



Effect of sugar type and concentration on the heat coagulation of oil-in-water emulsions stabilized by milk-protein-concentrate



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ABSTRACT

The influence of various sugars, on the heat stability of a milk-protein-concentrate (MPC)-stabilized emulsion (10% w/w protein, 10% w/w oil) was studied. Regardless of concentration, the addition of sugars during emulsification slightly increased the droplet diameter except the addition of 20–30% w/w maltodextrin significantly ($p < 0.05$) decreased the droplet diameter and was attributed to the larger change in disperse/continuous phase viscosity ratio. Generally, the addition of sugar reduced the heat coagulation time (HCT) determined at 140 °C. The increased concentration of glucose, maltose, sucrose, trehalose shifted the pH at heat stability maximum towards more acidic values whereas the increased concentration of maltodextrin shifted the pH at heat stability maximum towards more alkaline values. The extent of destabilization also varied between sugars, with trehalose being particularly effective in retaining the original heat stability of the MPC-stabilized emulsions. Reducing sugars (glucose, maltose, maltodextrin) decreased the heat stability maximum more significantly than non-reducing sugars (sucrose and trehalose). Particle size, microstructure, and rheological measurements showed good correlations with the heat stability. Several factors, including free calcium ion level, volume fraction of the continuous phase protein and solvent quality, will also affect the heat stability of MPC-stabilized emulsions with added sugars.

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1. Introduction

Dairy beverages for dietetic purposes usually include proteins, emulsifiers, minerals, oil, and sugars (Keowmaneechai & McClements, 2006). In the processing of these dairy beverages, emulsifiers and some milk proteins adsorb at the oil/water interface during homogenization to produce small oil droplets. The emulsion-based liquid slurry (pH ~ 6.8) is often heat sterilized (i.e., retort or ultrahigh-temperature processes) for long term shelf-life stability (Liang, Patel, Matia-Merino, Ye, & Golding, 2013a). Milk proteins, especially casein and caseinate, are often fortified into

dairy beverages because of their excellent nutritional value and heat stability (Belicium, Sauer, & Moraru, 2012; de Kort, Minor, Snoeren, van Hooijdonk, & van der Linden, 2012; Srinivasan, Singh, & Munro, 2002, 2003). Despite the remarkable heat stability of casein, under certain circumstances, such as high heating temperature and long heating duration, casein and caseinate may flocculate, coagulate or gel (Crujisen, 1996; Sauer & Moraru, 2012). Recently, protein–protein and protein–ingredient interactions in dairy colloids have attracted increased attention in food industries and food institutes (de Kort, Minor, Snoeren, van Hooijdonk, & van der Linden, 2011; McSweeney, Healy, & Mulvihill, 2008; Sağlam, Venema, de Vries, Shi, & van der Linden, 2013; Sauer & Moraru, 2012). In some dairy products such as Dulce de leche, heat-induced coagulation of concentrated milk and sucrose is favourable (Pauletti, Castelao, & Seguro, 1996). Therefore, it is of great practical importance to gain more understanding of the heat-induced physicochemical changes on casein-stabilized oil-in-water emulsion systems containing ternary ingredients.

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In previous work, the heat-induced instabilities of casein micelles and caseinates have been evaluated in milk, concentrated milk, whey-protein-free casein micelle systems, and casein-micelle-stabilized and sodium caseinate-stabilized oil-in-water emulsions (Crujisen, 1996; de Kort et al., 2012; McSweeney et al., 2008; Sauer & Moraru, 2012). Those systems share a number of parameters that affect their heat stability. These include compositional factors such as the initial heating pH (O'Connell & Fox, 2003; Singh, 2004; van Boekel, Nieuwenhuijse, & Walstra, 1989a, 1989b, 1989c), the protein concentration (Walstra, Wouters, & Geurts, 2006), the oil volume (Crujisen, 1996), the aggregation state of casein (Liang et al., 2013a), the calcium ion activity (de Kort et al., 2012), the addition of polyphosphate (Tsioulpas, Koliandris, Grandison, & Lewis, 2010), the addition of lecithin (Kasinos, Tran Le, & Van der Meeren, 2014; McSweeney et al., 2008), and the type of sugar (Crujisen, 1996; Tan-Kintia & Fox, 1996).

It has been reported the addition of sugar can be used to control the heat-induced denaturation and aggregation behaviour of globular proteins in solution (Panzica, Emanuele, & Cordone, 2012) and in emulsion (Kim, Decker, & McClements, 2003; Kulmyrzaev, Bryant, & McClements, 2000), to improve heat stability of milk and concentrated milk (Holt, Muir, & Sweetsur, 1978; Tan-Kintia & Fox, 1996), to prevent cold protein denaturation (Xiong, 1997), to improve freeze–thaw stability (Ghosh, Cramp, & Coupland, 2006), to control the texture (Chanamai & McClements, 2000; Li, Fu, Luo, & Huang, 2013) and creaming stability of food emulsions (Álvarez-Cerimedo, Iriart, Candal, & Herrera, 2010). Semenova, Antipova, and Belyakova (2002) concluded that the addition of sugars affects the thermodynamic properties of proteins, including heat stability, preferential hydration, self-assembly, conformational stability, gelation, and surface activity. A more recent study suggested that the addition of sugar causes a decrease in pH and an increase in calcium ion activity of milk because of a combination of volume exclusion effects and hydration effects (Gao et al., 2010). Over the past few years, considerable effort has been spent on understanding the protective effect of sugars against the unfolding of globular proteins and their gelation (Semenova et al., 2002). The generally accepted heat-induced physicochemical changes on globular proteins involve: (1) the presence of sugar (up to 40% w/w sucrose) increases the denaturation temperature of globular proteins; (2) the presence of sugar effectively increases the viscosity of the continuous phase, leading to reduced protein–protein interactions in continuous phase and between the oil/water interfaces (Baier & McClements, 2001; Kulmyrzaev et al., 2000).

The effect of sugars on the heat stability of casein micelles has also been studied. When added at low concentration, sugars react like aldehydes, stabilizing concentrated milk against prolonged heating at high temperatures (Holt et al., 1978). Non-reducing sugars, such as sucrose and trehalose, and the sugar alcohols have little effect on the heat stability of milk whereas reducing sugars, such as glucose, galactose, maltose, and fructose, and the thermal degradation products of lactose enhance the heat stability of milk (Tan-Kintia & Fox, 1996). In contrast, on the emulsion system containing sodium caseinate, the presence of sucrose has little effect on the heat stability whereas lactose and glucose decrease the heat stability (Crujisen, 1996). It is of interest to further characterize emulsions with high concentrations of sugar, especially trehalose, which has been shown to impart exceptional stability to the protein structure (Crowe, 2007; Jain & Roy, 2009).

The heat stability of protein solutions or protein-based emulsions is often studied as a function of the initial pH (van Boekel et al., 1989b, 1989c; McSweeney, Mulvihill, & O'Callaghan, 2004; Rattray & Jelen, 1997; Singh, 2004). The heat coagulation time (HCT) is the time required for a heat-induced coagulum to become visible during heating in an oil bath. It indirectly measures the resistance of milk

proteins against heat-induced coagulation (Singh, 2004; Walstra et al., 2006). Milk protein concentrate (MPC) is a spray-dried ingredient that is produced by ultrafiltration/diafiltration. It contains more than 10 times less lactose than skim milk and the forms of the casein micelles and whey proteins are similar to those found in milk (Ye, 2011). However, to our best knowledge, the heat stability of MPC-stabilized oil-in-water emulsions containing high protein (i.e., >6% w/w) and high sugar (i.e., ≥10% w/w) concentrations has not been studied yet. The objectives of this research were to study the effect of sugar type and concentration on the droplet size reduction, to study the impact of pH on the heat stability characteristics of MPC containing system and to obtain qualitative information on the heat-induced behaviour of oil droplets and proteins in the continuous phase in high protein and sugar conditions.

2. Materials and methods

2.1. Materials

MPC 485 (81.5% w/w protein, 0.07% w/w sodium, 2.23% w/w calcium) was obtained from Fonterra Co-operative Group Ltd, Auckland, New Zealand. Bulk corn oil and sucrose were purchased from Davis Trading Co., Palmerston North, New Zealand. Glucose, maltose hydrate, and trehalose dihydrate were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Maltodextrin (Md 180) with a dextrose equivalent (DE) value of 18 was obtained from Grain Processing Corporation (Muscatine, IA, USA). All of the chemicals used were of analytical grade, and were obtained from either BDH Chemicals (BDH Ltd., Poole, England) or Sigma Chemical Co. unless otherwise specified.

2.2. Preparation of model emulsions

MPC (10% w/w) was reconstituted in Milli-Q water at 50 °C for 60 min. Glucose, maltose, sucrose, trehalose, and maltodextrin (0–30% w/w) were added as required to MPC solutions. Corn oil (10% w/w) was mixed with the mixture of MPC and sugar and was then pre-homogenized at 24,000 rev/min for 1 min using an Ultra-Turrax T25 (IKA®-Werke GmbH & Co. KG, Staufen, Germany) to form a coarse emulsion. The coarse emulsion was heated to 60 °C and homogenized by passing it through a two-stage homogenizer (type Panda, Niro Soavi, Parma, Italy) for three passes at 20 MPa (first stage) and 4 MPa (second stage) to form the final emulsions, containing constant protein and oil concentrations (10% w/w protein, 10% w/w oil) and varied concentrations of sugar (from 0 to 30% w/w). The molar concentrations of the different sugars are shown Table 1. The amount of adsorbed proteins at oil/water interface was calculated to be 1.24 ± 0.13 g/100 g of emulsion (10% w/w oil) following the equation (McClements, 2005):

$$C_{ad} = C_{total} - C_{non-ad}, C_{non-ad} = \frac{6 \cdot \Gamma \cdot \varnothing}{d_{32}}$$

Table 1
Molar concentration for different sugar types at concentrations used in this study.

Sugar type	Molecular weight (g/mol)	Weight (g/kg)		
		100	200	300
		Molar concentration (M)		
Glucose	180.2	0.6	1.1	1.7
Maltose	342.3	0.29	0.58	0.88
Sucrose	342.3	0.29	0.58	0.88
Trehalose	342.3	0.29	0.58	0.88
Maltodextrin (DE 18)	1000	0.10	0.20	0.30

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