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The effect of sucrose on unfrozen water and syneresis of acidified sodium caseinate–xanthan gels

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Abstract

The influence of the ingredients of acidified Na caseinate–xanthan–sucrose gels on thermophysical properties and syneresis of the gels was studied. Sucrose concentration affected all of the gel equilibrium properties and the rate of syneresis. The positive effect of sucrose on syneresis and unfrozen water (UFW) values was attributed to different effects. The amount of UFW was governed mainly by the colligative properties of sucrose whereas the equilibrium syneresis behaviour was associated with the changes in network dynamics caused by the kosmotropic properties of sucrose. The latter could enhance xanthan–sucrose association or favour xanthan–protein interactions.

Keywords: Biopolymers; Interactions; Gel

1. Introduction

Sodium caseinate is a dairy ingredient in which casein is the major protein component. The micellar structure of casein is destroyed in Na caseinate solutions, which consist mainly of sub-micellar assemblies [1]. During milk/caseinate acidification at low temperature, a gel structure is formed by the dissociation/aggregation of casein fractions (α_{S1}-, α_{S2}-, β- and κ-). The casein network can show syneresis because of contraction of the gel, even without the application of external force [2]. The addition of polysaccharides to dairy systems modifies the functional properties of proteins and may also reduce the syneresis of gels.

Xanthan is an anionic polysaccharide that consists of a linear (1-4)-β-D-glucopyranose glucan backbone with charged side chains of (3-1)-α-linked D-mannopyranose, (2-1)-β-D-glucuronic acid and (4-1)-β-D-mannopyranose on alternating residues [3,4]. This polymer is widely used in the food industry as a stabilizer and thickener agent [5] and is considered a non-gelling hydrocolloid. However, some authors [6,7] have obtained hydrogels from annealed solutions and have suggested that gelation occurs after annealing of the solution [7].

The addition of sugars can change the thermodynamic properties of proteins or polysaccharides in aqueous solutions, through direct biopolymer–co-solute interactions or through modification of the water structure [8]. Such changes could modify the biopolymer interactions and, consequently, the system properties.

In complex hydrophilic systems, water is present in three states, namely, free water, freezable bound water and unfrozen water (UFW), with free water being related to syneresis [9,10]. Freezable bound water crystallizes at temperatures lower than 0 °C, while free water crystallizes at 0 °C [11]. About 90% of the water present in milk gels is mechanically enclosed between the casein strands that form the network and is classified as freezable bound and free water [12]. The UFW does not crystallize, even when the swollen matrix is cooled to 10 °C below the equilibrium freezing temperature in the presence of ice crystals [13]. The UFW can be quantified using differential scanning calorimetry based on the

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difference between the total mass of water and the freezable bound and free water.

The objective of this study was to assess the influence of composition and of the xanthan annealing temperature on the amount of UFW and free water (syneresis) in acidified sodium caseinate–xanthan gels containing sucrose. A factorial experimental design was used to quantify the influence of the concentration of ingredients and of annealing temperature on these properties.

2. Material and methods

2.1. Material

Sucrose (Synth, Brazil), xanthan gum, casein and gluconodelta-lactone (GDL) (Sigma Chemical Co., St. Louis, MO) were used to prepare the model systems. The amount of ions in both biopolymers was measured (Table 1) by atomic absorption (AA) spectroscopy (Institute of Chemistry, UNICAMP, Brazil).

2.2. Preparation of model systems

Sodium caseinate solution was prepared by dissolving casein in deionised water with the addition of NaOH to give a pH of 6.7. Glucono-δ-lactone and sucrose were mixed with the sodium caseinate solutions at 10 °C. The amount of glucono-δ-lactone (GDL) used in each formulation was calculated based on a GDL/caseinate ratio of 0.135 [14]. This value provides a pH value of 4.6 at equilibrium for pure sodium caseinate gels, while the mixed gels showed pH values in the range between 4.2 and 4.6. Xanthan gum solution was prepared by mechanical stirring for 1 h at temperatures varying from 20 to 80 °C. The xanthan solution was then cooled to 10 °C and mixed with the caseinate–sucrose–GDL system immediately after the addition of sucrose and GDL. The gels were formed at 10 °C in a hermetic aluminium pan for the temperature modulated differential scanning calorimetry (TMDSC) experiments or in cylindrical plastic tubes (30 mm × 30 mm) for syneresis and pH measurements.

2.3. Syneresis and pH measurements

The pH (Sentron 2001 pHmeter, Sentron Inc., USA) and syneresis of the systems were measured in triplicate at different time intervals for up to 9 days after the addition of GDL. The syneresis was considered as the amount (volume) of water spontaneously released and was determined according to Eq. (1):

$$S(\%) = \left(\frac{V_{out}}{V_{gel}}\right) 100 \quad (1)$$

where S is the gel syneresis, V_{out} the volume of water released and V_{gel} is the initial volume of water in the gels.

The syneresis values obtained as a function of time (after GDL addition) were fitted to first order reaction kinetics (Eq. (2)) in order to evaluate the differences in the process rates and equilibrium values of the formulations used.

$$S = S_{eq} + C\exp(-kt) \quad (2)$$

where S is the measured syneresis, S_{eq} the equilibrium value, k the kinetics constant, t the reaction time and C is a fitting parameter.

Table 1
Mean composition of casein and xanthan powders

	Moisture content (%)	Na^+ (%)	Ca^{2+} (%)	K^+ (%)
Casein	6.51	0.16	0.14	0.08
Xanthan	8.36	2.60	0.40	4.00

2.4. Temperature modulated differential scanning calorimetry (TMDSC)

The water melting temperature and enthalpy were determined using a differential scanning calorimeter DSC 2920 Modulated DSC (TA Instruments, New Castle, USA) fitted with a refrigerated cooling system (RCS). In this technique, two simultaneous heating programs (a linear and a sinusoidal ramp) are applied. Dry helium flowing through the DSC cell at a rate of 25 mL/min was used as the purge gas, whereas dry nitrogen (150 mL/min) was used through the RCS unit. Indium and water were used to calibrate the equipment temperature scale and enthalpic response. The mass of each empty sample pan was matched with the mass of the empty reference pan to ±0.1 mg.

A pan containing about 10–15 mg of sample was tightly sealed and immersed in liquid nitrogen in order to obtain a maximum amount of water frozen and was subsequently poured into DSC cell. The heating program (q) was set to be 1 °C/min from −45 to 20 °C, while the temperature amplitude (A_T) was ±0.1 °C and the period (p) of 15 s. The measurements were done in triplicate with samples that had already reached the equilibrium of syneresis. The melting temperature of water was considered as the onset temperature determined from the maximum slope of the enthalpy peaks (T_m). The melting enthalpy was calculated from the area of the endothermic peak. The amount of unfrozen water (UFW) in the gel was obtained according to Eq. (3):

$$\mathrm{UFW}(\%) = \left[\mathrm{Wb} - \frac{(\Delta H)_{exp}}{(\Delta H)_{lit}}\right] 100 \quad (3)$$

where Wb is the gel moisture fraction (wet basis), ΔH the melting enthalpy, and the subscripts exp and lit are experimental and literature values, respectively. The value of $(\Delta H)_{lit}$ for water was 335 J/g.