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Enhancing lactose crystallization in aqueous solutions by soluble soybean polysaccharide

Xueqian Shi, Qixin Zhong *

Department of Food Science and Technology, The University of Tennessee, Knoxville, TN 37996, United States

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ABSTRACT

Increasing the crystallization rate without compromising purity is critical to lactose recovery from cheese whey. In this study, soluble soybean polysaccharide (SSPS), a low viscosity polysaccharide, was studied for the impact on lactose crystallization. SSPS was dissolved at 0–1.0% w/w in 40% w/w lactose solutions to study spontaneous and seeded (with 0.5% w/w lactose crystals) crystallization at 30 °C. The addition of SSPS enhanced the crystallization that was the most significant at 0.1% w/w SSPS, resulting from the facilitation of nucleation. Further addition of SSPS to 0.5% and 1.0% w/w increased sample viscosity and reduced the crystal growth and therefore yield. The purity and structure of lactose crystals were not affected by addition of SSPS, based on DSC, FTIR, and XRD. A high (54.7%) yield of lactose crystals in 24 h after adding 0.1% SSPS and 0.5% w/w seed showed the great potential of SSPS to facilitate lactose recovery.

1. Introduction

Crystallization is the main method used in the dairy industry to recover lactose from cheese whey and crystallization rate is vital to the economic viability. Nucleation and crystal growth are generally the two steps involved in crystallization of lactose in an aqueous solution (Hartel, 2001). Supersaturation is the driving force in both steps, and the crystallization process proceeds until the concentration of a solute in the liquid phase reduces to its maximum solubility (Mullin, 2001). The formation of nuclei is a process of forming lactose molecule clusters because the lactose–lactose interactions are favored over those of lactose and water (Hartel, 2001). The growth of nuclei involves several steps initiated by the mutarotation of lactose from the β- to α-form followed by diffusion of lactose molecules from the continuous phase to water/crystal interfaces and then incorporation into the crystal lattice (Hartel, 2001). Heat generated by the phase change and impurity molecules is to be removed during crystallization (Hartel, 2001; Mullin, 2001).

Impurities may affect the crystallization rate of lactose positively or negatively. Protein (3.49–5.64 g/100 g), potassium (140 mg/100 g), chloride (90–127 mg/100 g), calcium (111–120 mg/100 g), sodium (47–77 mg/100 g), and phosphorus (61–79 mg/100 g) are the major non-lactose compounds in the whey (Jenness, 1988). Potassium, calcium, sodium, and phosphorus by themselves were observed to inhibit the nucleation or crystallization of lactose to different extents, while coexistence of calcium and phosphate showed the promotion effect (Guu & Zall, 1991). Calcium chloride (1–15 g/100 g water) promoted the lactose crystallization in spontaneous single crystal experiments (Bhargava & Jelen, 1996; Jelen & Coulter, 1973; Jelen & Samuel, 1973) but had no detectable effect in seeded crystallization (Smart & Smith, 1992). Potassium phosphate and potassium chloride were reported to inhibit crystallization (Bhargava & Jelen, 1996; Jelen & Coulter, 1973). Sodium phosphate showed no effect on lactose crystallization at 5% total solids (Guu & Zall, 1991) but showed a promotion effect at 20% of total solids (Smart & Smith, 1992). Lactic acid is a major organic acid in whey and was reported to act as an inhibitor of lactose crystallization (Guu & Zall, 1991; Jelen & Coulter, 1973; Nickerson & Moore, 1974). In comparison, calcium lactate (up to 5 g/100 g water) slightly increased the growth rate of lactose crystals (Bhargava & Jelen, 1996; Smart & Smith, 1992).

Different mechanisms have been proposed to explain the effects of different additives on crystallization. Additives can impact lactose solubility and thereby supersaturation and crystallization rate (Mullin, 2001). Lactose has a higher crystallization rate in alcohol–water mixtures than in water alone because of the reduction of lactose solubility by alcohol (Majd & Nickerson, 1976). Sucrose has also been reported to promote lactose crystallization, resulting from the decreased water solubility of lactose (Nickerson & Moore, 1972). In some cases, impurities can act as nuclei and be entrained in crystals (Guu & Zall, 1991). Sodium phosphate and calcium chloride were reported to promote lactose crystallization without changing the solubility of lactose, and both

* Corresponding author at: Department of Food Science and Technology, The University of Tennessee, Knoxville, TN 37996-4539, United States. Tel.: +1 865 974 6196; fax: +1 865 974 7332.
E-mail address: qzhong@utk.edu (Q. Zhong).

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salts were detected in lactose crystals (Smart & Smith, 1992). It was also proposed that crystal growth rate can be enhanced by increasing the ionic strength, but the effects become less significant at high concentrations of salts (Hook, 1944). This theory was supported by the maximum crystallization rate of lactose when calcium chloride was added at 10% of total solids (Jelen & Coulter, 1973).

The effects of polysaccharides on crystallization properties of lactose have only been studied in frozen dairy food systems. Hydrocolloids such as gelatin, guar gum, xanthan, and locus bean gum are commonly used as stabilizers in ice cream (Bahramparvar & Mazaheri Tehrani, 2011). They have been reported to inhibit the formation of ice and lactose crystals by increasing system viscosity (Nickerson, 1962) that constrains the formation of nuclei at low temperatures (McSweeney & Fox, 2009). In our preliminary studies, we also observed the inhibition of lactose crystallization in aqueous solutions at 30 °C by guar gum, locus bean gum, xanthan, and gum Arabic. However, soluble soybean polysaccharide (SSPS) was observed to promote lactose crystallization. SSPS is an acidic polysaccharide with a small fraction of conjugated polypeptide (Chivero, Gohtani, Ikeda, & Nakamura, 2014). The viscosity of SSPS is much lower than that of other polysaccharides and this is an important property that enables the wide use of SSPS as a functional additive to obtain a high content of dietary fiber (Maeda, Phillips, & Williams, 2000) and prevent the precipitation of proteins (Pan, Chen, Davidson, & Zhong, 2014).

The aim of this study was to evaluate the effects of SSPS on lactose crystallization with or without initially-added lactose seed. Nucleation and crystal growth were characterized by absorption spectroscopy and yield, respectively. The morphology of lactose crystals was studied using polarized light microscopy. The purity and physicochemical properties of lactose crystals were studied by X-ray diffraction spectroscopy (XRD), differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR).

2. Materials and methods

2.1. Chemicals

α-D-(+)-Lactose monohydrate was from Fisher Scientific (Pittsburgh, PA). SSPS was a gift from Fuji Oil Corp. (Osaka, Japan). The structure and composition of SSPS have been characterized previously (Nakamura, Furuta, Maeda, Nagamatsu, & Yoshimoto, 2001). Lactose crystal seed (100-mesh fineness) was from Hilmar Ingredients (Hilmar, CA). Other chemicals used in this study were obtained from either Sigma-Aldrich Corp. (St. Luis, MO) or Fisher Scientific (Pittsburgh, PA).

2.2. Crystal yield

The unseeded (spontaneous) and seeded crystallization experiments were conducted at the fixed lactose concentration and temperature. Briefly, 40% w/w α-lactose monohydrate and 0, 0.1, 0.5 or 1.0% SSPS w/w were dissolved in distilled water at 70 °C in a water bath until clear solutions were obtained. After cooling to 30 °C in an ice bath, samples for seeded crystallization were added with 0.05% w/w lactose seed. Samples were incubated at 30 °C in a water bath for 6, 12 and 24 h for unseeded crystallization and 3, 9, 12 and 24 h for seeded crystallization. Crystals were collected after decanting the upper serum, followed by washing with absolute ethanol two times and vacuum-drying overnight at 30 °C. The final crystals were collected, weighed, and stored in a desiccator until use. The net mass of lactose crystals was used to calculate the yield according to Eq. 1. Triplicate experiments were conducted at each combination of conditions.

$$\text{Yield}\ (\%) = 100\% \times [\text{Crystal obtained}\ (\text{g})/\text{total lactose in solution}\ (\text{g})] \quad (1)$$

2.3. Viscosity

The viscosity of solutions with 40% w/w lactose and 0, 0.1, 0.5, or 1.0% w/w SSPS prepared as above was measured using an AR2000 rheometer (TA Instruments, New Castle, DE). The cone-plate geometry, with a cone angle of 1° and a cone diameter of 40 mm, was adopted. The shear rate ramp was performed from 5 to 100 s^{-1} at 30 °C after equilibration at 30 °C for 2 min. Experiments were conducted in duplicate.

2.4. Determination of water solubility of lactose

The solubility of lactose without or with different amounts of SSPS was tested in distilled water at 30 °C. Lactose solutions prepared as in crystallization experiments were incubated in a water bath at 30 °C and the crystal mass was determined daily for 10 days to determine the equilibrium of crystallization. The crystal mass after reaching a constant was used to calculate solubility of lactose (Bhargava & Jelen, 1996) according to Eq. 2. Triplicate experiments were conducted.

$$\text{Solubility}\ (\text{g}/100\ \text{g water}) = \frac{\text{total lactose mass}\ (\text{g}) - \text{crystal mass}\ (\text{g})}{\text{water mass}\ (\text{g})}\ 100 \quad (2)$$

2.5. Nucleation studied by absorption spectroscopy

Lactose (40% w/w) solutions with 0 and 0.1% w/w SSPS, with and without 0.05% w/w seed, were prepared as above. Samples were placed in the plastic cuvette immediately after cooling to 30 °C. The absorbance of each sample at 500 nm was recorded every 5 min for 12 h using a spectrophotometer (BioMate 5, Thermo Electron Corporation, Rochester, NY) at ambient conditions (21 °C). Experiments were conducted in duplicate.

2.6. Crystal morphology

Crystals collected after 3, 9, 12 and 24 h incubation were observed using a polarized light microscope (model BX-51, Olympus America Inc., Center Valley, PA). Images were recorded with an Olympus DP70 camera (Ver.2.3.1.231, Olympus America Inc.).

2.7. Differential scanning calorimetry (DSC)

The DSC experiments were conducted using a model Q2000 instrument (TA Instrument, New Castle, DE). Around 5 mg powder was sealed in hermetic aluminum pans and heated from 25 to 250 °C at a rate of 10 °C/min. Nitrogen was used as the transfer gas at a flow rate of 50 mL/min.

2.8. X-ray diffraction spectroscopy (XRD)

X-ray powder diffraction experiments were performed using a model X'Pert instrument (PANalytical Inc., Westborough, MA). Crystals were ground to fine powder prior to analysis. Scanning at a 2θ scale from 5 to 35° was performed at a step size of 0.05°/s.

2.9. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra were measured using a Nexus670 spectrometer and smoothed using OMNIC spectra software (Thermo Nicolet Corp., Madison, MI). The background spectrum was calibrated using KBr for each sample. Pellets were prepared after grinding lactose crystals together with KBr at a mass ratio of 1:20. The scanning in the wavenumber range of 400–4000 cm^{-1} was conducted with a resolution of 4 cm^{-1}.