

STUDY OF THE PHASE TRANSITIONS OF SUCROSE MIXTURES
WITH MONOVALENT INORGANIC SALTS

Z. Palacha, K. Pawluczak

Department of Food Engineering and Process Management, Warsaw Agricultural University
ul. Nowoursynowska 159C, 02-787 Warszawa
e-mail: Palacha@sggw.waw.pl

S u m m a r y . The paper defines the parameters of the phase transitions (glass transition temperature, the temperature and heat of crystallization, melting temperature and heat) of sucrose and mixtures of sucrose with monovalent inorganic salts (NaCl and KCl). The end temperature of glass transition for sucrose/KCl and sucrose/NaCl mixtures was found to have fallen in comparison with pure amorphous sucrose only at low levels of water activity, while the crystallization and melting temperatures of these mixtures were found to have increased in comparison with pure amorphous sucrose in the overall range of water activity investigated.

K e y w o r d s: glass transition temperature, crystallization temperature, melting temperature, heat of crystallization, heat of melting, water activity.

INTRODUCTION

The physical state of food components plays an important role in food processing and shelf-life [8,9]. In dried or deep-frozen food, carbohydrates are in amorphous metastable state, which is very sensitive to changes in water content and temperature [3,7]. The interaction of these two parameters may cause a glass transition and then carbohydrates crystallization. These phenomena are generally undesirable in food technology.

Literature provides information on the effect of the degree of hydration and storage time of single carbohydrates on their phase transitions [2,5,6,8]. The addition of monosaccharides (glucose, fructose) to sucrose increases the glass

transition temperature and the crystallization temperature of amorphous sucrose in the mixture [4,6]. The presence of other sugars in the environment of amorphous sucrose is likely to increase the viscosity of the mixture solution and creates a steric hindrance to sucrose molecules and thus delays its crystallization. In literature there is no data on the effect of added ingredients of a small molecular weight on the phase transitions of carbohydrates.

Therefore the paper aims at establishing the parameters of the phase transitions of amorphous sucrose and amorphous mixtures of sucrose and monovalent inorganic salts (NaCl, KCl) using differential scanning calorimetry.

MATERIAL AND METHODS

The following chemicals were used in the experiments: D(+) sucrose (Fluka Biochemicals), analytically pure sodium chloride (PPH "POCh" S.A. Gliwice), analytically pure potassium chloride (PPH "POCh" S.A. Gliwice).

Preparation of amorphous forms

The amorphous forms of pure sucrose and sucrose mixtures with monovalent inorganic salts were obtained by preparing 10% aqueous solutions (for amorphous mixtures, prior to the preparation of the solutions, mixtures of salt and sucrose were made in the weight ratio of 1:20), which were subsequently frozen in a National Lab Profit Master freezer type PMU0380 at the air temperature of -80°C for 5 hours. Then frozen solutions were freeze-dried in a Christ Alpha 1-4 apparatus under a pressure of 70 Pa for 22 hours. The freeze-drying temperature was 10°C for the first 18 hours and was then raised to 25°C for the final 4 hours. Thus obtained amorphous forms were stored over P_2O_5 ($a_w = 0.0$ at 25°C) for two weeks in order to obtain absolute dryness of the material. Then the samples were stored for 24 hours over four different salt solutions with a specific a_w value: LiCl ($a_w = 0.11$, in 25°C), CH_3COOK ($a_w = 0.23$), MgCl_2 ($a_w = 0.33$), K_2CO_3 ($a_w = 0.43$).

Preparation of samples for analysis

The samples of dry amorphous materials and materials with a varied water content were placed in a standard aluminum pans (type 605 01V) with a known mass, which were hermetically sealed and their mass was evaluated on a Metler AE 240S balance with an accuracy of ± 0.01 mg. The mass of the samples ranged from 4 to 8 mg. The water content in the samples under study at specific water activity levels is shown in Table 1.

Table 1. Water content in freeze-dried mixture of sucrose and salts after rehumidification

Water activity	Water content [g water/100 g d.m.]		
	Sucrose	Sucrose/KCl	Sucrose/NaCl
0.00	0.0	0.0	0.0
0.11	1.5 ± 0.3	1.9 ± 0.2	2.1 ± 0.3
0.23	2.8 ± 0.1	3.2 ± 0.1	3.5 ± 0.1
0.33	5.2 ± 0.1	4.5 ± 0.2	4.2 ± 0.1
0.43	5.7 ± 0.2	5.9 ± 0.2	5.8 ± 0.2

Determination of temperature and heat of phase transitions by means of the DSC method

A UNIPAN 605M Differential Scanning Calorimeter (DSC) was used for the study. It was connected with a computer using the TRANSITION measurement program. The pan with the sample of the analyzed material was placed near an empty reference pan in the microcalorimeter chamber and the measurement program was started. The experiment was performed by means of the dynamic method (a programmed linear increase in temperature) with the heating equivalent rate 5K/min.

The samples were heated from 25°C to a properly selected end temperature (relative to the thermal properties of the substances in the sample).

After the completion of the measurement, based on the thermogram, the following transitions were established: glass transition temperature (T_{g1} – onset temperature of glass transition, T_{g2} – end temperature of glass transition), crystallization temperature ($T_{c\text{onset}}$ – onset temperature of crystallization, T_{cr} – peak temperature of crystallization), melting temperature ($T_{m\text{onset}}$ – onset temperature of melting, T_m – peak temperature of melting) and latent heat of crystallization (ΔH_{cr}) and melting (ΔH_m).

For each experimental variant, the measurements were performed in at least three replicates.

RESULTS AND DISCUSSION

Glass transition temperature of sucrose and its mixtures with monovalent salts

The values of glass transition temperature (T_{g1} and T_{g2}) were established only for the first three levels of water activity. It was found that for all the samples analyzed the values of glass transition end temperature (T_{g2}) (Fig. 1) were decreasing with the increase in water activity. Typically, at low levels of water activity T_{g2} was higher for pure amorphous sucrose than for its mixtures with

monovalent inorganic salts. On the other hand, at higher levels of water activity the tendency was reversed.

The decrease in glass transition temperature of amorphous materials related to an increase in water content confirms the plasticizing effect of water [6,8]. Additionally, there is a linear dependency between glass transition temperature and water activity, as confirmed by the studies of Roos and Karel [6] on α -lactose and sucrose.

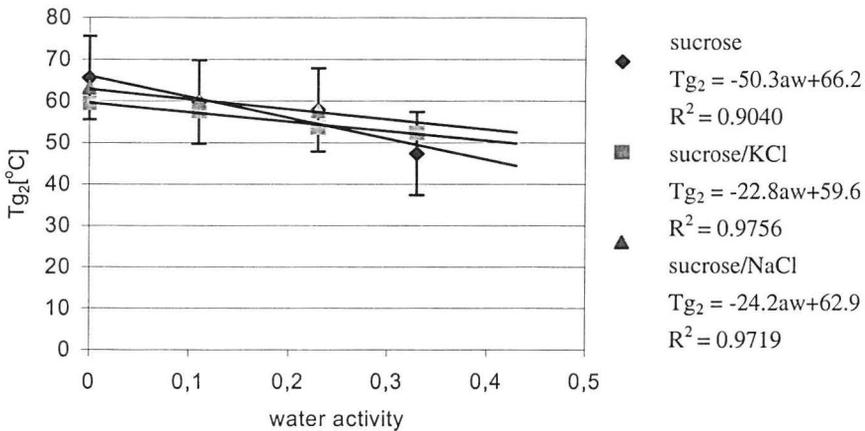


Fig. 1. Dependence of the end temperature of glass transition on the level of water activity.

Temperature and heat of crystallization of sucrose and its mixtures with monovalent salts

Figure 2 shows the dependency of crystallization peak temperature (T_{cr}) on water activity for amorphous sucrose and its mixtures with inorganic salts. It was found that, as for glass temperature, crystallization temperature decreased with increasing water content. A more marked decrease was noted for pure amorphous sucrose and its mixture with KCl. An addition of monovalent inorganic salts to sucrose led to an increase in the crystallization temperature of the resultant mixture, and so at $a_w = 0.0$ the amorphous mixtures of sucrose/KCl and sucrose/NaCl had a crystallization temperature of about 25°C higher than the crystallization temperature of pure amorphous sucrose. Moreover, the more active the environmental water was, the higher the crystallization peak temperature of the sucrose/NaCl mixture became. The phenomenon of the increase in amorphous sucrose crystallization temperature as a result of the addition of monovalent salts is probably due to an increase in the viscosity of the obtained mixture beyond the

glass transition temperature and an appearance of a steric hindrance inhibiting crystallization. Another important factor is the molecular weight of the salts added. A smaller molecular weight of NaCl compared to KCl probably determined the greater impact of the salt on the increase in crystallization temperature.

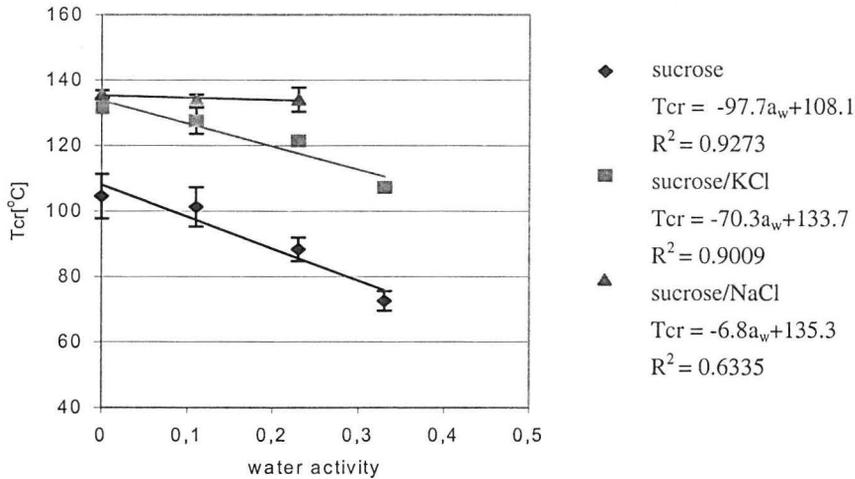


Fig. 2. Dependence of the peak temperature of crystallization of amorphous sucrose and its mixtures with inorganic salts on the level of water activity.

The values of the heat of crystallization of amorphous sucrose and its amorphous mixtures with monovalent inorganic salts are presented in Fig. 3. In all the cases there was a decrease in the heat of crystallization related to an increase in water content. This phenomenon should be explained by the fact that the higher the water content, the smaller portion of the sample analyzed was in an amorphous state capable of crystallization. With water activity of 0.43, the samples of sucrose and sucrose/KCl and sucrose/NaCl crystallized completely already at room temperature.

Another finding was that the presence of KCl and NaCl in the mixture led to a decrease in the absolute value of heat of crystallization in relation to amorphous sucrose heat of crystallization, whereas NaCl had a greater effect on the heat of crystallization of the mixture than KCl. In addition, the dynamics of heat of crystallization decrease was much greater for mixtures than for pure amorphous sucrose, which is evident from the higher regression coefficients of the equations obtained.

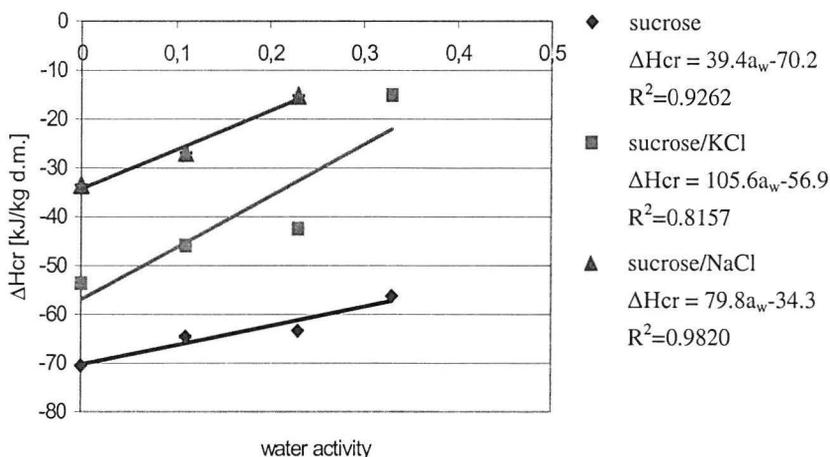


Fig. 3. Dependence of the latent heat of crystallization of amorphous sucrose and its mixtures with inorganic salts on the level of water activity.

Melting temperature and heat of melting of sucrose and its mixtures with monovalent salts

The values of melting peak temperature of amorphous sucrose and its amorphous mixtures with KCl and NaCl after their hydration are presented in Fig. 4. A very small decrease in the melting temperature with the increase in water content was found. For all the water activity levels, the sample of pure amorphous sucrose demonstrated the lowest value of melting temperature and the lowest dynamics of the decrease. As regards the amorphous mixture of sucrose/KCl, the melting temperature increased approximately by 8°C ($a_w = 0.00$) and for sucrose/NaCl by approximately 6°C ($a_w = 0.00$). The highest melting temperature was noted for sucrose/KCl, and slightly lower for sucrose/NaCl. The dynamics of the melting temperature decrease was much higher than for pure sucrose, yet the kind of added salt did not significantly affect it.

The increase in the melting temperature of the mixtures analyzed (sucrose/KCl, sucrose/NaCl) was probably due to the high melting temperature of the salts themselves. Bubicz *et al.* [1] state the following melting temperatures: KCl - 767.8°C and NaCl - 800.8°C.

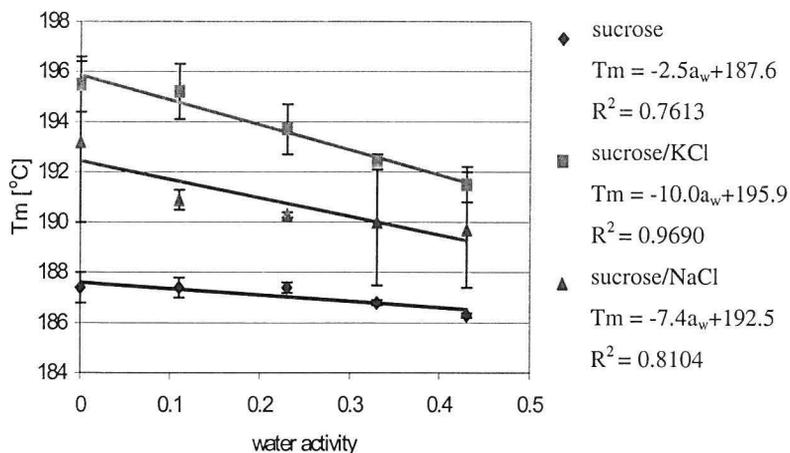


Fig. 4. Dependence of the peak temperature of melting of sucrose and its mixtures with inorganic salts on the level of water activity.

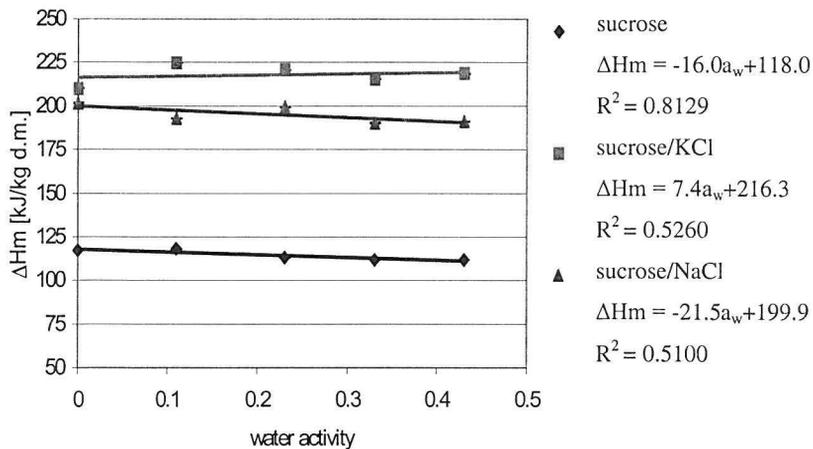


Fig. 5. Dependence of the latent heat of melting of sucrose and its mixtures with inorganic salts on the level of water activity.

A similar relationship between the decrease in the melting temperature of amorphous sucrose and the amorphous mixture of sucrose/fructose and the increase in water content had been noted by Roos and Karel [6]. The researchers explained this phenomenon, like the decrease in glass transition and crystallization temperatures, with the plasticizing effect of water.

There was practically no effect of the hydration degree of both pure sucrose and its mixture with monovalent inorganic salts on the value of their heat of melting (Fig. 5). However, an addition of salt to the sucrose led to an almost twofold increase in the heat of melting of the mixture, irrespective of the kind of salt added.

CONCLUSIONS

1. The increase in water content had an effect on the decrease in the glass transition temperature of both amorphous sucrose and its mixture with monovalent inorganic salts. The analyses performed on sucrose and salt (KCl and NaCl) mixtures proved that the end temperature of glass transition of those mixtures was lower than that for pure amorphous sucrose at low water activity levels, while at higher levels of a_w a reverse tendency was observed.
2. The addition of monovalent inorganic salts caused an increase in the crystallization temperature of the amorphous mixture in comparison to pure amorphous sucrose. On the other hand, the higher the water activity, the crystallization temperature of the amorphous mixture of sucrose/KCl decreased more significantly than T_{cr} of the mixture of sucrose/NaCl. Moreover, the presence of monovalent salts in the mixture with sucrose led to a decrease in heat of crystallization.
3. The addition of KCl and NaCl to sucrose increased the melting temperature of the amorphous mixture by 7°C on average. The highest melting temperature was noted for the mixture of sucrose/KCl and a slightly lower one for the mixture of sucrose/NaCl as compared to pure sucrose.
4. The increase in water activity had practically no effect on the heat of melting of amorphous mixtures, while the presence of monovalent inorganic salts in the mixture caused almost a twofold increase in the value of melting heat as compared to pure amorphous sucrose.

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BADANIE PRZEMIAN FAZOWYCH MIESZANIN SACHAROZY Z JEDNOWARTOŚCIOWYMI SOLAMI NIEORGANICZNYMI

Z. Pałacha, K. Pawluczak

Katedra Inżynierii Żywności i Organizacji Produkcji, Szkoła Główna Gospodarstwa Wiejskiego
ul. Nowoursynowska 159C, 02-787 Warszawa
Pałacha@sggw.waw.pl

S t r e s z c z e n i e. W pracy określono parametry przemian fazowych (temperatura przemiany szklistej, temperatura i ciepło krystalizacji, temperatura i ciepło topnienia) sacharozy oraz mieszanin sacharozy z dodatkiem jednowartościowych soli nieorganicznych (NaCl i KCl). Stwierdzono, że temperatura końcowa przemiany szklistej dla mieszanin sacharoza/KCl i sacharoza/NaCl obniżyła się w porównaniu do czystej sacharozy amorficznej tylko przy niskich poziomach aktywności wody, natomiast temperatura krystalizacji oraz temperatura topnienia tych mieszanin wzrosła w odniesieniu do czystej sacharozy amorficznej w całym badanym zakresie aktywności wody.

S ł o w a k l u c z o w e: temperatura przemiany szklistej, temperatura i ciepło krystalizacji, temperatura i ciepło topnienia, aktywność wody.