BATCH PRECIPITATION OF LEAD IODIDE

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Lead iodide was precipitated by a procedure in which an aqueous solution of potassium iodide at a concentration of 0.03, 0.10 or 0.20 mol l^{-1} was stirred while an aqueous solution of lead nitrate at one-half concentration was added at a constant rate. The mean size of the PbI_2 crystals was determined by evaluating the particle size distribution, which was measured sedimentometrically. The dependence of the mean crystal size on the duration of the experiment exhibited a minimum for any of the concentrations applied. The reason for this is discussed.

One of our previous papers[1] dealt with the precipitation of lead iodide in a continuous stirred crystallizer. A steady state can be expected to establish during the continuous precipitation, i.e. the supersaturation to be virtually constant throughout the experiment. In contrast to this, all parameters of crystallization change appreciably during batch precipitation. For well-soluble substances the mean size of the crystal product will increase with increasing batch time[2] or, if secondary nucleation occurs, the mean size plot will exhibit a maximum[3]. The mean crystal size can be expected to diminish with increasing concentration of the solutions mixed[4]. These trends, however, may not be so straightforward if low-soluble substances are precipitated because micromixing plays a major role in this case whereas secondary nucleation by the collision mechanism will have a negligible effect[5]. Since many industrial products are precipitated by the batch process, it was the aim of the present work to examine the effect of the batch time and/or of the rate of component mixing on the product crystal size.

EXPERIMENTAL

Chemicals. Lead nitrate and potassium iodide of reagent grade purity were supplied by Lachema, Brno. Distilled water was used. Lead iodide was precipitated in a 500 cm^3 beaker which was fitted with a double-blade glass stirrer and held at room temperature. A volume of 200 ml of a KI solution at a concentration of 0.03, 0.1 or 0.2 mol l^{-1} was added, and 200 ml of a solution of $Pb(NO_3)_2$ at a concentration of 0.015, 0.05 or 0.1 mol l^{-1}, respectively, were fed just above the level by means of a peristaltic pump applying a rate of 35, 85, 170, 330, 600 or 1 330 ml/h. After adding all the solution, the suspension was stirred for another 30 min. The crystals were separated and dried. A representative sample was then suspended in a saturated solution of PbI_2 and deagglomerated in an

ultrasonic bath for 1 min, and the crystal size distribution was determined on an Analysette 20 photosedimentograph (Fritsch).

Calculations. The data were linearized by means of the relation[6]

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

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

$$z = 3\,L/\dot{L}t_c\,, \tag{2}$$

i.e. as the triple actual size L (in μm) divided by the product of the average linear rate of crystallization $\dot{L}$ (in μm s^{-1}) and the batch time t_c (in s). The mean crystal size corresponding to $M(L)$ = 64.7 wt.% is calculated from the relation

$$\bar{L} = \dot{L}t_c\,. \tag{3}$$

RESULTS AND DISCUSSION

The results of measurement are summarized in Table I. The dependence of the mean crystal size on the duration of the experiment is shown in Fig. 1. The curves corresponding to the 2nd order polynomial are seen to pass through a minimum for all of the concentrations used. This surprising behaviour can be explained as follows.

As the one reaction component is added to the solution of the other component, a high supersaturation develops at the "interface" of the drops added. Supersaturation will also occur in the bulk phase, and this supersaturation will be the higher, the higher the rate of addition of the solution[7]. The supersaturation at the "interface" of the fed drops will cause nucleation. As the number of precipitated particles increases, the concentration of the component in the vessel decreases gradually and so does the supersaturation, until the latter drops to below the metastable region boundary and nucleation virtually ceases to proceed. The number of crystals formed will depend on the rate of nucleation

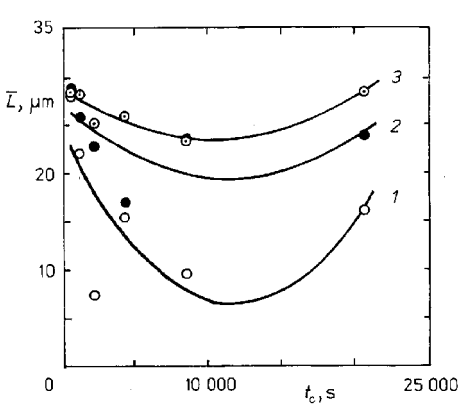

FIG. 1
Mean crystal size $\bar{L}$ (in μm) plotted against batch time t_c. Lead nitrate concentration (mol l^{-1}): *1* 0.015, *2* 0.05, *3* 0.1

and on the time for which the nucleation proceeded. The size of the resulting crystals then is a complex function of the number of crystals formed, the growth rate (which is dependent on the supersaturation in the bulk phase), and the time during which the crystals were in contact with the supersaturated solution. If the rate of addition is reduced, i.e. the t_c value is increased, more crystals are formed and are smaller in size. At high t_c values, however, the crystal growth begins to play a major role and the mean crystal size will also increase with increasing t_c. All those effects combine to give rise to a minimum in the plot of mean crystal size vs the batch time t_c.

The concentrations of the reacting solutions manifest themselves in two ways: a higher concentration brings about a higher supersaturation and hence, a more intense nucleation, but also a faster growth, and moreover, provides higher quantities of substance precipitated and so a higher increment of the crystal size. Figure 1 demonstrates that the favourable effect of a higher concentration on the product crystal size predominates in the concentration region investigated. At the same time, the effect of the batch time decreases with increasing concentration, and the scatter of the experimental data

TABLE I
Parameters of the experiments and resulting mean product crystal size

Experiment No.	$c_{Pb(NO_3)_2}$, mol l^{-1}	t_c, s	$\bar{L}$, μm
1	0.015	8 470	9.54
2	0.015	4 235	15.46
3	0.015	2 182	7.41
4	0.015	1 200	22.13
5	0.015	541	27.86
6	0.015	20 570	16.09
7	0.05	8 470	23.33
8	0.05	4 235	17.01
9	0.05	2 182	22.83
10	0.05	1 200	25.82
11	0.05	541	28.93
12	0.05	20 570	23.73
13	0.1	4 235	25.90
14	0.1	2 182	25.17
15	0.1	8 470	23.48
16	0.1	1 200	28.31
17	0.1	20 570	28.35
18	0.1	541	28.36

reduces. This is apparently due to the stochastic nature of nucleation in more dilute solutions.

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