \left(\frac{4 \cdot 5 m_c^c}{\alpha \varrho_c \dot{N}_N}\right)^{s/n} L \qquad (14)$$

is the system constant characterizing the crystallization (nucleation and growth) kinetics under given experimental conditions. Substituting for $\dot{N}_N$ from Eq. (11), we obtain

$$B_N = B_N' \frac{L}{(1 - w_{0A})^s} n_m^{-0.75s/n} , \qquad (15)$$

where

$$B_N' = \left(\frac{4 \cdot 5 m_c^c}{\alpha \varrho_c K_N}\right)^{s/n} . \qquad (16)$$

Equation (15) relates the system constant B_N, and hence also the crystal size L, to the precipitation parameters.

EXPERIMENTAL

A 400-cm^3 glass crystallizer of 70 mm diameter equipped with a cooling jacket, a four-bladed stirrer of 40 mm diameter with horizontal blades, and four baffles 10 mm wide, was charged with 150 cm^3 of an aqueous solution of $KAl(SO_4)_2$ saturated at 25°C. At this temperature, 150 cm^3 of methyl alcohol (100%, 70% or 50%) was added to the solution at a constant rate of 330 cm^3/h. The suspension was stirred for a further 30 min and then filtered. The crystals were washed with methyl alcohol and dried at room temperature. Results of sieve analyses are given in Table I, and the dependence of L on the stirrer speed is represented in Fig. 1.

RESULTS AND DISCUSSION

As seen from Fig. 1, the mean crystal size of the salted-out product depends on both the methyl alcohol concentration and the stirrer speed. A correlation analysis has shown that the variation in the mean crystal size with the stirrer speed can best be represented by the empirical equation

$$L . 10^6 = 1/(a + bn_m) \qquad (17)$$

or

$$L . 10^6 = n_m/(a + bn_m) . \qquad (18)$$

TABLE I

Sieve analyses of products from salting-out of $KAl(SO_4)_2 . 12 H_2O$

CH$_3$OH %	Exp. No	n_m	$M(L)$ for $L =$							$\bar{L} . 10^6$
			0·6	0·5	0·4	0·3	0·2	0·1	0·08	
100	1	240	2·36	6·76	12·53	23·25	57·35	89·80	95·85	196
	2	240	0·85	2·95	6·42	12·11	53·82	87·22	94·60	166
	3	360	0·44	4·04	16·10	26·56	55·15	84·54	93·46	176
	4	360	2·54	8·76	16·79	29·96	61·97	88·89	95·16	201
	5	360	4·07	12·32	17·61	33·16	68·87	90·03	95·85	214
	6	600	—	1·88	6·15	14·76	42·72	73·81	85·66	151
	7	960	—	—	1·07	9·54	23·07	64·56	79·47	118
	8	1 200	—	0·4	1·61	6·87	38·48	68·76	83·81	127
70	11	240	1·42	6·96	17·10	30·97	64·46	90·17	96·56	196
	12	240	6·51	19·53	28·64	44·39	79·93	95·55	98·29	250
	13	360	2·29	9·53	17·98	33·32	68·42	87·72	92·06	208
	14	360	1·63	9·98	14·51	24·80	62·02	89·38	95·13	198
	15	600	—	1·89	11·95	19·64	42·34	79·35	90·51	167
	16	960	0·12	0·43	1·04	4·75	41·23	70·60	84·20	131
	17	960	—	0·61	2·44	8·55	25·05	65·82	81·10	134
	18	1 200	—	0·40	1·66	5·26	22·60	58·22	74·85	125
50	21	240	11·46	19·24	26·20	38·49	70·45	90·12	95·85	272
	22	240	11·60	18·63	27·77	45·15	78·92	95·10	97·91	259
	23	360	3·53	9·69	25·11	45·54	80·23	95·03	97·65	230
	24	600	—	3·31	16·72	22·88	45·23	81·46	92·20	181
	25	960	—	0·71	4·29	11·45	29·58	63·84	83·62	141
	26	960	—	0·36	3·63	10·53	30·16	68·34	85·79	134
	27	1 200	0·37	1·48	3·33	9·99	46·65	69·61	82·94	151

TABLE II

Constants of empirical equations (17) and (18) (the parenthesized figures are smoothed values obtained by correlation of the data for all alcohol concentrations)

CH$_3$OH %	(17)			(18)		
	$a . 10^5$	$b . 10^8$	R	a	$b . 10^5$	R
100	433	342	0·881	−1·179	907	0·993
70	361	390	0·974	−1·303	891	0·997
		(360)		(−1·150)	(850)	
50	305	378	0·936	−1·096	796	0·992

Equation *(17)* can be used to extrapolate L to a fictitious unstirred solution, L. $. 10^6(n_m \to 0) = 1/a$, while in the limit of very high stirrer speed the value of L becomes zero. Equation *(18)*, on the other hand, can be used to extrapolate L to very high stirrer speeds, $L. 10^6(n_m \to \infty) = 1/b$. The values of the constants in Eqs *(17)* and *(18)* are listed in Table II.

FIG. 1

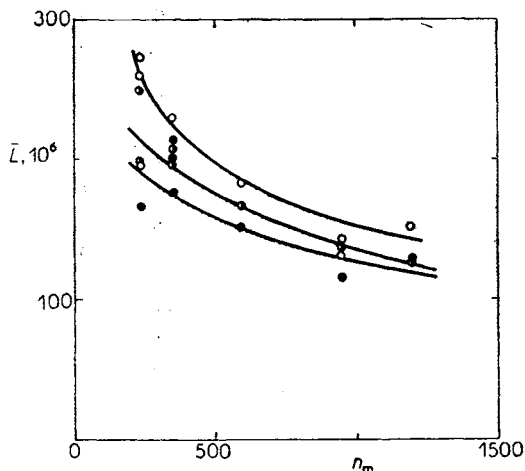Dependence of mean particle size on stirrer speed. O, 100% MeOH; ◑, 70% MeOH; ●, 50% MeOH
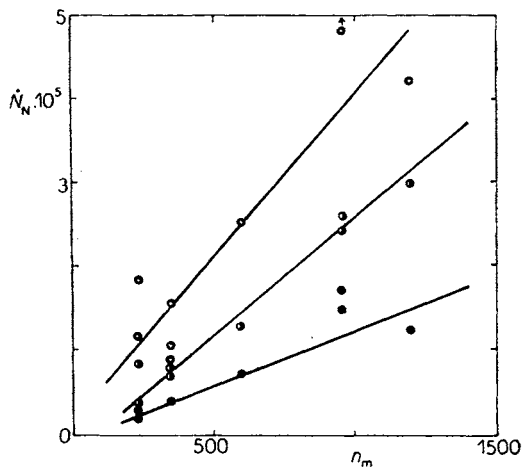
FIG. 2

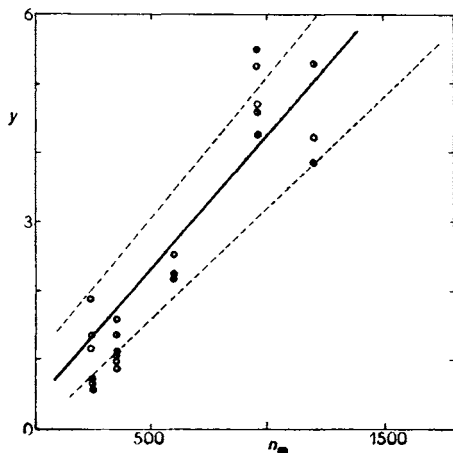Dependence of nucleation rate on stirrer speed. O, 100% MeOH; ◑, 70% MeOH; ●, 50% MeOH

FIG. 3

Dependence of nucleation rate on stirrer speed according to Eq. *(11)*. A plot of $y = \dot{N}_N/(1 - w_{0A})^{1.6}$ *vs* $n^{3/4}$.   O,   100% MeOH; ◑, 70% MeOH; ●, 50% MeOH

System constants B_N were calculated from Eq. (13) for suspension concentrations $m_c = 0.135\ kg/kg_0$ ($100\%\ CH_3OH$), 0.0909 ($70\%\ CH_3OH$), and 0.065 ($50\%\ CH_3OH$), using parameter values determined in a previous work[5]: $\alpha = 0.471$; $\varrho_c = 1\ 760\ kg$ . . m^3; $t_c = 1\ 800 + 750 = 2\ 550\ s$; $c = 0$; $g/n = 0.423$ (100%), 0.595 (70%), and 0.827 ($50\%\ CH_3OH$). The linear growth and nucleation rates were obtained from the equations

$$\dot{L} = \bar{L}/t_c \tag{19}$$

and

$$\dot{N}_N = \frac{27 m_c \dot{L}}{2\alpha\varrho_c \bar{L}^4}, \tag{20}$$

respectively. The results are summarized in Table III.

TABLE III
Kinetic parameters calculated from Eqs (13), (19), and (20)

Exp. No	n_m	$\dot{L} \cdot 10^8$	$\dot{N}_N \cdot 10^5$	$B_N \cdot 10^{14}$	$B'_N \cdot 10^6$
1	240	6·51	1·88	4 206	3 677
2	240	7·69	1·14	6 132	4 538
3	360	6·90	1·58	4 803	4 505
4	360	7·88	1·06	6 493	5 333
5	360	8·39	0·88	7 485	5 774
6	600	5·92	2·50	3 393	4 362
7	960	4·63	5·25	1 939	3 626
8	1 200	4·98	4·21	2 291	4 361
11	240	7·69	0·771	426·6	374
12	240	9·80	0·371	840·2	578
13	360	8·16	0·645	503·4	499
14	360	7·76	0·748	438·9	457
15	600	6·55	1·25	273·1	423
16	960	5·14	2·58	138·9	329
17	960	5·25	2·41	147·9	343
18	1 200	4·90	2·97	121·9	344
21	240	10·67	0·206	38·60	38·2
22	240	10·16	0·239	32·55	33·9
23	360	9·02	0·341	21·53	32·5
24	600	7·10	0·700	9·35	24·6
25	960	5·53	1·48	3·92	17·0
26	960	5·25	1·73	3·28	15·0
27	1 200	5·92	1·21	4·98	24·2

It can be seen from Table III that the rate of stirring affects primarily the nucleation rate (Fig. 2). As the rate of stirring is increased, the number of crystal nuclei generated increases and the supersaturation decreases; this is also connected with a slight decrease in the linear growth rate. The nucleation rate is largely affected by the concentration of methyl alcohol. By plotting $y = \dot{N}_N/(1 - w_{0A})^{1\cdot6}$ vs $n^{3/4}$ according to Eq. (11), we obtain a single straight line for all alcohol concentrations (Fig. 3), with a correlation coefficient $R = 0\cdot93$ confirming the applicability of the equation. The value of the system constant B_N depends strongly on the concentration of methyl alcohol. This is due primarily to the values of the relative kinetic exponent g/n, which vary according to alcohol concentration[5] from $0\cdot423$ to $0\cdot827$. The constant B_N' calculated from Eq. (15) (Table III) is independent, within experimental error, of the rate of stirring for each alcohol concentration:

$$100\% \text{ CH}_3\text{OH}: \ B_N' = (4\,522 \pm 736) \cdot 10^{-6}$$

$$70\% \text{ CH}_3\text{OH}: \ B_N' = (418 \pm 88) \cdot 10^{-6}$$

$$50\% \text{ CH}_3\text{OH}: \ B_N' = (26\cdot5 \pm 8\cdot7) \cdot 10^{-6}$$

Thus the simple model presented in this paper is adequate to describe the effect of the rate of stirring on the size of crystals salted out by the addition of a second solvent.

LIST OF SYMBOLS

A	interfacial area
a, b	empirical constants in Eqs (17) and (18)
B_N	system constant of crystallization
B_N'	constant in Eq. (16)
c	secondary nucleation exponent
c_i	concentration
d_m	stirrer diameter
g	growth exponent
K_N	constant in Eq. (11)
K_{12}	constant in Eq. (5)
k_m	micromixing coefficient
k_N	nucleation rate constant
$\bar{L}$	mean crystal size (m)
$\dot{L}$	linear growth rate
m	mass
m_c	suspension concentration
$\dot{m}_c$	specific output of crystallizer
$\dot{N}_N$	nucleation rate
n_m	stirrer speed

n	nucleation exponent
R_i	loss of mass from solution due to crystal growth
t	time (s)
t_c	batch time
w	concentration (kg/kg of solvent)
Δw	supersaturation
w_{0A}	mass fraction of water in component A
α	volume shape factor
δ	size of segregated volumes reduced by shearing forces
δ_0	size of segregated volumes
ε	dissipated energy
λ_K	size of elementary eddies
ν	kinematic viscosity
ϱ_c	crystal density

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