

CRYSTALLIZATION OF PENTAERYTHRITOL II. MODEL EXPERIMENTSMiloslav KAREL^a, Jaroslav NYVLT^a and Angelo CHIANESE^b^a *Institute of Inorganic Chemistry,**Academy of Sciences of the Czech Republic, 160 00 Prague 6, The Czech Republic*^b *University of Rome "La Sapienza",**Via Eudossiana 18, I-00184 Rome, Italy*

Received March 2, 1993

Accepted November 2, 1993

Kinetics of crystallization of the pentaerythritol has been determined in laboratory experiments: MSMPR (Mixed Suspension–Mixed Product Removal) crystallizer experiments served for determination of the kinetics of secondary nucleation and of the kinetics of crystal growth.

Crystallization of the pentaerythritol (PE, i.e. 2-bis(hydroxymethyl)-1,3-propanediol) from mother liquors is complicated by the presence of impurities coming from the chemical reaction, in particular formaldehyde, its derivatives, formiates, dipentaerythritol (DPE) and other polypentaerythritols. These impurities can affect the kinetics of crystallization. In the first part of this study¹ we investigated the effect of DPE on the metastable zone width of PE, i.e. on its primary nucleation. The aim of this paper is to present the results of crystallization studies performed in a laboratory model of continuous crystallizer, investigating the effect of the DPE admixture on the kinetics of PE crystallization from aqueous solutions.

EXPERIMENTAL

Continuous laboratory MSMPR experiments have been performed on the small-scale crystallizer described earlier². It consists of a 400 cm³ vessel made of glass, with a jacket for keeping constant temperature, two-blade agitator, side outlet controlled by a magnetic valve, platinum resistance thermometer and electrodes controlling the level. Slightly overheated solution is fed using a peristaltic pump, discharge is periodically controlled by the electronic circuit comprising the electrodes, controller and magnetic valve. The amount of suspension removed during one valve opening is less than 10% of the crystallizer volume. The solution has been prepared from PE (Aldrich, 98%, melting point 256 °C) in distilled water. Representative sampling has been checked by a wash-out test^{2,3} and found to be satisfactory.

Experiments have been performed under the conditions listed in Table I. Samples have been taken after elapse of 6 to 10 retention times of solution, when the steady state has been established⁴. Crystals of PE were separated using a glass filter, dried and sieved.

RESULTS AND DISCUSSION

The results of sieve analyses have been fitted^{5,6} using the equation

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

where the dimensionless crystal size is

$$z = L/(\bar{L}\bar{t}_1) . \quad (2)$$

TABLE I
Conditions of MSMPR experiments

Experiment No.	T , °C	ΔT , K	m_c	\bar{t}_1 , s	$\dot{m}_c \cdot 10^5$, s ⁻¹
2% DPE					
1	61.0	11.4	0.0293	1 200	2.44
2	60.9	11.5	0.0334	1 200	2.78
3	61.4	10.9	0.0561	2 400	2.34
4	60.7	11.7	0.0444	1 200	3.70
5	60.5	11.9	0.0452	1 200	3.77
6	42.4	18.5	0.0480	2 400	2.00
7	42.4	18.5	0.0451	1 200	3.76
8	42.5	18.4	0.0383	1 620	2.36
9	42.5	18.4	0.0395	1 620	2.44
10	30.6	19.0	0.0252	2 400	1.05
11	31.1	18.5	0.0280	1 680	1.67
12	31.7	17.9	0.0289	1 488	1.94
6% DPE					
13	45.0	15.9	0.0452	1 872	2.41
14	45.0	15.9	0.0324	1 980	1.64
15	46.1	14.8	0.0476	1 578	3.02
16	42.5	18.4	0.0483	1 620	2.98
17	42.5	18.4	0.0559	3 000	1.86
18	25.8	23.8	0.0436	1 200	3.63
19	24.7	24.9	0.0351	1 500	2.34
20	24.1	25.4	0.0369	1 500	2.46

For $z = 3$, the mean crystal size

$$\bar{L} = 3 \dot{\bar{L}}_1 \quad (3)$$

has been calculated and together with the corresponding suspension concentration, m_c , and specific production rate of the crystallizer, \dot{m}_c , used for the determination of the system constant of crystallization^{5,7} B_N :

$$\bar{L}^{1+3g/n} = 3 B_N m_c^{1-cg/n} \dot{m}_c^{g/n-1} \quad (4)$$

The ratio of kinetic exponents of growth and nucleation, g/n , can be determined from this equation the condition of constant suspension concentration:

TABLE II
Results of MSMPR experiments

Experiment No.	L , mm	$B_N \cdot 10^{12}$	$\dot{L} \cdot 10^8$, m s ⁻¹	$\dot{N}_N \cdot 10^{-3}$, kg s ⁻¹
1	0.19	4.13	5.28	19
2	0.18	3.86	5.00	26
3	0.20	4.12	2.78	16
4	0.164	3.52	4.55	46
5	0.169	3.80	4.69	43
6	0.20	3.85	2.78	14
7	0.198	5.45	5.50	26
8	0.196	4.18	4.03	17
9	0.209	4.91	4.30	15
10	0.21	3.27	2.92	6.2
11	0.16	2.26	3.17	22
12	0.18	3.21	4.03	18
13	0.15	8.03	2.67	39
14	0.148	6.67	2.49	28
15	0.137	7.53	2.89	64
16	0.142	8.03	2.92	57
17	0.148	6.27	1.64	31
18	0.108	5.25	3.00	57
19	0.179	(12.2)	3.98	22
20	0.142	7.64	3.16	47

$$\frac{d \log \bar{L}}{d \log \dot{m}_c} = \frac{g/n - 1}{1 + 3g/n} \quad (5)$$

Applying this equation to experimental data with PE + 2% DPE we have found

$$g/n = 0.427$$

and for experiments with PE + 6% DPE

$$g/n = 0.369.$$

It is known from earlier investigations⁸ that the PE crystals in concentrated suspensions are subjected to an attrition. This is why we may expect a predominant role of the crystal-crystal contacts and thus the coefficient of secondary nucleation should be $c = 2$. This presumption has been verified by the small spread of constants B_N calculated for various values of c . The constants B_N obtained from Eq. (4) are summarized in Table II.

The analysis of the MSMPR experiments offers also values of the linear crystal growth rate, \dot{L} , and of the nucleation rate, \dot{N}_N . For these quantities it holds⁵

$$\dot{L} = \bar{L}/(3\bar{t}_1) \quad (6)$$

and

$$\dot{N}_N = 9 \dot{m}_c / (2\alpha \rho \bar{L}^3), \quad (7)$$

where $\alpha = 0.59$ and $\rho = 1396 \text{ kg m}^{-3}$. Calculated values are summarized in Table II.

The drawback of the MSMPR experiments is that they can express the nucleation rate only as a function of the linear growth rate

$$\dot{N}_N = \text{const } \dot{L}^{n/g}, \quad (8)$$

but for more detailed description of the kinetics of crystallization they need additional information on the supersaturation under given conditions. Direct measurement of the supersaturation is usually tedious and time consuming. This is why the supersaturation has not been experimentally determined in our experiments. We can expect, however, that the linear crystal growth rate \dot{L} is proportional to some power of the supersaturation Δw :

$$\dot{L} = k'_G \Delta w^g. \quad (9)$$

Unfortunately, literature data⁹⁻¹¹ on the growth order vary from $g = 1$ to $g = 2$ (an extremal value $g = 14$ can be even found¹²) so we have to take into preliminary considerations both of these limiting values. As the supersaturation has been determined by density measurements in two of our MSMR experiments¹¹ with 2% DPE at 60 °C

$$\Delta w = 0.033 \dots \dot{L} = 1.46 \cdot 10^{-7}$$

$$\Delta w = 0.015 \dots \dot{L} = 8.63 \cdot 10^{-8},$$

we obtain for these conditions $k'_G = 5.09 \cdot 10^{-6}$ for $g = 1$ and $k'_G = 2.59 \cdot 10^{-4}$ for $g = 2$. These values can then be recalculated using other published data⁹ to give coefficients which are shown in Table III.

Using these coefficients, supersaturations Δw could be obtained for all of our experiments. As the experimental growth rates are affected by incidental errors and so are also the nucleation rates, we used Eq. (8) for smoothing the data in a way that is shown as an example in Fig. 1. Smoothed values of linear growth rates and corresponding supersaturations are given in Table IV. A rough estimate of the true supersaturation in our experiments can be obtained from the materials balance:

$$w_0 \dot{m}_0 = \dot{m}_c + w_f \dot{m}_f = \dot{m}_c + w_f (\dot{m}_0 - \dot{m}_c) \quad (10)$$

and hence

$$\Delta w = \frac{w_0 \dot{m}_0 - \dot{m}_c}{\dot{m}_0 - \dot{m}_c} - w_{\text{eq}} \quad (11)$$

TABLE III
Temperature dependence of modified growth rate constants

$T, ^\circ\text{C}$	% DPE	$k'_G \cdot 10^6$ $g = 1$	$k'_G \cdot 10^4$ $g = 2$
60	2	5.09	2.59
42.5	2	1.3	0.7
31	2	0.55	0.35
45	6	0.45	0.27
25	6	0.35	0.20

TABLE IV
Assessment of the supersaturation

Experiment No.	$\dot{L} \cdot 10^8, \text{ m s}^{-1}$		$\Delta w \cdot 10^2, \text{ kg/kg solvent}$		
	experimental	smoothed	$g = 1$	$g = 2$	materials balance
1	5.28	4.51	0.89	1.32	3.43
2	5.00	4.93	0.97	1.38	3.18
3	2.78	2.70	0.53	1.02	1.17
4	4.55	6.21	1.22	1.55	2.44
5	4.69	6.05	1.19	1.53	2.47
6	2.78	2.70	2.08	1.96	3.52
7	5.50	5.25	4.04	2.74	3.75
8	4.03	3.73	2.87	2.31	4.30
9	4.30	3.62	2.78	2.27	4.16
10	2.92	2.12	3.85	2.46	4.09
11	3.17	3.48	6.33	3.15	3.62
12	4.03	3.73	6.78	3.26	3.37
13	2.67	2.56	5.69	3.08	2.71
14	2.49	2.29	5.09	2.91	3.74
15	2.89	2.89	6.42	3.27	2.18
16	2.92	2.95	6.56	3.31	3.29
17	1.64	1.63	3.62	2.45	2.68
18	3.00	3.91	11.17	4.42	3.27
19	3.98	3.55	10.14	4.21	4.23
20	3.16	3.05	8.71	3.91	4.16

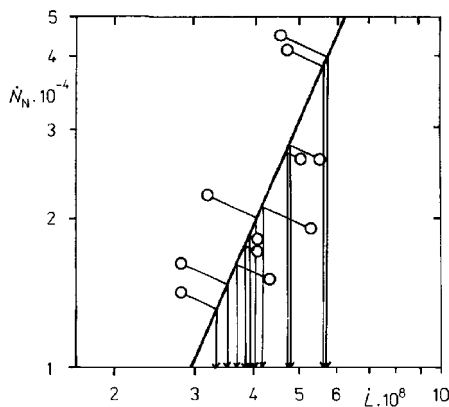


FIG. 1
Example of smoothing of the linear growth rate data for assessment of the supersaturation

The values of supersaturation obtained from the materials balance (included also in Table IV) are probably overestimated as the mass of solute deposited as incrustations has been neglected. Nevertheless, it can be seen from Table IV that these experimental values are close to those calculated for $g = 2$. We may thus conclude that the growth order of PE can be assumed to be $g = 2$. This value agrees with $g = 2.06$, obtained by investigating growth rate of PE crystals suspended in a fluidized bed¹³.

The dependence of the linear crystal growth rate on supersaturation and that of the nucleation rate on supersaturation can be expressed using equations

$$\log \dot{L} = a_L + 2 \log \Delta w \quad (12)$$

and

$$\log \dot{N}_N = a_N + n \log \Delta w \quad (13)$$

TABLE V
Constants of kinetic equations (12) and (13)

Experiment No.	a_L	a_N	n
1 - 5	-3.6187	13.196	4.68
6 - 9	-4.1190	11.906	4.68
10 - 12	-4.4111	11.302	4.68
13 - 17	-4.5576	12.883	5.42
18 - 20	-4.7157	12.213	5.42

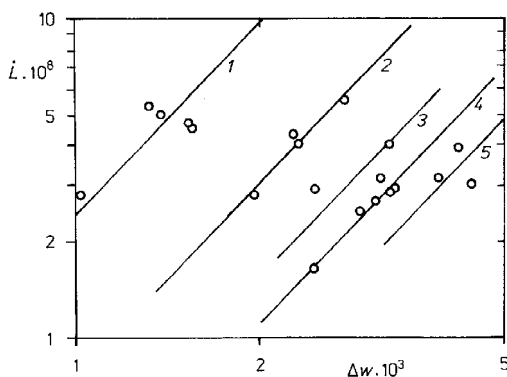


FIG. 2
Linear crystal growth rate as a function of supersaturation. 1 Experiments 1 - 5, 2 6 - 9, 3 10 - 12, 4 13 - 17, 5 18 - 20

with corresponding plots shown in Figs 2 and 3. The order of nucleation, n , has been calculated from previously found values g/n , given above. Straight lines drawn through the experimental points are represented by constants given in Table V. It can be seen from the Figs 2 and 3 that the data are well fitted.

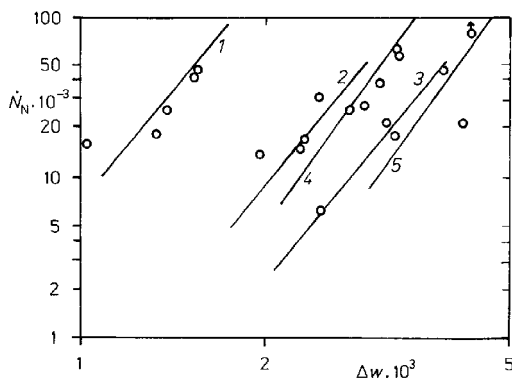


FIG. 3
Nucleation rate as a function of super-saturation. Notation of lines as in Fig. 2

This work has been supported by the University of Rome and the Grant Agency of the Academy of Sciences of the Czech Republic, grant No. 43211.

SYMBOLS

a_L, a_N	constants
B_N	system constant of crystallization
c	exponent of secondary nucleation
DPE	dipentaerythritol
g	growth rate order
k_G	modified growth rate constant, m s^{-1}
k_N	nucleation rate constant, s^{-1}
k'_N	modified nucleation constant, $\text{kg}^{-1} \text{s}^{-1}$
L	crystal size, m
\bar{L}_N	original crystal size, m
\bar{L}	mean crystal size, m
\dot{L}	linear crystal growth rate, m s^{-1}
$M(L)$	size distribution function, % oversize
m_c	suspension density
\dot{m}_c	specific production rate of the crystallizer, s^{-1}
\dot{m}_0	feed rate, s^{-1}
\dot{m}_f	rate of discharge of mother liquors, s^{-1}

\dot{N}_N	nucleation rate, $\text{kg}^{-1} \text{s}^{-1}$
n	nucleation order
PE	pentaerythritol
T	temperature, K or $^{\circ}\text{C}$
T_{eq}	equilibrium temperature, $^{\circ}\text{C}$
t_1	mean retention time of solution, s
w	concentration, kg/kg solvent
w_{eq}	solubility, kg/kg solvent
w_0	concentration of feed, kg/kg solvent
w_f	concentration of mother liquors, kg/kg solvent
Δw	supersaturation, kg/kg solvent
z	dimensionless crystal size
α	volume shape factor
ρ_c	crystal density, kg m^{-3}

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Translated by the author (J. N.).