SCALE-UP OF STIRRED CRYSTALLISERS. BATCH PRECIPITATION OF ALUMINIUM POTASSIUM SULPHATE

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Aluminium potassium sulphate has been precipitated batchwise by mixing equal volumes of 0·6 mol/l solutions of potassium sulphate and aluminium sulphate with eventual addition of water in advance. The experiments were performed at 20 and 25°C in the volume 100 to 200 cm^3 and in the volume 0·021 m^3. From the size distribution of product crystals, the mean size of crystals has been evaluated and calculated the system kinetic constant of crystallisation B_N. The system constant is different in both series of experiments and can be correlated with the size of the crystallizer or with mixing intensity. Its value and the value of relative kinetic exponent g/n is comparable with the values obtained in experiments with cooling of solutions.

The batch cooling of solutions of potassium aluminium sulphate has been studied in the first paper[1] of the series in which the effect of scale-up of crystallisation units at different crystallisation modes has been considered. Another possibility of preparation of crystals of this compound is precipitation from the reactants[2] according to the reaction

$$K_2SO_4 + Al_2(SO_4)_3 \xrightarrow{aq} 2\,KAl(SO_4)_2\,.\,12\,H_2O\,. \tag{A}$$

This method of preparation of aluminium potassium sulphate is possible as its solubility is significantly smaller than the solubility of both initial components.

In this paper, the effect of scale-up of crystallisers on mean size of crystals of aluminium potassium sulphate at batch precipitation is studied.

THEORETICAL

The equation

$$(\bar{L} - L_N)^{1+3g/n} f(z_N)^{g/n} = 3B_N m_c^{(1-c)g/n} (t_c/3)^{1-g/n} \tag{1}$$

has been given in the last study[1] for the dependence of mean size of product crystals on process parameters in which

$$z_N = 3L_N/(\bar{L} - L_N) \tag{2}$$

and

$$f(z_N) = 1 + z_N + z_N^2/2 + z_N^3/6\,. \tag{3}$$

The values $\bar{L}$ and L_N can be simply determined by analysis of crystal size distribution based on relations

$$M(L) = 100(1 + z + z^2/2 + z^3/6)\exp(-z) \tag{4}$$

and

$$z = 3(L - L_N)/(\bar{L} - L_N) \tag{5}$$

Eq. (*5*) is an equation of a straight line in coordinates z *vs* L and values of $\bar{L}$ or L_N can be obtained from this straight line for values $M(\bar{L}) = 64{\cdot}7\%$ and $M(L_N) = 100\%$.

From Eq. (*1*) it is possible to derive the relation for dependence of mean size of product crystals $\bar{L}$ on crystalliser output: The crystalliser output can be defined for this purpose as $\dot{m}_c = 3m_c/t_c$ and it is then possible to write the usual relation[1]

$$\frac{\mathrm{d}\log\bar{L}}{\mathrm{d}\log\dot{m}_c} = \frac{g/n - 1}{1 + 3g/n} \tag{6}$$

which can be used for evaluation of the relative kinetic exponent, g/n.

EXPERIMENTAL

Aluminium potassium sulphate has been precipitated at 20 and 25°C by quick mixing of 0·6 mol/l solutions of potassium and aluminium sulphate. To be able to study the effect of supersaturation on crystallisation, both these solutions, kept at constant temperature, were mixed in a crystalliser equipped with an effective stirrer with the preset required amount of water. Mixing took place for 1 h after finishing the induction period, *i.e.* after precipitation of first crystals. The precipitated aluminium potassium sulphate has been then filtered, shortly washed with alcohol, dried at the laboratory temperature and weighed. Distribution of crystal sizes has been determined by sieving.

In all, two series of measurements were performed. The first series was mixing of 50 cm^3 of each initial solution and preset amount of water[2] in the beaker 250 cm^3, equipped with a two-blade stirrer of diameter 20 mm at 400 rev/min. The second series of experiments was performed identically but in a crystalliser with effective volume 0·021 m^3 equipped with a stirrer of diameter 100 mm at 300 rev/min. For the sieve analysis were used 6—7 sieves in the first series of experiments, 15 or 13 sieves in the second series of experiments. Parameters of individual experiments as well as the results of evaluation of data are summarised in Table I.

TABLE I

Precipitation of aluminium potassium sulphate; parameters of experiments and results. In all experiments was used the amount of salt which corresponds to 28·46 g $KAl(SO_4)_2.12\ H_2O$

Series	I						II		
Experiment No	11	12	13	14	17	18	21	22	23
T, °C	20	20	20	20	25	25	25	25	25
Preset H_2O, g	—	20	90	100	—	60	—	40	75
Total H_2O, g	85·2	105·2	175·2	185·2	85·2	145·2	85·2	125·2	160·2
w_0	0·334	0·270	0·162	0·153	0·334	0·210	0·334	0·227	0·178
w_{eq}	0·1127	0·1127	0·1127	0·1127	0·1343	0·1343	0·1343	0·1343	0·1343
$S = w_0/w_{eq}$	2·96	2·40	1·44	1·36	2·49	1·56	2·49	1·69	1·33
m_c	0·2213	0·1573	0·0493	0·0403	0·1997	0·0757	0·1997	0·0927	0·0437
$L_N \,.\, 10^3$	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02	0·02
$L \,.\, 10^3$	0·220	0·231	0·261	0·307	0·229	0·264	0·308	0·307	0·333
$B_N \,.\, 10^{13}$, $c = 1$	10·3	11·8	16·9	26·7	11·5	17·4	27·0	26·9	33·9
$c = 1·5$	6·55	6·76	6·85	10·19	7·09	8·04	16·67	13·15	13·25
$c = 2$	4·16	3·88	2·78	3·89	4·37	3·71	10·28	6·44	5·18

RESULTS AND DISCUSSION

Similarly as in the first contribution of this series[1] the sieve analyses were approximated by a simple function (Eq. (*4*), Fig. 1). Distributions were expressed satisfactorily by this function up to crystal sizes 0·6 mm. The mean crystal sizes $\bar{L}$ and initial crystal sizes L_N were evaluated from so obtained smoothed data (for the whole series of experiments the average value L_N was selected). From Eq. (5) the value $g/n = 0{\cdot}6$ was determined which was very close to the exponent g/n, found for crystallisation by cooling of aluminium potassium sulphate[1]. By use of Eq. (*1*) individual constants B_N were then evaluated for each experiment for different arbitrary values of exponents of secondary nucleation $c = 0$, $c = 1$, $c = 1{\cdot}5$ and $c = 2$, and the average relative deviation B_N determined in individual series of measurements. The minimum deviation B_N was found for the selected $c = 1{\cdot}5$ which corresponded to the combined effect of collisions of the type crystal–stirrer and crystal–crystal. As is obvious from Table I, the value B_N differs in both series of experiments: the average value with the series I is $7{\cdot}58 \pm 1{\cdot}38) \,.\, 10^{-13}$ and with the series II $(14{\cdot}35 \pm 2{\cdot}00) \,.\, 10^{-13}$, *i.e.* $B_N(\text{II}) = 1{\cdot}85 B_N(\text{I})$. It is not possible to decide definitely on basis of the made experiments if the effect of scale-up of the crystalliser size had been positive, *i.e.*

$$B_N = 2{\cdot}28 \,.\, 10^{-12} V^{0.12}$$

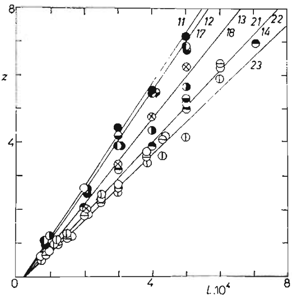

FIG. 1

Distribution of crystal sizes for individual experiments 11 ●, 12 ◐, 13 ◑, 14 ◓, 17 ◒, 18 ⊗, 21 ○, 22 ⊖, 23 ⦶.

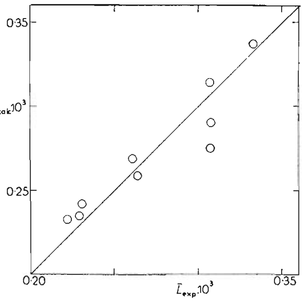

FIG. 2

Comparison of the calculated and experimental mean crystal sizes; ○ experimental points or if the difference was due to differing mixing intensity, *i.e.*

$$B_N = 1{\cdot}13 \,.\, 10^{-12}(n_m d_m^2)^{0.22} \,.$$

When the system constant B_N obtained in this study is compared (from Table I the average value for $c = 1$ is $B_N = 2{\cdot}03 \,.\, 10^{-12}$) with the value $B_N = 2{\cdot}09 \,.\, 10^{-12}$ ($c = 1$) calculated from cooling experiments[1], a quite good agreement has been reached in spite of a significant spread of values calculated here for $c = 1$. This fact seems to point to the conclusion that it does not matter significantly whether the supersaturation is formed by cooling of the solution or by a chemical reaction.

Mean crystal sizes $\bar{L}$ were calculated from Eq. (*1*) for conditions of individual experiments and they were compared with experimental values. From Fig. 2 is obvious that the results of experiments are reasonably well approximated by relation (*1*) and thus that this relation can be applied also in crystallisation by precipitation.

LIST OF SYMBOLS

B_N	system constant (kg, m, s)
c	exponent of secondary nucleation
d_m	stirrer diameter (m)
$f(z_N)$	function defined by Eq. (*3*)
g	kinetic exponent of crystal growth
L	crystal size (m)
$\bar{L}$	mean crystal size (m)
L_N	initial crystal size (m)
$M(L)$	oversize crystal fraction (% wt.)
m_c	concentration of suspension (kg/kg of free solvent)
$\dot{m}_c$	specific crystalliser output (kg/kg s)
n	kinetic exponent of nucleation
n_m	speed of rotation of stirrer (min^{-1})
$S = w_0/w_{eq}$	supersaturation ratio
t_c	batch time
V	volume of crystalliser (m^3)
w_0	concentration of potassium aluminium sulphate in solution (kg/kg free water)
w_{eq}	solubility of aluminium potassium sulphate in solution (kg/kg free water)
z	dimensionless residence time of crystals
z_N	dimensionless initial crystal size

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