Journal of Thermal Analysis, Vol. 12 (1977) 351–360

THERMAL INVESTIGATIONS ON THE CRYSTALLIZATION OF SORBITOL

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(Received January 25, 1977)

The melting and crystallization of sorbitol were investigated with the DSC method and thermal microscopy. Sorbitol was found to have two crystalline modifications (confirmed by X-ray diffraction) with different melting points, while rapid cooling of molten sorbitol resulted in an amorphous form.

The effect of inoculation on the crystallization of the melt was studied too. Powders of both crystalline modifications were used for this purpose.

A new technological process for rapid crystallization of molten sorbitol has been worked out on the basis of the thermal analysis results.

The present work is a part of a research program on solid-liquid transformations with the aid of thermoanalytical methods. These investigations primarily concern slowly-crystallizing substances, so they have a technological purpose too, i.e. determining the optimum conditions for crystallization.

Some solid modifications of sorbitol have been reported in the literature, e.g. by Lóránt and Boros [1]. Melting point data and suggested structures were in contradiction; the existence of various crystal forms was ascribed to different water contents by Schwartz and co-workers [2] and by Lenth and DuPuis [3].

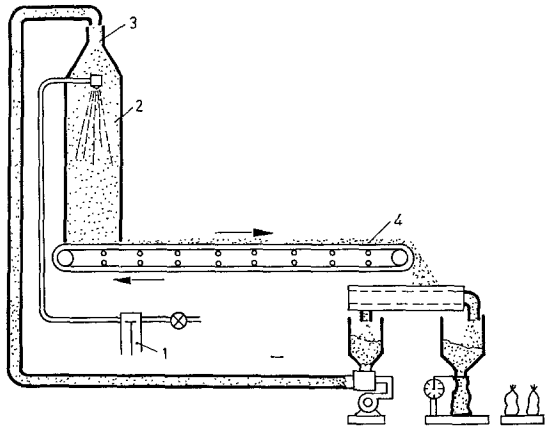


Fig. 1. Scheme of express crystallizer: 1 – metering pump for the melt; 2 – tower; 3 – inoculator feeding with air; 4 – conveyor

At the Institutes for Agricultural Chemical Technology and for General and Analytical Chemistry of the Technical University and the planning office VEGYTERV (Budapest) a new process has been worked out for the crystallization of slowly-crystallizing melts [4].

The scheme of the process, which has been applied for the continuous crystallization of sorbitol in industrial practice, is shown in Fig. 1. The melt is supplied by a metering pump and atomized in the tower. At the same time crystalline powder is fed with air at the top of the tower as inoculator. The inoculated melt passes down to a conveyor, where the crystallization is completed within 5 – 10 minutes, whereas molten sorbitol without inoculation can easily be undercooled, the spontaneous crystallization of the undercooled melt (applied in the old technology) takes some days.

Experimental

Pure sorbitol (Merck) of different types was used. DSC investigations on melting and crystallization and TG measurements on the water contents of samples were carried out on the Du Pont 990 Thermal Analysis system. The heating rate of non-isothermal DSC runs was 5°/min. This type of measurement was suitable for determination of the degree of crystallization after isothermal treatment of inoculated melts.

The morphology of the different forms and the progress of isothermal crystallization were studied with the aid of a Leitz hot-stage microscope. X-ray studies were carried out on a Siemens Kristalloflex-4 diffractometer with CuK_α rays. The scanning rate was 2 degree/min.

Water contents of samples were determined by the Karl Fischer method too.

Results and discussion

Several pure sorbitol products were studied with the DSC method. On the basis of the DSC measurements two forms of crystalline sorbitol could be distinguished (see Fig. 2). All the samples belonged either to the "*A*" form or to the "*B*" form, or contained a mixture of the two types. The melting peak temperature of the "*A*" form was 86°, that of the "*B*" form 97°, while the heat of melting was found to be 7.23 and 6.83 kcal/mole for the "*A*" and "*B*" forms, respectively. The third curve of Fig. 2 demonstrates the behaviour of the congealed melt (molten sorbitol was cooled down to room temperature, and the DSC run of the sample was started some hours later). The first peak is connected with softening of the frozen melt, while the second represents real melting.

Figures 3, 4 and 5 show photomicrographs of the three forms. X-ray diffraction patterns (see Table 1) showed both "*A*" and "*B*" forms to be crystalline. The frozen melt was found to be amorphous, but microscopic investigations with polarized light pointed to some regularity which ceased at 75° (see Fig. 5).

It is of practical importance that only the "*B*" form meets the requirements of pharmacopoeias (minimum melting point 94°), while with spontaneous crystallization usually the "*A*" form is obtained.

Crystallization of molten sorbitol inoculated with "*A*" and "*B*" crystals was studied under the microscope. Figures 6a–e show how the process progressed with the "*A*" type at 80°. "*B*" type product could also be obtained after inoculation with "*B*" crystals.

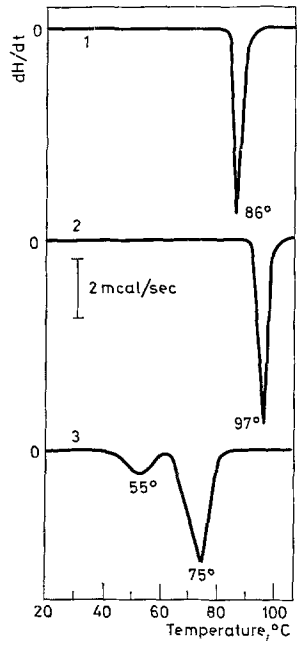


Fig. 2. DSC curves of sorbitol modifications. Heating rate: 5° C/min. 1 – form "A"; 2 – form "B"; 3 – frozen melt

The effect of inoculation was further investigated in the DSC cell. The samples for the model experiments were mixtures of pure "*A*" and "*B*" crystals of grain sizes between 100 and 140 micrometres. Non-isothermal runs showed the phenomenon qualitatively. Figure 7 gives the DSC curve of a mixture obtained with constant heating rate. The melting endotherm of the "*A*" modification is followed by the exothermic effect of crystallization of the resulting melt on "*B*" type crystals. The third peak, at 95°, represents melting of the "*B*" form.

Quantitative investigation of the problem was carried out in isothermal runs. Model mixtures of different composition were treated at 90° for different periods, and rapidly cooled down to room temperature. The amount of "*B*" type crystals in the sample was determined in faster DSC runs (5°/min heating rate) on the basis of the measured melting heat. In these cases the exothermic effect before

Table 1

X-ray diffraction patterns of sorbitol modifications

Form "A"		Form "B"	
d, Å	I/I_0	d, Å	I/I_0
		4.77	6
		3.95	17
		3.81	50
3.21	36	3.23	12
		3.06	14
		3.00	13
2.70	12	2.65	13
		2.56	20
2.47	12		
		2.40	100
		2.37	23
		2.32	19
		2.24	29
2.21	72	2.21	38
2.16	100		
2.10	12	2.11	25
2.03	93	2.07	38
1.97	26	2.00	39
1.94	54	1.94	35
1.81	33	1.87	7
		1.79	44
		1.75	24
		1.70	15
1.67	10		
1.62	8	1.62	7
1.58	27	1.59	29
1.513	14		
1.499	30		
1.487	10		
1.472	20		
1.160	19	1.460	18
1.447	25		
1.400	47		
		1.385	29
1.370	7	1.370	6
		1.340	14
1.320	21	1.320	13
1.293	6		
		1.283	6
		1.233	9
		1.210	13
1.204	10	1.205	12
1.197	9	1.191	9
1.172	18		
		1.169	10

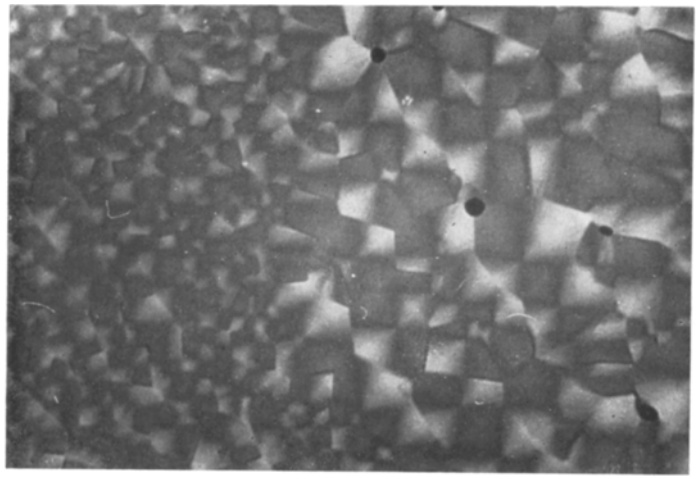


Fig. 5. Photomicrograph of the frozen melt in polarized light (0.5 mm full width)

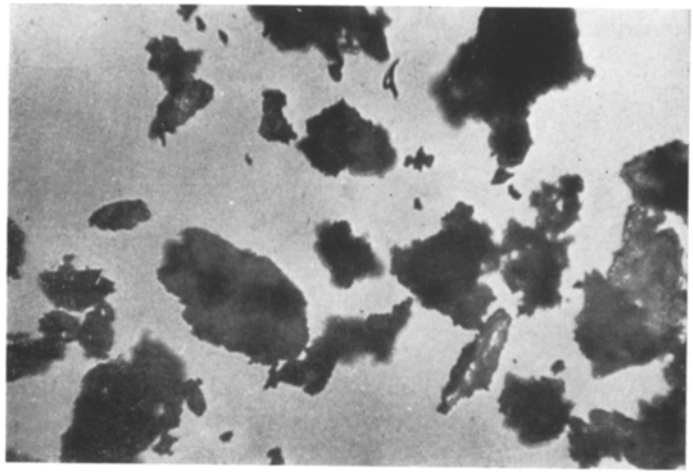
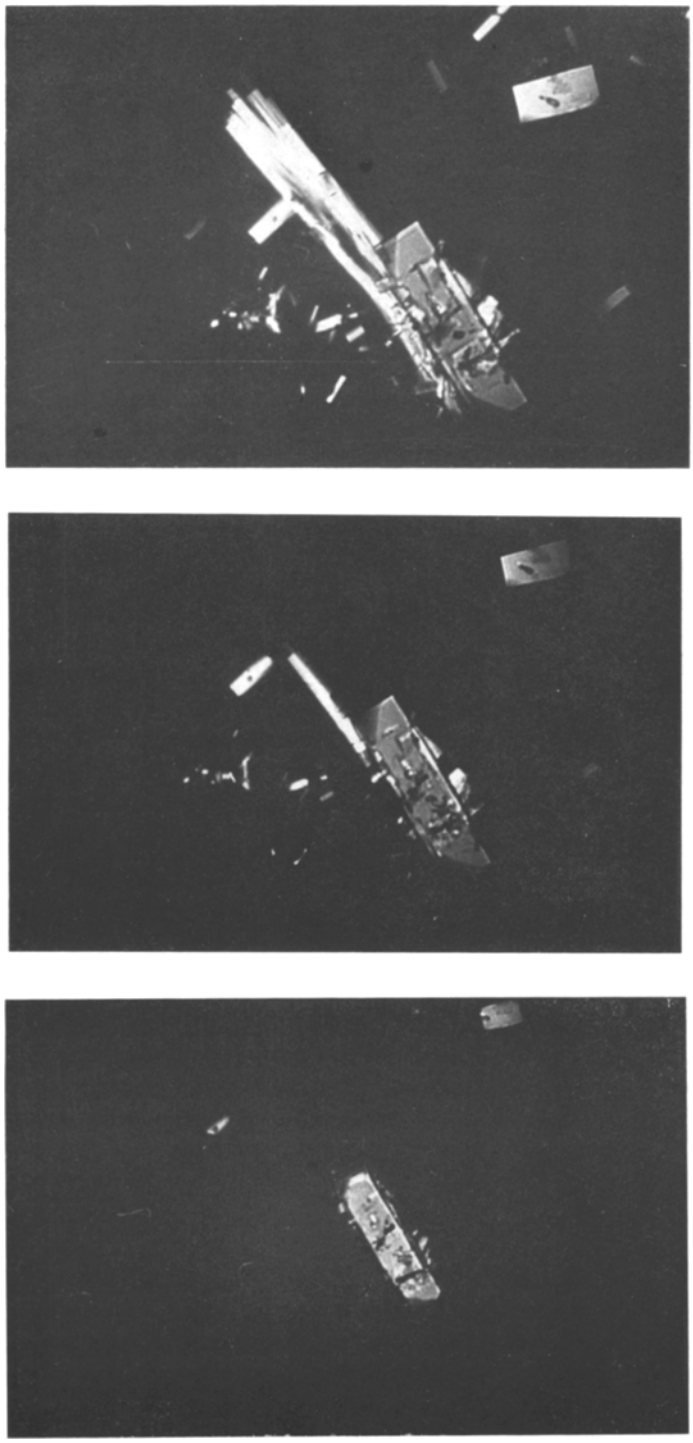


Fig. 4. Photomicrograph of "B" sorbitol (0.5 mm full width)

Fig. 3. Photomicrograph of "A" sorbitol (0.5 mm full width)



c

b

a

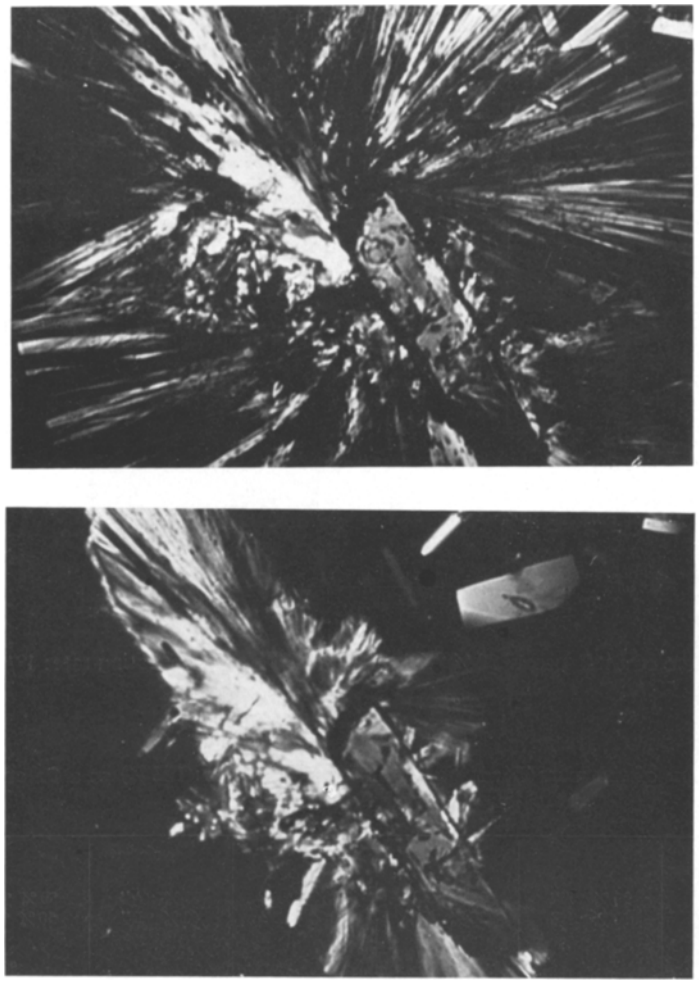


Fig. 6. Crystallization of molten sorbitol inoculated with "A" crystals at 80° (in polarized light, 0.5 mm full width); a — at the beginning; b — 3 minutes after inoculation; c — 6 minutes after inoculation; d — 12 minutes after inoculation; e — 20 minutes after inoculation

the melting of the "*B*" crystals was negligible, i.e. the crystalline fraction was not influenced by the DSC measurement.

The compositions of the samples and the increase of the crystallized fraction are listed in Table 2, and some of the data are plotted in Fig. 8. Clearly, the greater the amount of inoculator crystals the higher the yield of crystallization from the melt.

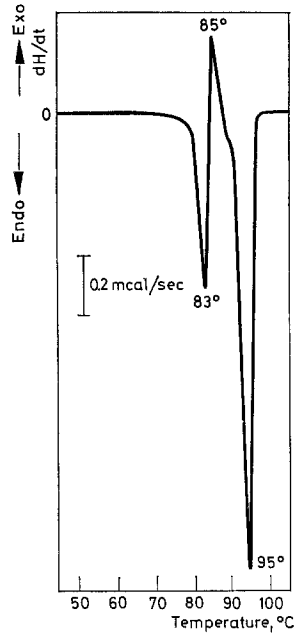


Fig. 7. DSC curve of a mixture of 50% "A" + 50% "B" sorbitol. Heating rate: 1°/min

Table 2

Crystallized fraction of the melt (%; initial amount of "A" form: 100%) as a function of the time of thermal treatment

Initial sample composition / Time of thermal treatment at 90°C min	90% "A" 10% "B"	80% "A" 20% "B"	70% "A" 30% "B"	60% "A" 40% "B"	50% "A" 50% "B"
3	30.5	42.4	51.9	59.3	69.6
6	36.9	52.8	57.3	65.4	67 5
12	44.0	60.6	73.5	76.8	78.2
30	61.0	72.3	74.3	75.8	76.2
90	67.9	80.4	84.8	83.1	85.5
720	76.4	90.0	83.2	83.1	81.4

The process started very rapidly, but later became very slow. The degree of crystallization from the melt did not approximate to 100% in any of the samples, while as mentioned before, under the conditions of the new crystallization technology the whole process takes about 10 minutes. This points to the fact that in the DSC sample pan the contact of the inoculator crystals and the melt was not good; in fact, the melt formed discrete drops, and some of the droplets had only a very small contact surface with the crystals.

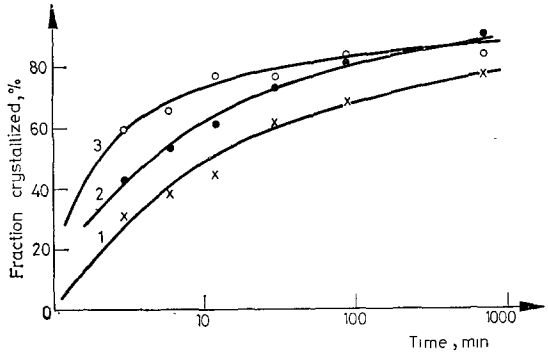


Fig. 8. Progress of crystallization in mixtures of molten sorbitol and "B" sorbitol crystals at 90°

Under the conditions of the new technology the fine droplets of melt meet the inoculator crystals with relatively high speed, causing a large contact surface.

Our further aims are to study the thermal behaviour of some other slowly-crystallizing substances of practical importance (e.g. $Na_2SiO_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $NaOCOCH_3 \cdot 3H_2O$) and to apply the new technology for their industrial production.

References

1. B. Lóránt and M. Boros, Lebensm.-Untersuch.-Forsch., 128 (1965) 22.
2. E. M. Schwarz, V. V. Grundstein and A. F. Levins, J. Thermal Anal., 4 (1972) 331.
3. C. W. Lenth and R. N. DuPuis, Ind. Eng., Chem., 37 (1945) 152.
4. L. Fodor et al., Hungarian Patent No. 162367.

Résumé — On a étudié par DSC et microscopie avec platine chauffante, la fusion et la cristallisation du sorbitol. On a trouvé que le sorbitol présente deux modifications cristallines, confirmées par diffraction des rayons X, avec des points de fusion différents, tandis que le refroidissement rapide du sorbitol fondu conduit à une forme amorphe.

On a étudié également l'effet de l'introduction de germes sur la cristallisation du produit fondu, en utilisant la poudre provenant des deux modifications cristallines.

Les résultats obtenus par analyse thermique ont permis de mettre au point un procédé technologique nouveau pour obtenir la cristallisation rapide du sorbitol fondu.

ZUSAMMENFASSUNG — Schmelzen und Kristallisation von Sorbit wurde mittels der DSC-Methode und Thermomikroskopie untersucht. Es wurde festgestellt, daß Sorbit zwei, durch Röntgendiffraktion bestätigte Kristallmodifikationen mit verschiedenen Schmelzpunkten besitzt, während schnelles Abkühlen des geschmolzenen Sorbits zu einer amorphen Form führt.

Der Einfluß von Impfkristallen auf die Kristallisation der Schmelze wurde ebenfalls untersucht. Pulver beider Kristallmodifikationen wurden für diesen Zweck eingesetzt.

Ein neuer technologischer Prozeß zur schnellen Kristallisation von geschmolzenem Sorbit wurde auf Grund der Ergebnisse der Thermoanalyse erarbeitet.

Резюме — Методами ДСК и термической микроскопии было исследовано плавление и кристаллизация сорбита. Было найдено, что сорбит имеет две кристаллические модификации (подтверждено диффракцией рентгеновских лучей) с различными температурами плавления. Быстрое охлаждение расплавленного сорбита приводит к аморфной форме. Было изучено также влияние затравки на кристаллизацию расплава. Для этой цели были использованы порошки обеих кристаллических модификаций. На основании результатов термического анализа был разработан новый технологический процесс для быстрой кристаллизации расплавленного сорбита.