WIDTH OF THE METASTABLE REGION IN THE PRECIPITATION OF LEAD IODIDE

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Nucleation kinetics in the precipitation of lead iodide from dilute solutions of lead nitrate and potassium iodide was derived from measurements of the metastable region width when adding KI solution to $Pb(NO_3)_2$ solution, and also from induction period measurements on instantaneous mixing of batches of the two solutions. The nucleation order values obtained lay within the region of m = 3.5 to 4.6, which is a satisfactory agreement in view of the different nature of the two approaches.

Batch precipitation can be conducted in two ways: either one solution is slowly added to the other, or equivalent quantities of the two solutions are mixed at once. A higher-quality product can be expected in the former case because supersaturation takes place slowly and does not reach so high a level as in the latter case. Hence, nucleation is controlled to an extent, and agglomeration and entraining of impurities in the product crystal lattice are limited as well. The quality of the product will be affected appreciably by the starting stage of precipitation, during which the majority of particles are formed. Investigation of the starting stage thus can bring information which is of significance in the precipitation process control. The present work was performed with the aim to find how the metastable region width, and thus the primary nucleation kinetics, is affected by the manner the other component is added, and to what extent the information concerning the metastable region width for aqueous solutions of well-soluble substances is applicable to the precipitation of low-soluble substances.

THEORETICAL

Precipitation of lead(II) iodide from solutions of lead(II) nitrate and potassium iodide was chosen as the model system:

$$Pb(NO_3)_2\,(aq) + 2\,KI\,(aq) \longrightarrow PbI_2\,(s) + 2\,KNO_3\,(aq) \qquad (A)$$

The solubility of PbI_2 is very low, only 0.738 g/1 000 g H_20 at 22 °C (ref.[1]). If the precipitation is conducted so that a solution of KI is added to a solution of $Pb(NO_3)_2$, the excess Pb^{2+} ions will lower the solubility of PbI_2 for the solubility product to remain constant, whereas K^+ and NO_3^- ions present in the solution will increase the solubility of PbI_2. Their effect will be expressed by the activity change, which can be calculated, for instance, from the Davies equation[2].

The solubility product of PbI_2 in water will be calculated from the solubility data $w^0_{PbI_2}$. Furthermore we have $C^0_{Pb} = C^0_{PbI_2}$ and $C^0_I = 2\,C^0_{PbI_2}$, so that conventional calculation for 22 °C gives a value of $S_0 = 6.911\,.\,10^{-12}$.

Assume that a volume V_I of KI solution at a concentration of C^0_I is added to a volume V_{Pb} of solution of $Pb(NO_3)_2$ having a concentration C^0_{Pb}. The input amounts of $Pb(NO_3)_2$ and KI can be calculated from the balance. Also assume that all KI is spent during the reaction.

The total water content in the system can be calculated from the water balance in the input solutions; the requisite solution densities can be obtained, e.g., from tables[3].

The solubility of lead iodide in the reaction mixture then is calculated from the solubility product, taking into account the relations

$$C_{Pb(NO_3)_2} = 1\,000\; m_{Pb(NO_3)_2}/m_{H_2O}\, M_{Pb(NO_3)_2} \tag{1}$$

$$C_{Pb} = C_{Pb(NO_3)_2} + x \tag{2}$$

$$C_I = 2\,x \tag{3}$$

so that

$$S = (C_{Pb(NO_3)_2} + x)\; 4\,x^2 \;. \tag{4}$$

By solving this equation in x and substituting in the relation

$$w_{PbI_2,eq} = x\, M_{PbI_2}/1\,000 \tag{5}$$

we obtain the unknown solubility of PbI_2. The supersaturation of the solution then can be calculated as

$$\Delta w = m_{PbI_2}/m_{H_2O} - w_{PbI_2,eq} \;. \tag{6}$$

Two approaches exist to achieve supersaturation during precipitation reactions. Either a solution of substance A is added to a solution of substance B at a constant rate until first crystals appear, or batches of the two solutions are mixed at once at time $t = 0$ and the time elapsed to the appearance of first crystals is measured.

Treatment in the former case is based on the assumption that at the moment of appearance of the first visible crystals, the rate of formation of supersaturation is compensated by the nucleation rate[4], that is,

$$\dot{m}_\mathrm{c} = \dot{m}_{\mathrm{PbI_2}} = k_\mathrm{N}\, \Delta w^m_\mathrm{max} \ , \tag{7}$$

which can be written in the form

$$k_\mathrm{N}\, \Delta w^m_\mathrm{max} = (C^0_\mathrm{I}\, M_{\mathrm{PbI_2}}/2\,000)\, \dot{V}_\mathrm{I} \tag{8}$$

or, after rearrangement, as

$$\log \Delta w_\mathrm{max} = A + (1/m) \log \dot{V}_\mathrm{I} \ , \tag{9}$$

where

$$A = (1/m) \log [C^0_\mathrm{I}\, M_{\mathrm{PbI_2}}/(2\,000\, k_\mathrm{N})] \ . \tag{10}$$

Equation (*9*) is an analogy of the equations derived for constant-rate cooling[4] and for precipitation with an addition of the other solvent[5,6].

For induction period measurements we have[4]

$$k_\mathrm{N}\, \Delta w^m = K/t_\mathrm{N} \tag{11}$$

or

$$\log t_\mathrm{N} = \log (K/k_\mathrm{N}) - m \log \Delta w \ , \tag{12}$$

where K is a proportionality constant between the nucleation rate and the inverse induction period[7].

The procedures of gradual addition and instantaneous mixing, however, differ with respect to the mixing. We can assume that at the first moment after mixing the solutions, regions of predominating concentration of A and regions of predominating concentration of B will exist, and these regions will diminish with time until the system is completely homogeneous[8]. If solution of B is added slowly, the regions of predominating concentration of B will be small and homogenization will take place rapidly, whereas if the solutions are mixed at once, larger inhomogeneities will appear and their homogenization will take a longer time. In the first moments after mixing, supersaturation with PbI_2 will take place at the "interface" of the phases and will be apparently higher than as corresponds to the perfectly mixed system[8]. Assume that water which is added with the other solution plays no role at the "interface", hence, that the effective supersaturation Δw_{eff} will lie somewhere between that for a perfect mixing of the undiluted solutions Δw_0 and for solutions with the corresponding dilution Δw^*:

$$\Delta w_{eff} = \varphi \, \Delta w_0 + (1 - \varphi) \, \Delta w^* . \tag{13}$$

This value is then employed in Eq. (*12*). The φ value in this model corresponds to the volume fraction of the added solution in the system after mixing.

EXPERIMENTAL

Lead nitrate and potassium iodide were reagent grade chemicals obtained from Lachema, Brno. Solutions were prepared with distilled water.

The metastable region width was measured at 22 °C in a procedure where a 0.016 M solution of KI was pipetted by drops at a constant rate into a 50 cm^3 Erlenmeyer flask containing 25 cm^3 of a 0.008 M solution of $Pb(NO_3)_2$. The volume V_I and time t were recorded when the first haze became visible. The mass balance is given in Table I, the results of measurement are summarized in Table II.

The induction period was measured using the same apparatus. A mixture containing 4 cm^3 of a 0.016 M KI and a known volume of water was added at once to 4 cm^3 of a 0.008 M solution of $Pb(NO_3)_2$ and time was measured from that moment on. The mass balance and results of measurement are given in Table III.

RESULTS AND DISCUSSION

Inserting experimental data (Table II) in Eq. (*9*) we obtain

$$\log (\Delta w \,.\, 10^4) = 1.2281 + 0.2635 \log \dot{V} \tag{14}$$

with a correlation coefficient of R = 0.962. The correlation is shown in Fig. 1. Similarly, insertion of experimental data (Table II) into Eq. (*7*) gives

TABLE I

Mass balance of precipitation of 25 cm^3 of a 0.008 M solution of $Pb(NO_3)_2$ with a 0.016 M solution of KI

KI, cm^3	PbI_2, mg	KNO_3, mg	$Pb(NO_3)_2$, mg	H_2O, g	$w_{PbI_2,eq}$ kg/kg H_2O
0	0.00	0.00	66.24	24.89	0.000481
1.0	3.69	1.62	63.59	25.89	0.000493
2.0	7.38	3.24	60.94	26.88	0.000505
3.0	11.06	4.85	58.29	27.88	0.000518
4.0	14.75	6.47	55.64	28.87	0.000530
5.0	18.44	8.09	52.99	29.87	0.000543
6.0	22.13	9.71	50.34	30.86	0.000556
7.0	25.82	11.32	47.69	31.86	0.000570
8.0	29.50	12.94	45.04	32.85	0.000584
8.5	31.35	13.75	43.72	33.35	0.000591
9.0	33.19	14.56	42.39	33.85	0.000598
10.0	36.88	16.18	39.75	34.85	0.000613
10.5	38.72	16.99	38.42	35.34	0.000621
11.0	40.57	17.79	37.10	35.84	0.000628
11.5	42.41	18.60	35.77	36.34	0.000636
12.0	44.26	19.41	34.45	36.83	0.000644
12.5	46.10	20.22	33.12	37.34	0.000651
13.0	47.94	21.03	31.80	37.83	0.000660
13.5	49.79	21.84	30.47	38.33	0.000668
14.0	51.63	22.65	29.15	38.83	0.000676
15.0	55.32	24.26	26.50	39.82	0.000693
16.0	59.01	25.88	23.85	40.82	0.000710
17.0	62.70	27.50	21.20	41.82	0.000728
18.0	66.39	29.12	18.55	42.81	0.000746
19.0	70.07	30.74	15.90	43.81	0.000765
20.0	73.76	32.35	13.25	44.80	0.000784
21.0	77.45	33.97	10.60	45.80	0.000804
22.0	81.14	35.59	7.95	46.79	0.000824
23.0	84.83	37.21	5.30	47.79	0.000845
24.0	88.51	38.82	2.65	48.78	0.000866
25.0	92.20	40.44	0	49.78	0.000887

TABLE II
Results of experiments in which a 0.016 M solution of KI was gradually added to 0.008 M solution of $Pb(NO_3)_2$

Experiment No.	$\dot{V}$, cm^3/min	0.016 M KI cm^3	*t*, s	$\dot{m} . 10^6$ kg/kg s	$\Delta w . 10^4$ kg/kg
1	0.85	8.5	600	1.57	3.49
2	1.4	9.0	386	2.54	3.82
3	1.5	9.0	360	2.72	3.82
4	4.4	11.0	150	7.55	5.04
5	12.5	12.5	60	20.58	5.83
6	7.7	11.5	90	12.97	5.31
7	5.25	10.5	120	9.13	4.75
8	9.75	13.0	80	15.84	6.08
9	12.0	15.0	75	18.52	6.96
10	27.5	23.0	50	35.50	9.30
11	10.1	13.5	80	16.24	6.31
12	11.25	15.0	80	17.36	6.96

TABLE III
Mass balance of experiments and results of induction period measurement

Experiment No.	PbI_2 mg	KNO_3 mg	H_2O		$w_{PbI_2,eq}$ kg/kg H_2O	$t_N{}^a$, s	$\Delta w . 10^4$ kg/kg
			Addition g	Total g			
21	0.01475	0.00647	0	7.96	0.000887	<1.5	9.66
22	0.01475	0.00647	0.68	8.64	0.000881	5.9	8.25
23	0.01475	0.00647	1.36	9.32	0.000876	11.2	7.06
24	0.01475	0.00647	2.04	10.00	0.000872	13.9	6.03
25	0.01475	0.00647	2.72	10.68	0.000867	16.9	5.14
26	0.01475	0.00647	3.40	11.36	0.000864	23.5	4.35
27	0.01475	0.00647	4.08	12.04	0.000860	33.3	3.65
28	0.01475	0.00647	5.44	13.40	0.000854	43.4	2.47
29	0.01475	0.00647	6.80	14.76	0.000848	53.4	1.51

[a] The t_N value is the average of 7 to 9 measurements with a mean square deviation of ±1.2 s.

$$\log (\Delta w \,.\, 10^4) = 1.0538 + 0.2823 \log (\dot{m}_c \,.\, 10^6) \qquad (15)$$

with a correlation coefficient of $R = 0.949$. The inverse values of the coefficients correspond to the nucleation order $m = 3.54$ and 3.80, respectively (the difference is due to rounding errors).

Equation (*12*), with data from Table III and for a volume fraction $\varphi = 0.5$, takes the form

$$\log t_N = 11.98 - 4.56 \log (\Delta w_{eff} \,.\, 10^4) \qquad (16)$$

($R = -0.988$). The slope of this dependence (Fig. 2) gives a nucleation order of $m = 4.57$. In view of the different nature of the two approaches, the agreement of the data derived from the metastable region width measurements and from the induction period measurements is satisfactory.

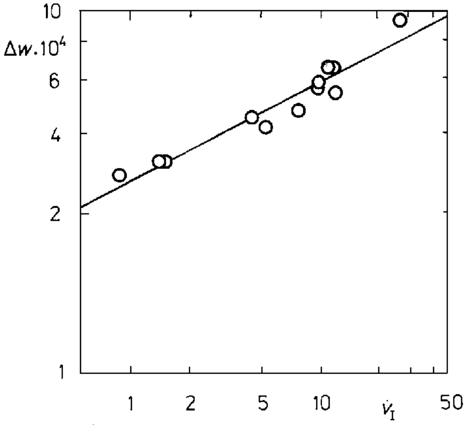

FIG. 1
Dependence of the metastable region width Δw on the rate of addition of the KI solution $\dot{V}_I$

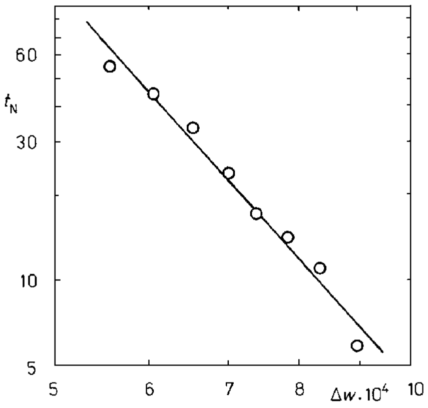

FIG. 2
Dependence of the induction period t_N on supersaturation Δw

SYMBOLS

A	constant in Eq. (*9*)
C_i	concentration of component *i*
C_i^0	concentration of component *i* in aqueous solution
K	proportionality constant

k_N	nucleation rate constant
M_i	molecular weight of component *i*
m	apparent nucleation order
m_i	weight of component *i*
m_i^0	input weight of component *i*
$\dot{m}_c$, $\dot{m}_{PbI_2}$	lead iodide precipitation rate
R	correlation coefficient
S	lead iodide solubility product in the system
S_0	lead iodide solubility product in water
t	time
t_N	induction period
V_i	volume of solution of component *i*
$\dot{V}_I$	rate of addition of potassium iodide solution
$w_{PbI_2}^0$	lead iodide concentration in water
$w_{PbI_2,eq}$	lead iodide solubility
Δw	supersaturation
Δw_{eff}	effective supersaturation
Δw_{max}	maximum supersaturation
Δw_0	supersaturation after mixing undiluted solutions
Δw^*	supersaturation after mixing dilute solutions
φ	volume fraction of solution added

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