Crystallization of the supersaturated sucrose solutions in the presence of fructose, glucose and corn syrup

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Abstract

The crystallization of supersaturated sucrose solutions (boiling point 120°C, ≤ 22% moisture, w/w) at 20°C in presence of fructose (80:20, 85:15, 90:10, 95:5), glucose (40:60, 60:40, 80:20, 85:15, 90:10, 95:5) and corn syrup (DE=37.5) (20:80, 40:60, 60:40, 80:20, 85:15, 90:10, 95:5) was investigated. The presence of fructose, glucose and corn syrup inhibited the sucrose crystallization. The crystallization time increased with the concentration of the additive. There is a great difference between the water activity of boiled sugar mixture solution and the same composition when crystallized. So measurement of water activity was successfully used to characterize the crystallization process. The microscope equipped with polarizing filters was used to see the structural changes in crystallization.

Keywords: crystallization, sugars, water activity, polarized microscopy

1. Introduction

Aqueous solutions of sugars have been studied for many years due to their both scientific and practical importance (molecular biology and biochemistry, food chemistry and technology, sugar industry, etc.). Sugars in foods are usually present as mixtures. The most common sugar composition is a mixture of fructose, glucose and sucrose. Prepared foods may also contain mixtures of lactose, galactose, sucrose or corn syrup. While providing a sweet sensation to the food products, the sugars also act to provide certain characteristic textural properties desirable in foods. Crystallization of the sugars is controlled in such way that either the sugar is maintained in the solution phase or the formation of the solid crystalline phase is controlled to give the desired texture (Hartel & Shastry, 1991). Since the textural quality of a food product depends on the crystal size distribution, the rate of growth of the sugar crystals is critical to the final product characteristics (Roos, 1995). According to Hartel (2001), there is four steps occuring in crystallization: generation of a supersaturated phase, nucleation, crystal growth and recrystallization. Once the solution or melt has been become supersaturated, there is thermodynamic driving force for crystallization. That is, the molecules tend toward crystalline state to lower the energy level of the system. During nucleation, the molecules in the liquid state rearrange and eventually form into a stable cluster that organizes into a crystalline lattice. The ordered arrangement of molecules in the lattice involves a release of latent heat as the phase change occurs. Nucleation also depends on the formulation (types and concentrations of nucleating promoters or inhibitors) and on the processing conditions (heat and mass transfer rates). Nuclei that form can grow to larger size based on the available supersaturation in the solution. Growth continues until all of the available supersaturation has been depleted and the system approaches an equilibrium in phase volume, which depends on temperature and composition of the system. Once equilibrium in phase volume has been attained, changes still may take place in the crystalline structure during long-term sotrage. This approach to a more global equilibrium is called recrystallization.

An understanding of the principles that control the prevention or formation of the crystalline sugar system phase is quite important in developing satisfactory food products. Although the presence of many of the other coumpounds, including other sugars, is known to impede sucrose crystallization (Bhandari & Hartel, 2002; Gabarra & Hartel, 1998; Hartel, 2001), our understanding of exactly when this inhibition occurs is still lacking.

The objective of the present work was to provide an extended understanding of the influece of fructose, glucose and corn syrup on the crystallization of sucrose by appling the polarized light microscopy and measuring the water activity shift due to isotermal crystallization.

2. Materials and methods

Materials

The raw materials used were crystalline sucrose (Wielkopolski Cukier S.A, Poland), glucose (Cerestar, Germany), fructose (Algol Latvia SIA, Latvia) and corn syrup (DE=37.5) (Roquette, France).

Preparation of supersaturated sugar solutions

Sugars were dissolved in distilled water during heating and gentle stirring in the boiling vessel and the solution was boiled up to 120ºC. Samples were then poured into preheated uniform size cups (d=40mm, h=10mm) and sealed with lids. A Parafilm^{TM} was completely taped around the cup/lid junction to prevent the water transfer. The cups were then hermetically sealed in the glass jar and stored at controlled temperature (18±2ºC) until the analysis.

Water content

To measure the water content of the sugar solutions, a Karl Fischer titration (Mettler Toledo DL38, Switzerland) was used. Three samples were analyzed for each measurement.

Water activity

Water activity of supersaturated sugar solutions (crystallized or liquefied) was measured at 20°C using an electronic dew-point water activity meter, Aqualab Series 3 model CX (Decagon Devices, USA). For each determination three replicates were obtained and the average reported.

Polarized light microscopy

Polarized light microscopy was used to determine the isothermal crystallization kinetics. Images were acquired using Nikon eclipse E200 light microscope (Nikon, Japan) with polarizer filters. To prevent the water transfer, the junction of microscope glass and cover glass was sealed with the water-proof silicone. Images were taken with a 4-X objective.

3. Results and discussion

The water contents of supersaturated sugar solutions boiled up to 120°C are shown in Table 1. The moisture content of crystallizing samples did not changed in time, showing that the applied storage conditions were hermetic and there were no water transfer processes.

When sucrose is dissolved to water, entropy is decreased as water molecules become organized under the effect of the sugar. Water molecules are less free to escape into the vapour phase and this is at the origin of vapor pressure depression. As water activity is by definition the ratio of vapor pressure of solution and solvent (P/Po), and by convention a_w=1.0 for water, the increase in sugar concentration provokes a decrease in a_w (Mathlouthi & Reiser, 1995). Each sugar possesses its own constant equilibrium water activity value at saturation. However if a saturated solution gets supersaturated the water activity decreases down to this value. As supersaturation is a thermodynamically non-equilibrium state, the excess solute above saturation will tend to crystallize out and the water activity of the solution will increase up to the level of the equilibrium solubility concentration (Zamora & Chirifie, 2006). Water activity of sucrose supersaturated solution boiled up to 120°C (water content 9%) was 0.272±0.025 that is in correlation with Norrish (1967) work. Crystallization of pure sucrose supersaturated solution occurred very quickly, within few minutes and the

Table1. Water content of different sugar solutions

Sugar solution	Water content (%)
Sucrose/glucose	14.74±1.55
Sucrose/corn syrup	16.74±2.23
Sucrose/fructose	22.46±2.65

water activity increased to saturation value a_w = 0.863±0.002. In contrast, crystallization of sucrose in presence of glucose (Figure 1), fructose (Figure 2) or corn syrup (Figure 3) led to slower crystallization. The a_w values of the up to 120°C boiled supersaturated solution increased during 84 days storage from initial 0.3-0.35 up to 0.86 corresponding to the a_w of saturated sucrose solution. Increasing the sucrose/glucose ratio, the water activity increased more rapidly (Figure 1a). The water activities close to 0.85 show complete of crystallization of sucrose from supersaturated solution. According to a_w values the crystallization process was not completed within 84 days for 40:60 and 60:40 of sucrose/glucose solutions. For 80:20 of sucrose/glucose solution the main process occurred within 84, for 85:15 within 28, and for 95:5 within 7 days.

The a_w results were confirmed with polarized light microscopy. Figure 1b shows a sequence of images obtained by polarized light microscopy for sucrose crystallization from sucrose/glucose supersaturated solution at isothermal conditions (20°C) within 84 days. The use of polarized light allowed one to enhance the visualzation of the sugar crystals and to distinguish them from the material. The crystals appared as a bright region surrounded by the dark backround. No crystallization observed in sucrose/glucose solution if the sucrose concentration was less than 60%. The more the solution consisted of sucrose, the faster the solution started to crystallize. The crystals grew until they became in contact with one another. For example the solution with the 90% of sucrose had crystallized completely by 7-th day, but the solution with the 95% of sucrose had completely crystallized by the next day of storage.

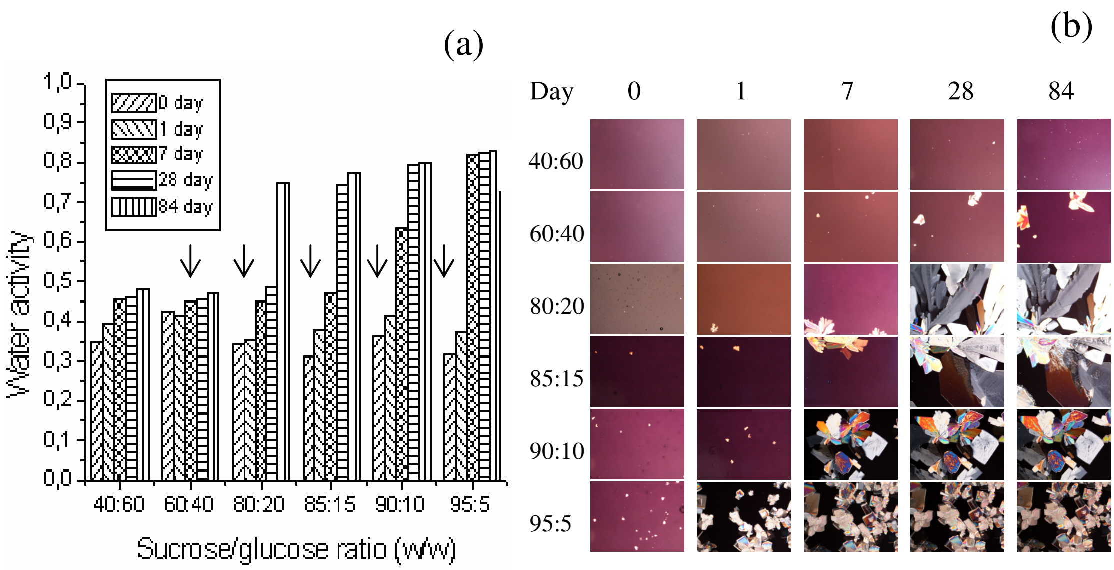

Figure 1. (a) Water activity and (b) images of polarized light microscopy of solutions with different sucrose/glucose ratios within 84 days

The crystallization of sucrose was more inhibited by addition of fructose than glucose. The sucrose/fructose solutions ratios 80:20 and 85:15 did not crystallize within 84 days and there was noticed only a slight increase in water activity (from 0.337±0.004 to 0.493±0.01) (Figure 2a). The polarized light microscopy confirmed the results and no crystals can be seen in the sucrose-fructose solutions if there was less than 90% of sucrose (Figure 2b). In case of 90:10 of sucrose/fructose solution, there was observed a rapid increase in water activity after one month of storage from 0.323±0.01 to 0.761±0.005 indicating the crystallization process and the polarized light microscopy showed large crystals in 84th day. The solution consisting 95:5 sucrose/fructose in the solution, there was observed a rapid increase in water activity between one week and by 28-th day, showing large crystals by microscopy.

The water activitys for different ratios of supersaturated sucrose/corn syrup solutions in time are given in Figure 3. There were no remarkable changes in water activity within 84 days when the sucrose content was under 85%. Therefore there was no significant crystallization process present. As the sucrose content increased in the solution, the increase of water activity was observed. A main crystallization had happened for 85:15 and 90:10 of sucrose/corn syrup solution within 28 days but for 95:5 of sucrose/corn syrup solution already within 7 days.

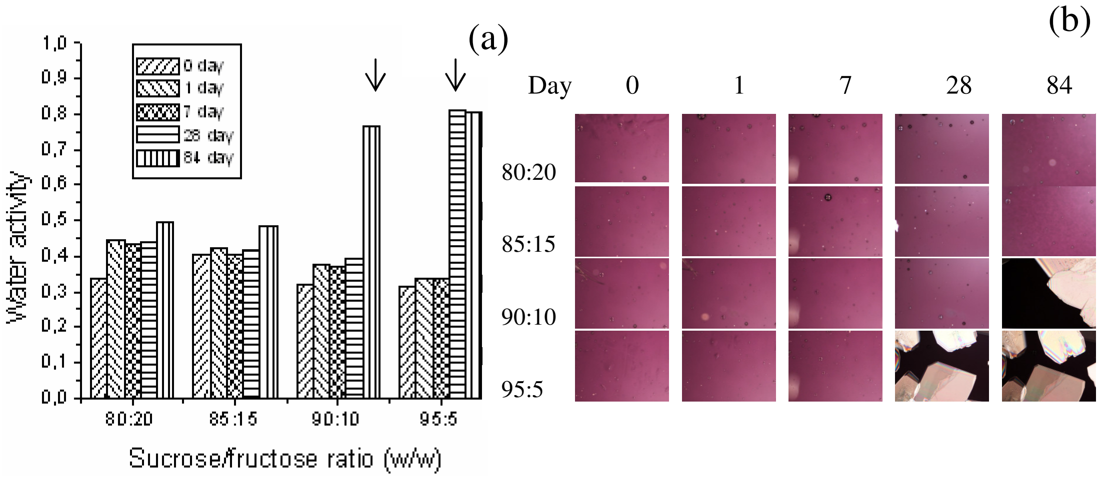

Figure 2. (a) Water activity and (b) images of polarized light microscopy of solutions with different sucrose/fructose ratios witin 84 days

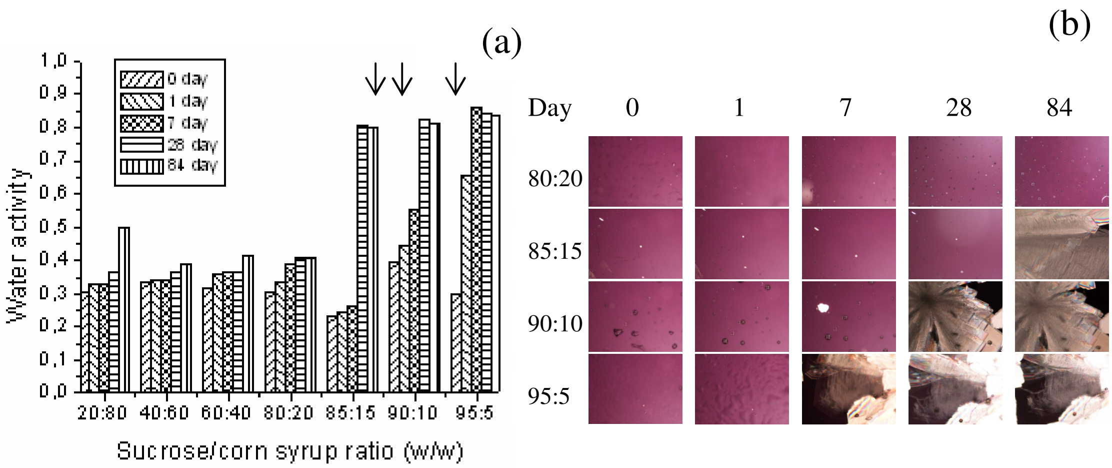

Figure 3. (a) Water activity and (b) images of polarized light microscopy of solutions with different sucrose/corn syrup ratios within 84 days

The inhibition of crystallization rates of sucrose by addition of other sugars can be explain that monosaccharides, glucose and fructose and glucose polymers in corn syrup adsorb to the sugar crystal surface and inhibit incorporation of the sucrose molecules (Hartel, 2001). Levenson and Hartel (2005) also suggested that added corn syrup may have contributed to the additional energy required for crystallization as it increased the viscosity and lowered the molecular mobility of the amorphous sugar matrix. The corn syrup may have also interacted with the sucrose molecules by hydrogen bonding, thereby affecting both translational and rotational diffusion. More energy would thus be required for the sucrose molecules to diffuse through the bulk solution for nucleation to occur.

4. Conclusions

The presence of fructose, glucose and corn syrup inhibited the sucrose crystallization in supersaturated solution. Minimal crystallization was noticed in presence of fructose and glucose syrup but the crystallization rate depended on the concentration of the additive.

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