

**CRYSTALLIZATION OF PENTAERYTHRITOL I. SOLUBILITY, DENSITY AND METASTABLE ZONE WIDTH**Miloslav KAREL<sup>a</sup>, Jaroslav NYVLT<sup>a</sup> and Angelo CHIANESE<sup>b</sup><sup>a</sup> *Institute of Inorganic Chemistry,**Academy of Sciences of the Czech Republic, 160 00 Prague 6, The Czech Republic*<sup>b</sup> *University of Rome "La Sapienza",**Via Eudossiana 18, I-00184 Rome, Italy*

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Solubility of pentaerythritol in water has been determined using literature data, the polythermal method and the dry residue method. Densities of its aqueous solutions have been measured using a pycnometer. Kinetics of crystallization of the pentaerythritol has been determined in laboratory experiments. In this paper, metastable zone width measurements have been employed for the assessment of the primary nucleation rate.

Crystallization is used in industries for separation of the pentaerythritol (PE, i.e. 2-bis(hydroxymethyl)-1,3-propanediol) from the mother liquors and for following purification by recrystallization. Mother liquors contain several by-products and components coming from the chemical reaction, in particular formaldehyde, its derivatives, formiates, dipentaerythritol (DPE) and other polypentaerythritols. Some of them are trapped into crystals and are present even in the step of recrystallization. These impurities can affect the kinetics of crystallization, as has been shown in the case of the formaldehyde<sup>1-3</sup> or calcium formiate<sup>4</sup>. The aim of this paper is to present the results of crystallization studies investigating the effect of the DPE admixture on the PE solubility, density of its aqueous solutions and the kinetics of PE crystallization from aqueous solutions.

**RESULTS AND DISCUSSION***Solubility of Pentaerythritol in Water*

The solubility of the PE in water has been published in the literature<sup>1,3,5</sup>. Several values were determined by the polythermal method<sup>1,3</sup>: known excess of the substance (recrystallized PE) has been added to a known amount of distilled water, the suspension has been very slowly heated until last crystals of the pentaerythritol dissolved and the tem-

perature has then been taken as the equilibrium temperature. Using the method of least squares the data have been fitted by the equation<sup>6</sup>

$$\log x_1 = A + B/T + C \log T, \quad (1)$$

where  $x_1$  is the molar fraction of pentaerythritol in solution and  $T$  is the absolute temperature (K). The values of the constants are as follows<sup>3</sup>:

$$A = -61.5083, \quad B = 1\ 607.731, \quad C = 21.8599. \quad (2)$$

The purity of PE employed for measurements has not been specified in the original paper exactly and is said to be better than 99%.

In this study, solubility data of PE with 2% DPE have been measured using the method of dry residue: PE in slight excess in water has been kept at constant temperature for several hours and after establishing the equilibrium a sample has been taken, weighed, dried at 120 °C and the dry residue weighed again. Solubility data so obtained were correlated again according to Eq. (1). Corresponding constants are:

$$A = 1.3787, \quad B = -1\ 338.9 \quad C = 0.43961. \quad (3)$$

Standard deviation of measured and calculated data is  $\pm 0.0030$  kg/kg H<sub>2</sub>O. In spite of the fact that the constants in sets (2) and (3) differ significantly, the values of solubilities calculated from Eq. (1) for both the sets of constants are almost identical so we can take our measurements as reliable data for further calculations.

Another set of data of PE solubility has been determined<sup>5</sup> for various contents of DPE. Fitting the original data for the contents of DPE 6% by Eq. (1) again we obtain constants

$$A = -35.0875, \quad B = 165.0776, \quad C = 13.1638. \quad (4)$$

Molar fractions  $x_1$  calculated from Eq. (1) using constants in sets (3) and (4) have been then converted into concentration units  $w_1$  (kg/kg water); selected values are summarized in Table I. It can be seen that DPE causes a slight increase in the PE solubility. Values obtained from these equations have then been used in the metastable zone width measurements.

*Density of Aqueous Solutions of PE*

The density of aqueous solutions of PE (Aldrich, 98%, m.p. 256 °C) has been determined using a 10 cm<sup>3</sup> pycnometer calibrated with distilled water and recalculated in a usual way to  $d_4^t$ . These densities are then used for the determination of solution concentration. The best correlation equations for individual temperatures are

$$30\text{ °C: } w = -4.42 + 4.33 d_4^t \quad (5)$$

$$42.5\text{ °C: } w = -4.30 + 4.33 d_4^t \quad (6)$$

$$49.6\text{ °C: } w = -4.98 + 5.02 d_4^t \quad (7)$$

$$61\text{ °C: } w = -5.15 + 5.21 d_4^t \quad (8)$$

or a general correlation

$$w = -3.164 + 3.134 d_4^t - 0.03338 T + 0.3484 d_4^t T \quad (9)$$

with  $T$  = temperature in °C. Selected values are given in Table II and shown in Fig. 1.

TABLE I  
Solubility of the pentaerythritol in water

$T, \text{ °C}$	PE with 2% DPE		PE with 6% DPE	
	$w_1, \text{ kg/kg water}$	$dw_1/dT$	$w_1, \text{ kg/kg water}$	$dw_1/dT$
25	0.0722	0.0027	0.0855	0.0026
30	0.0864	0.0031	0.0993	0.0030
35	0.1028	0.0036	0.1152	0.0035
40	0.1218	0.0041	0.1335	0.0040
45	0.1436	0.0047	0.1546	0.0046
50	0.1685	0.0054	0.1790	0.0053
55	0.1969	0.0061	0.2071	0.0061
60	0.2292	0.0070	0.2394	0.0070
65	0.2657	0.0079	0.2767	0.0081
70	0.3071	0.0089	0.3197	0.0094
75	0.3537	0.0100	0.3693	0.0108

### Volume Shape Factor

The volume shape factor, defined as

$$\alpha = \frac{\text{mass of crystal}}{\rho_c L^3} \quad (10)$$

can be assessed<sup>7</sup> from the formula

$$\alpha = \frac{m_c}{N_c \rho_c L^3}, \quad (11)$$

where  $m_c$  is the mass of chosen crystals,  $N_c$  their number,  $\rho_c$  crystal density (1 396 kg/m<sup>3</sup>) and  $L$  their characteristic dimension.

PE crystals were prepared in a batch cooling crystallizer. They were separated, dried and sieved. From the sieve fractions 0.5 – 0.6 mm (average size 0.55 mm, repeated twice), 0.325 – 0.425 mm (average size 0.375 mm), and 0.250 – 0.300 mm (average size 0.275 mm) from 250 to 450 crystals with a regular habit have been selected under a microscope and weighed. Values of the so determined shape factor are given in Table III. The most representative value is  $\alpha = 0.59$ .

When crystallized from aqueous solutions, the habit of PE crystals is a tetragonal bipyramid. Roger and Creasy<sup>2</sup> report for PE crystals a diameter of a sphere of equal volume  $d = 0.9655 L$  which corresponds to the shape factor  $\alpha = 0.471$ . This value is within the range of shape factors determined in this work.

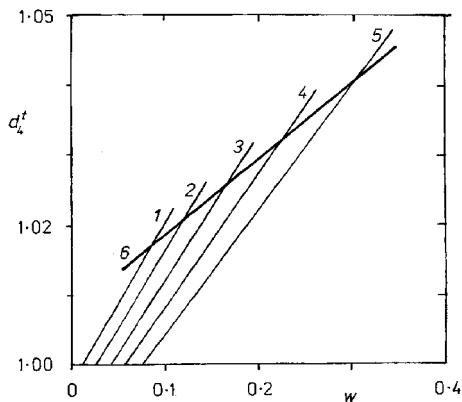


FIG. 1  
Density of pentaerythritol aqueous solutions as a function of concentration,  $w$  (kg/kg H<sub>2</sub>O), and temperature,  $T$ : 1 30, 2 40, 3 50, 4 60, 5 70 °C. 6 Saturated solutions

*Metastable Zone Width*

The metastable zone width of aqueous solutions of PE + DPE has been measured in a way described earlier<sup>8,9</sup>. With the help of the solubility data, nearly saturated solution of PE (Aldrich, about 2% of DPE) in distilled water has been prepared and eventually a calculated amount of DPE added in order to obtain the required DPE concentration. This solution has been rapidly cooled until a cloud of crystals precipitated and then

TABLE II  
Density of saturated aqueous PE solutions

$T, ^\circ\text{C}$	$w, \text{kg/kg water}$	$d_4^t$	$dd_4^t/dw$
25	0.0722	1.0156	0.2363
30	0.0864	1.0170	0.2299
35	0.1028	1.0188	0.2234
40	0.1218	1.0209	0.2170
50	0.1685	1.0261	0.2042
55	0.1969	1.0293	0.1978
60	0.2292	1.0328	0.1913
65	0.2657	1.0367	0.1849
70	0.3071	1.0410	0.1785
75	0.3537	1.0457	0.1721

TABLE III  
Volume shape factors of PE crystals

$L_{av}, \text{mm}$	$N_c$	$m_c, \text{g}$	$\alpha$
0.55	249	0.0342	0.59
0.55	300	0.0432	0.62
0.375	370	0.0144	0.53
0.275	450	0.0059	0.45
Cube			1.00
Sphere			0.524
Octahedron			0.471

very slowly heated up to dissolution of last crystals. This temperature has been taken as the equilibrium temperature,  $T_{\text{eq}}$ . Using temperature programmer<sup>9</sup>, the temperature of the solution was then decreased with a required constant cooling rate ( $-\dot{T}$ ) and appearance of first visible crystals indicated the maximum allowable undercooling,  $\Delta T_{\text{max}}$ . Experimental data have been then treated using the equation<sup>7,8</sup>

$$\log \Delta T_{\text{max}} = a + b \log (-\dot{T}) , \quad (12)$$

where

$$a = [(1-m)/m] \log (dw_{\text{cd}}/dT) - (1/m) \log k_{\text{N}} \quad (13)$$

and

$$b = 1/m , \quad (14)$$

where the nucleation rate constant  $k_{\text{N}}$  and the apparent nucleation order  $m$  correspond to the power-law of nucleation

$$\dot{N}_{\text{N}} = k'_{\text{N}} \Delta w^m \quad (15)$$

with  $k'_{\text{N}} = k_{\text{N}}/(\alpha \rho_{\text{c}} L_{\text{N}}^3)$ . Results of measurements are summarized in Table IV and depicted in Figs 2 and 3.

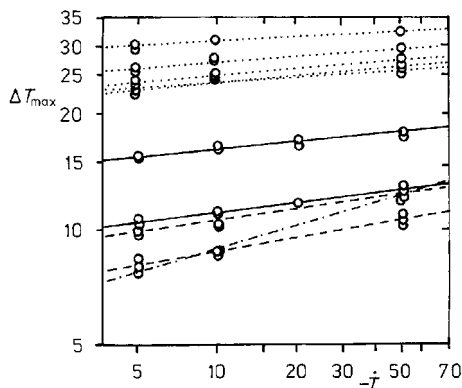


FIG. 2

Dependence of maximum undercooling  $\Delta T_{\text{max}}$  on cooling rate  $-\dot{T}$  for data in Table IV. (.....) 51.6 and 51.5 °C, (—) 59.8 °C, (---) 70.6 °C, (-.-.-) 72.4 °C. Upper lines in every bunch correspond to higher % DPE

TABLE IV  
 Metastable zone width measurements

$T_{\text{eq}}$ , °C	% DPE	$-\dot{T}$ , K h <sup>-1</sup>	$\Delta T_{\text{max}}$ , K			$a$	$b \cdot 10^2$	$m$
51.6	2	5	22.7	23.0				
		10	24.0	24.7		1.3330	4.524	22.1
		50	25.2	25.9	25.7			
51.5	3	5	22.4	22.4				
		10	24.4	24.2		1.3127	6.292	15.9
		50	26.0	26.2				
51.6	4	5	24.0	23.7	23.3			
		10	25.1	25.1		1.3368	5.712	17.5
		50	27.1	27.0				
51.6	6	5	25.4	26.2				
		10	27.4	27.1		1.3815	4.845	20.6
		50	29.1	28.9				
51.6	8	5	29.1	29.7				
		10	30.8	30.7		1.4440	3.915	25.5
		50	32.2	32.4				
59.8	2	5	10.5	10.3				
		10	10.9	10.9	10.9	0.9504	8.949	11.2
		20	11.5					
		50	12.8	12.7				
59.8	6	5	15.1	15.1	15.2			
		10	16.2	16.3		1.1346	6.908	14.5
		50	17.5	17.9	18.0			
70.6	2	5	8.4	7.9	8.4			
		10	8.7	8.7	8.6			
				8.6		0.8249	11.880	8.4
		50	10.9	10.9	10.4			
70.6	6	5	9.9	10.0	10.1			
		10	10.4	10.5	10.2	0.9250	9.844	10.2
		50	12.5	12.4	12.4			
72.4	2	5	7.9	7.8				
		10	8.7	8.7		0.7530	19.476	5.1

It can be seen from the results that the measurements correspond to primary (heterogeneous) nucleation. The data can be compared with the results of induction period measurements<sup>10</sup> of PE where  $m = 14.0$ . The DPE admixture rises the maximum undercooling and thus reduces the nucleation rate. This can be probably explained by an inhibiting action of DPE molecules which prevents the growth of PE clusters to the critical nuclei size. Temperature has a dramatic effect not only on the values of  $\Delta T_{\max}$  but also on the nucleation order. The significant decrease of  $m$  with increasing temperature has been also reported in the literature<sup>1,2</sup> for MSMPR measurements: e.g., at 42.8 °C Sabados<sup>1</sup> found  $m = 6.65$  whereas at 60 °C only  $m = 4.06$ .

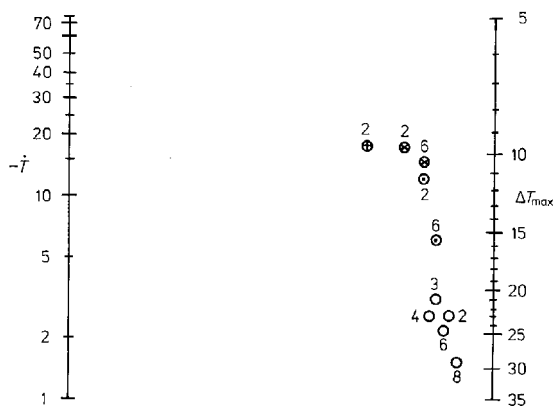


FIG. 3

Nomographic representation of the metastable zone width measurements.  $\bigcirc$  51.5 and 51.6 °C,  $\bigcirc$  59.8 °C,  $\bigcirc$  70.6 °C,  $\bigcirc$  72.4 °C. Numbers correspond to DPE concentrations in Table IV. The line connecting the cooling rate value  $-T$  with the point representing the particular system intersects the smoothed value of  $\Delta T_{\max}$ .

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## SYMBOLS

$A, B, C$	constants
$a, b$	constants
DPE	dipentaerythritol
$d_4^0$	density of solution related to water at 4 °C
$k_N$	nucleation rate constant, $s^{-1}$
$k'_N$	modified nucleation constant, $kg^{-1} s^{-1}$
$L$	crystal size, m
$L_{av}$	average crystal size, mm
$L_N$	original crystal size, m
$m$	apparent nucleation order



$m_c$	mass of crystals, kg
$N_c$	number of crystals
$\dot{N}_N$	nucleation rate, $\text{kg}^{-1} \text{s}^{-1}$
PE	pentaerythritol
$T$	temperature, K or $^{\circ}\text{C}$
$T_{\text{eq}}$	equilibrium temperature, $^{\circ}\text{C}$
$\Delta T_{\text{max}}$	maximal undercooling, K
$-T$	cooling rate, $\text{K s}^{-1}$
$w, w_1$	concentration, kg/kg solvent
$w_{\text{eq}}$	solubility, kg/kg solvent
$\Delta w$	supersaturation, kg/kg solvent
$x_1$	molar fraction
$\alpha$	volume shape factor
$\rho_c$	crystal density, $\text{kg m}^{-3}$

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