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Thermodynamic behavior of erythritol in aqueous solutions and in gelatine gels and its quantification

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ABSTRACT

As crystallization of erythritol can cause a sandy mouth-feel in sugar-free products, strategies to avoid crystallization or adaption of food formulation should be elucidated. However, until now erythritol crystallization was only quantified in aqueous solutions, but not in model food systems. Differential scanning calorimetry (DSC) is a simple method for the quantification of phase transition in various systems. However, no methods for the quantification of crystallization from aqueous systems based on DSC have been published until now. In the present study DSC was found to be suitable for the quantification of crystallization using supersaturated aqueous solutions of erythritol and erythritol containing gelatine gels for the first time. The developed method was validated by comparing the crystallization values determined by gravimetric measurement of erythritol crystals and the values obtained by DSC. No significant differences ($p < 0.05$) have been obtained between the results of the two methods if an appropriate design of measurements was applied. Additionally, the method was adapted to gelatine gels to elucidate the transferability to model food systems. Hence, the method is suitable for quantification of the amount of erythritol crystals present in aqueous solutions and gels, respectively.

1. Introduction

Erythritol belongs to the group of chemical substances known as polyols and exhibits a sweetness of 60–80% the sweetness of sucrose [1,2]. The interest in the formulation of food products containing erythritol has grown over the last few years due to its calorific value of 0 kcal g^{-1} according to the European directive on food additives 2008/100/EC. Erythritol occurs naturally at levels of up to 0.2% (w/v) in fermented products such as wine and soy sauce [3,4], and also in fruit [5], seaweed, and mushrooms [6]. At present, erythritol is mainly produced using a natural fermentation process, in contrast to other polyols that are usually produced using catalytic hydrogenation. Apart from the manufacturing method, the metabolic behavior of erythritol differs from that of other polyols as it is excreted in the urine. Therefore, erythritol does not cause any digestive dysfunction, is 2–3 times more tolerable than sorbitol in human beings, and thus barely has any laxative effect in contrast to other polyols [7].

The physical, chemical and sensory characteristics of erythritol in its solid phase, in melt and in pure aqueous solutions have been studied in detail by few researchers [8–12]. Erythritol shows a sweetening profile comparable to sucrose, but with lower sweetness and a strong cooling effect due to its high enthalpy of solution of +24.1 kJ mol^{-1} [8]. In some products this cooling effect is desirable, for example in peppermint or menthol flavored products, but it is objectionable in many other products, such as baked goods and chocolate [9]. The moderate solubility of erythritol of about 35 g per 100 g at 20 °C is about half that of sucrose (about 70 g per 100 g) [10,11]. A further drawback is the rapid crystallization from aqueous solutions or food matrices at concentrations above the maximum solubility of erythritol. This crystallization results in a sandy mouth-feel for sugar-free products sweetened with erythritol. For this reason, it is important to monitor the crystallization behavior of erythritol, particularly in food matrices, over various storage periods at defined temperatures.

Generally, there are two different physical processes (crystallization and re-crystallization), which can occur in food systems. Re-crystallization is characterized by phase transition from amorphous state to the energetically and thermodynamically more stable crystalline state, which is typical for lactose or isomalt [13,14]. In contrast to the re-crystallization, crystallization occurs in supersaturated aqueous solutions upon cooling and is subject of the present study as erythritol crystallizes rapidly from supersaturated solutions as described previously [9,11].

Different methods for elucidating the crystallization processes as well as for the quantification of the crystallization can be applied. Differential scanning calorimetry (DSC), X-ray

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diffraction (XRD), nuclear magnetic resonance (NMR), solution calorimetry, near-infrared (NIR) spectrometry as well as scanning electron microscopy (SEM) are feasible for the determination of re-crystallization processes (e.g. Jesus et al. [12]), whereas crystallization was monitored gravimetrically (e.g. Ohmori et al. [10]). However, the latter named method is feasible for aqueous solutions, but cannot be applied to complex food systems [10,11]. Therefore, erythritol crystallization in both aqueous solutions and gelatine gels was determined and quantified by means of DSC in the present study.

Research on erythritol in aqueous solutions and in model food matrices is scarce, probably due to the relatively recent approval of erythritol in food products, except beverages. As a consequence, few sugar-free products containing erythritol are commercially available in Europe. Their development is largely hindered by challenges which arise during product development – in particularly the occurrence of erythritol crystals. To facilitate product development, the crystallization behavior of erythritol in food matrices must be investigated. Prior to such development activities, the quantification of the erythritol crystals in model food systems must first of all be studied. To facilitate this, a simple and versatile method for quantitative analysis of erythritol crystals in aqueous solutions using DSC has been developed. In addition, gelatine gels were also used as sample materials in order to evaluate the transferability of the method to model food matrices.

2. Materials and methods

2.1. Materials

The following compounds were used in this study: crystalline erythritol (Jungbunzlauer AG, Switzerland), powdered polydextrose (Litesse Ultra, Danisco Inc., USA), gelatine (220 Bloom, Gelita GmbH, Germany), maltitol powder (C*Maltidex CH, Cargill GmbH, Germany). To minimize the effect of moisture on the solubility, all the powder samples were stored in a dry desiccator.

2.2. Sample and reference preparation

2.2.1. Erythritol solutions for DSC analysis and gravimetric measurements

2.2.1.1. Reference solution for DSC analysis. Erythritol was mixed with water and stirred for about 30 min at room temperature (23 °C) until complete dissolution in order to obtain a saturated erythritol solution containing 35% (w/w) erythritol.

2.2.1.2. Sample solutions for DSC and gravimetric measurements. Saturated erythritol solutions were prepared at 30 °C and 50 °C with 41% and 53% (w/w) of erythritol as described in a previous study [11]. Subsequently, after preparation, aliquots of the solutions were accurately (±0.1 mg) weighed into DSC pans and into 1.5 mL safe-lock tubes, respectively.

In the first experimental series, the DSC pans were sealed hermetically immediately after filling. To simulate the considerably larger headspace of the 1.5 mL safe-lock tubes, the pans were left open for exactly 7 min after weighing in a second experimental series. The DSC pans and the safe-lock tubes were stored at room temperature for 15, 30, and 60 min prior to DSC analysis.

2.2.2. Gelatine gels for DSC analysis

2.2.2.1. Reference gels for DSC analysis. Two reference gels were produced containing 33% (w/w) erythritol and 30% (w/w) of a polydextrose–maltitol–gelatine mixture (Table 1). In detail, gelatine was soaked in cold water (1:8, w/w) for at least 15 min. Erythritol, maltitol as well as polydextrose (Table 1) were dissolved in demineralized water and heated to 60 °C. After complete dissolution, the soaked gelatine was added and melted at 60 °C. About 20 mg of each gelatine solution were accurately (±0.1 mg) weighed into the DSC pans and these were sealed hermetically prior to DSC analysis.

2.2.2.2. Spiked gels for DSC analysis. Reference gels containing 33% (w/w) erythritol and 30% (w/w) of a polydextrose–maltitol–gelatine mixture (Table 1) were produced as described above. About 20 mg of each gelatine solution were accurately (±0.1 mg) weighed into the DSC pans. Afterwards, erythritol crystals (1.0–2.4 mg) were added to the gels in order to validate the usage of the calibration curve for aqueous solutions and to determine the recovery percentage. Finally, the pans were sealed hermetically and the samples were analyzed in triplicate by solution endotherms directly after preparation.

2.2.2.3. Sample gels for DSC analysis. Both sample gels were prepared as described above. After complete dissolution of all the compounds (Table 1), about 20 mg of each gelatine solution were accurately (±0.1 mg) weighed into the DSC pans. The pans were then sealed hermetically and stored at room temperature for 1 h and 24 h, respectively. After the storage period each sample was analyzed by DSC and at least duplicate analyses were carried out.

2.2.3. Gravimetric measurements for aqueous solutions

In order to compare the results obtained by differential scanning calorimetry, the crystallization of erythritol from aqueous solutions was also quantified using the gravimetric method described in our previous study [11]. Aliquots of the aqueous erythritol solutions of 20 mg and 1.5 g, respectively were accurately (±0.1 mg) weighed into 1.5 mL safe-lock tubes directly after the preparation of the solutions. The tubes were then closed and stored at room temperature for 15, 30 and 60 min as described above. To characterize the influence of the small sample weight in the DSC pans on the crystallization of erythritol, equal sample weights of about 20 mg were used for DSC analyses and gravimetric measurements in a first experimental series according to Section 2.2.1. In a further experimental series, the sample weight was increased to 1.5 g to simulate similar ratios of headspace to solution volume and air–water interfaces to the DSC measurements. After each storage period, the samples were centrifuged at 12,100 × *g* for 3 min in a Mini Spin centrifuge (Eppendorf AG, Germany). Afterwards, the supernatant was separated from the erythritol crystals remaining in the tubes. The crystals were dried to weight constancy at 40 °C for 24 h in a drying oven (Heraeus Instruments, Kendro Laboratory Products GmbH, Germany). Finally, the relative crystallization was calculated using the following equation:

$$\text{Crystallization}_{\text{grav}}\ (\%) = \frac{c_{\text{cryst}}}{c_0} \times 100 \quad (1)$$

where c_{cryst} is the concentration of crystallized erythritol (mg erythritol crystals per 100 mg solution) and c_0 is the initial concentration of erythritol (mg per 100 mg solution).

2.3. DSC analysis

DSC analysis was carried out using a DSC Q 2000 system from TA Instruments (New Castle, USA). The DSC analyzer was calibrated using indium (melting point: 156.6 °C) at the same scanning rate and at the same constant nitrogen purge gas flow of 50 mL min^{-1} as used for the samples. Thermograms of the erythritol samples were obtained using a linear scanning rate of 5 K min^{-1}, starting at 20 °C up to a final temperature of 100 °C or 120 °C, respectively. For the determination of the recovery percentages heating was continued until 120 °C. As references, the corresponding solutions (Section