CONTINUOUS PRECIPITATION OF LEAD IODIDE

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Lead iodide was precipitated from aqueous solutions of 0.015 – 0.1 M Pb(NO$_3$)$_2$ and 0.03 – 0.2 M KI in the equimolar ratio using a laboratory model of a stirred continuous crystallizer at 22 °C. After reaching the steady state, the PbI$_2$ crystal size distribution was measured sedimentometrically and the crystallization kinetics was evaluated based on the mean particle size. Both the linear crystal growth rate and the nucleation rate depend on the specific output of the crystallizer. The system crystallization constant either points to a significant effect of secondary nucleation by the mechanism of contact of the crystals with the stirrer blade, or depends on the concentrations of the components added due to the micromixing mechanism.

The precipitation process has been attracting interest[1–4] due to its importance in the chemical, food and pharmaceutical industries and also to the fact that, although a kind of crystallization, precipitation occurs under specific conditions, so that a number of effects which can be neglected in the case of crystallization of well-soluble substances play a role in precipitation. The basic difference between precipitation and crystallization of well-soluble substances is in the fact that considerably higher degrees of supersaturation are usually involved in the former. The way of mixing the two reactants is then of importance because micromixing gives rise to local concentration gradients which can induce intense nucleation[5]. Among factors which are of importance is the concentration of the solutions added. Precipitation of lead iodide was examined in this work as a model process with the aim to identify and quantitatively describe the effect of concentrations of the starting solutions on the precipitation kinetics.

THEORETICAL

If two reacting components are added to a continuous stirred crystallizer in the turbulent mode, the mixing process can be divided into several stages[5,6]. In the first stage, the component added forms macroscopic regions which are rich in it, whereas in the second stage, turbulences cause each macroscopic region to separate into smaller regions which form a sufficiently large "interface" that can contribute appreciably to the rate of the reaction between the component prevailing in the microregion and the other

component in the solution bulk. The microregions diminish in the next stage to the size of Kolmogoroff vortices; this stage involves the major part of the reaction between the two components combined with intense nucleation. The nucleation rate will, naturally, depend on the supersaturation developing at the "interface", i.e. on the concentrations of the entering components. Thus, the conventional relation for the nucleation rate[4],

$$\dot{N}_N = k_N m_c^c \Delta w^n \quad , \tag{1}$$

modifies to a form involving the effect of concentrations of the solutions, viz.

$$\dot{N}_{NC} = k_N m_c^c \Delta w^n C^d \quad , \tag{2}$$

where k_N is the nucleation rate constant, m_c is the concentration of the suspension playing a role in secondary nucleation, c is an empirical exponent of secondary nucleation ($c = 0$ in the surface layer mechanism or if secondary nucleation does not take place, $c = 1$ in the collision mechanism if collisions of the particles with the stirring blade predominate, and $c = 2$ in the collision mechanism if collisions between the particles predominate), Δw is supersaturation, C is the concentration of one of the solutions added (a single value is sufficient because the components are added in the stoichiometric ratio), and d is an empirical exponent.

The following relation between the mean crystal size $\overline{L}$ and the process parameters, viz. the suspension concentration m_c and the specific crystallizer output $\dot{m}_c$ has been derived[4,7]:

$$\overline{L}^{1 + 3g/n} = 3 \, B_N m_c^{1 - cg/n} \dot{m}_c^{(g/n) - 1} \quad , \tag{3}$$

where g is the kinetic exponent of growth, n is the kinetic exponent of nucleation, and B_N is the system crystallization constant, which can be written as

$$B_N = [4.5 \, m_c^c (\alpha \rho_c \dot{N}_N)]^{g/n} \, \dot{L} \quad . \tag{4}$$

By combining Eqs (*1*), (*2*) and (*4*) we obtain

$$B_{NC} = B_N / C^{dg/n} \quad . \tag{5}$$

This equation describes the dependence of the experimental system constant B_{NC} on the concentration of the entering solutions, C.

Secondary nucleation is usually supposed not to occur during precipitation[1]. This is warranted particularly in the collision mechanism involving very small particles (on the order of micrometers); at best, the surface layer mechanism can play a role in this case. We formally have $c = 0$ in both cases and denote the corresponding system constant B_{N0}. For larger particles (tens of micrometers), collisions with the stirrer blade are conceivable; then we have $c = 1$, for which the system constant will be denoted B_{N1}.

EXPERIMENTAL

Lead nitrate and potassium iodide were chemicals of reagent grade purity (Lachema, Brno). Distilled water was used.

Lead iodide was precipitated in a glass crystallizer possessing a working volume of 220 cm^3 with overflow at the liquid level height. The crystallizer was equipped with a two-blade glass stirrer whose perpendicular blades were 60 mm in diameter. Preliminary experiments showed that the homogenization of the suspension was sufficient at 400 rpm and that sampling from the overflow was representative. Solutions of the two components were added in the 1 : 1 ratio at a constant rate to an aqueous solution of PbI$_2$ saturated at 22 °C; the condition $C_I = 2\ C_{Pb}$ was met for the solutions added. The parameters of the experiments are given in Table I. A volume of 250 cm^3 of the suspension was sampled after elapse a 6 – 8-fold multiple of the mean residence time $\bar{t}_1$, the PbI$_2$ crystals were filtered out on a folded filter, dried in air, and after suspending in a saturated solution of PbI$_2$, the crystal size distribution was determined on an Analysette 20 photosedimentograph (Fritsch). A typical distribution diagram is shown in Fig. 1.

Linearization of sedimentographic data was achieved by using the relation[8]

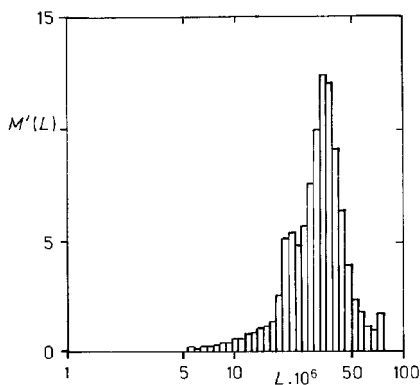$$M(L) = 100\,(1 + z + z^2/2 + z^3/6)\,\exp(-z)\ , \tag{6}$$

FIG. 1
Crystal size distribution in experiment No. 11

where $M(L)$ is the oversize fraction and the dimensionless crystal size z is defined as

$$z = L/(\dot{L}\,\bar{t}_1) \ , \tag{7}$$

that is, as the ratio of the true particle size L to the product of the linear crystallization rate $\dot{L}$ and the mean solution residence time $\bar{t}_1 = V/\dot{V}_{1+2}$. The mean crystal size values $\bar{L}$ corresponding to the value of $z = 3$, i.e. $M(L) = 64.7\%$, are given in Table II, an example of linearization is shown in Fig. 2. The mean crystal size can be employed to calculate the linear crystallization rate and nucleation rate[4] for individual experiments:

$$\dot{L} = \bar{L}/3\,\bar{t}_1 \tag{8}$$

$$\dot{N} = 9\,\dot{m}_c/(2\alpha\rho_c\bar{L}^3) \ . \tag{9}$$

Table I
Balance data of precipitation experiments

Experiment No.	$\dot{m}_c \cdot 10^6$ kg/(kg$_{H_2O}$ s)	c_{Pb} mol/kg H$_2$O	$\dot{V}_{1+2}$ cm^3/h	$m_c \cdot 10^3$ kg/kg H$_2$O	$\bar{t}_1$ s
1	0.52	0.015	180	2.29	4 380
2	1.43	0.015	384	2.92	2 040
3	1.43	0.015	384	2.92	2 040
4	2.35	0.05	180	10.3	4 380
5	2.84	0.015	700	3.17	1 116
6	2.84	0.015	700	3.17	1 116
7	4.93	0.1	180	21.6	4 380
8	4.95	0.1	180	21.7	4 380
9	4.95	0.1	180	21.7	4 380
10	5.34	0.05	384	10.9	2 040
11	5.34	0.05	384	10.9	2 040
12	8.00	0.015	1 878	3.36	420
13	10.0	0.05	700	11.2	1 116
14	11.0	0.1	384	22.5	2 040
15	20.4	0.1	700	22.8	1 116
16	20.4	0.1	700	22.8	1 116
17	27.1	0.05	1 878	11.4	420
18	54.8	0.1	1 878	23.0	420

RESULTS AND DISCUSSION

Equation (*3*) shows that based on experimental data, the relative kinetic exponent g/n can be calculated from experiments with a constant concentration of the suspension m_c:

$$(\mathrm{d} \ln \bar{L})/(\mathrm{d} \ln \dot{m}_c) = (g/n - 1)/(1 + 3g/n) \quad . \tag{10}$$

The value of $g/n = 0.514$ was obtained from the average of all experiments. Assume, in analogy to similar substances, that the kinetic growth order is $g = 2$; then the resulting

TABLE II
Results of experiments and evaluation of precipitation kinetics

Experiment No.	$\bar{L} \cdot 10^6$ m	$B_{NO} \cdot 10^{14,a}$	$B_{N1} \cdot 10^{14,a}$	$B_{NC} \cdot 10^{14,b}$	$\dot{L} \cdot 10^9$ m/s	$\dot{N}_N \cdot 10^6$ 1/kg
1	40.03	85.21	3.74	1.53	3.05	0.021
2	30.25	53.47	2.66	0.96	4.94	0.13
3	29.87	51.78	2.58	0.93	4.88	0.14
4	29.53	18.15	1.73	1.03	2.25	0.23
5	30.90	72.53	3.76	1.31	9.23	0.25
6	30.46	69.94	3.63	1.26	9.10	0.26
7	25.30	8.37	1.17	0.92	1.93	0.78
8	33.49	17.04	2.38	1.87	2.55	0.34
9	28.18	10.98	1.53	1.21	2.14	0.57
10	20.88	10.58	1.04	0.60	3.41	1.50
11	22.01	12.10	1.19	0.69	3.60	1.28
12	22.74	51.90	2.78	0.93	18.05	1.74
13	23.82	19.56	1.94	1.11	7.11	1.90
14	21.92	8.25	1.17	0.91	3.58	2.68
15	27.92	20.32	2.91	2.23	8.34	2.40
16	22.55	11.81	1.69	1.30	6.74	4.56
17	15.21	9.96	1.00	0.57	12.07	19.75
18	13.53	5.16	0.74	0.57	10.74	56.61
Mean value		29.8	2.09	1.11		
δ, %		86	46	40		

[a] B_{N0} and B_{N1} in $\mathrm{m}^{2.524}\ \mathrm{s}^{-0.486}$; [b] B_{NC} in $\mathrm{m}^{2.524}\ \mathrm{s}^{-0.486}\ \mathrm{kg}^{-0.957}\ \mathrm{mol}^{0.957}$.

nucleation order is $n = 3.89$, which compares well with the values[8] of $n = 3.54$ and 3.80 derived from metastable region width measurements and $n = 4.56$ from induction period measurements.

The shape factors of the PbI_2 crystals were estimated[9] from microscopic measurements. Lead iodide forms hexagonal platelets. The diameter of the circle inscribed in the hexagonal base was chosen as the characteristic dimension L, and the platelet thickness was approximated by $v = L/5$. Then the volume shape factor is

$$\alpha = L^3 (3^{1/2}/5)/L^3 = 0.29 \tag{11}$$

and the surface shape factor is

$$\beta = [L^2 \cdot 3^{1/2} + 6 L^2/(5 \cdot 3^{1/2})]/L^2 = 2.27. \tag{12}$$

The crystal density, $\rho_c = 6\ 060$ kg m^{-3}, was taken from tables[10].

The dependences of the linear crystal growth rate $\dot{L}$ and nucleation rate $\dot{N}_N$ on the specific crystallizer output, calculated from Eqs (8) and (9), are shown in Fig. 3.

Data of the system constant B_{N0}, calculated from Eq. (3), are given in Table II. The values are strongly dependent on the concentration of the entering solutions. The dependence was linearized in logarithmic coordinates (Fig. 4) to obtain the equation

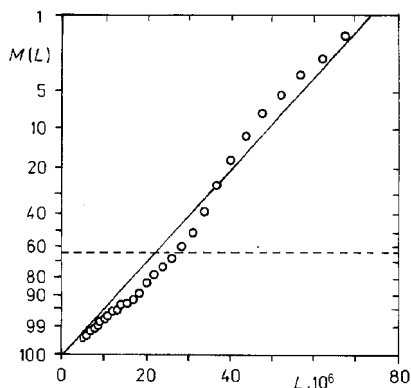$$\ln B_{N0} = 3.1577 - 0.957 \ln C_{Pb} \tag{13}$$

Fig. 2

Linearized crystal size distribution in experiment No. 11

with a correlation coefficient of $R = -0.90$. The system constant B_{NC} was calculated from the equation

$$B_{NC} = B_{NO} \, C_{Pb}^{0.957} \; . \tag{14}$$

The values are given in Table II, which also includes the B_{N1} values calculated for $c = 1$ for the assumption of secondary nucleation by the contact mechanism. The deviations from the mean indicate that the model accounting for the effect of concentration gradients during micromixing suits best, although the model of secondary nucleation with the assumption of contact with the stirrer blades may be applicable as well.
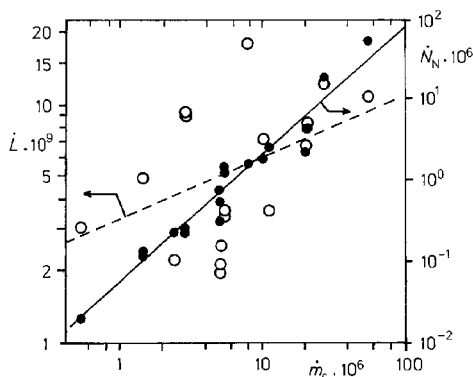

FIG. 3
Dependence of the linear crystal growth rate $\dot{L}$ (○) and nucleation rate $\dot{N}_N$ (●) on the specific crystallizer output
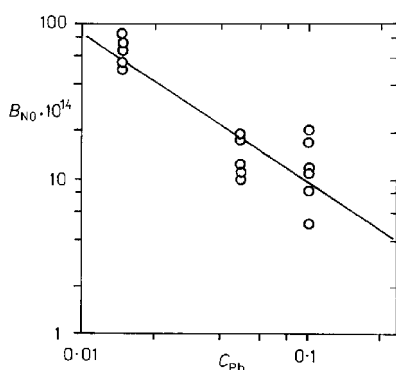
FIG. 4
Dependence of the system constant B_{N0} on the concentration C_{Pb}

SYMBOLS

B_N	system crystallization constant
B_{N0}	system constant for $c = 0$
B_{N1}	system constant for $c = 1$
B_{NC}	system constant for the micromixing model
C	concentration, mol/kg H_2O
C_I	iodide ion concentration
C_{Pb}	lead ion concentration
c	secondary nucleation exponent
d	empirical coefficient in Eq. (2)
g	order of the kinetic equation of growth

k_N	nucleation rate constant
L	crystal size
$\overline{L}$	mean crystal size
$\dot{L}$	linear crystal growth rate
$M(L)$	oversize crystal fraction exceeding size L
m_c	suspension concentration, amount of crystals separated
$\dot{m}_c$	specific crystallizer output
$\dot{N}_N$	nucleation rate
N_{NC}	nucleation rate taking into account the effect of micromixing
n	kinetic order of nucleation
R	correlation coefficient
$\overline{t}_1$	mean solution residence time in crystallizer
V	crystallizer volume
$\dot{V}_{1+2}$	total feeding rate of the two reagents
v	crystal thickness
Δw	supersaturation, kg/kg H_2O
z	dimensionless crystal size
α	volume shape factor
β	surface shape factor
δ	percent mean square deviation
ρ_c	crystal density

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