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The effect of hexametaphosphate addition during milk powder manufacture on the properties of reconstituted skim milk

Skelte G. Anema*

Fonterra Research and Development Centre, Private Bag 11029, Palmerston North, New Zealand

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ABSTRACT

Skim milk powders with various levels of sodium hexametaphosphate (NaHMP) were prepared. Reconstituted skim milk samples were prepared from these powders. NaHMP slightly reduced the pH, markedly reduced the serum and ionic calcium and markedly increased the serum phase orthophosphate levels of the milks. This shift in the mineral equilibrium resulted in a drastic reduction in casein micelle integrity, with a marked dissociation of casein from the micelles. κ-Casein was the predominant casein dissociated, although significant levels of α_S-casein and β-casein were also transferred to the serum phase. This dissociation of the casein micelles caused a marked decrease in size and scattering properties of the casein micelles. In addition, a small decrease in the zeta potential of the casein micelles in the milk was observed. Heat treatment of the milks with added NaHMP induced further dissociation of κ-casein, although much of the α_S-casein and β-casein re-associated with the micelles.

1. Introduction

Sodium hexametaphosphate (NaHMP) is a food grade polyphosphate. NaHMP is recognised as a cyclic compound with the molecular formula of $Na_6P_6O_{18}$; however, commercial food grade NaHMP may be a linear polyphosphate chain or possibly a mixture of the linear and cyclic compounds (Gao et al., 2010). NaHMP has the potential to bind up to 3 calcium atoms per molecule, and therefore is a very effective calcium chelator compared with simple monophosphates or citrates (de Kort, Minor, Snoeren, van Hooijdonk, & van der Linden, 2009; Odagiri & Nickerson, 1965).

In addition to chelating calcium, NaHMP can bind to the casein micelles in milk. Vujicic, deMan, and Woodrow (1968) found that most of the NaHMP added to milk was bound to the casein micelles. Lower levels were found to be bound to the micelles in the studies of Odagiri and Nickerson (1965). de Kort, Minor, Snoeren, van Hooijdonk, and van der Linden (2011) proposed that, as NaHMP has six negative charges homogeneously distributed around the molecule, this charge distribution allowed the interaction of the NaHMP with both calcium ions and casein molecules. The NaHMP can bind to adjacent casein molecules either directly through the negative charges on the NaHMP interacting with the positive changes on the caseins or indirectly through the NaHMP and casein binding to the same calcium molecule. Thus this dual interaction of NaHMP can facilitate a cross-linking behaviour between proteins and mineral components.

NaHMP and other polyphosphates or calcium chelators are often added to dairy systems to improve the processing ability of the dairy system or to impart desired functional properties to the derived products. For example, polyphosphates or other calcium chelators are routinely added during processed cheese manufacture to chelate calcium and aid emulsification of the cheese melt (Kapoor & Metzger, 2008). The fouling of heat exchanger surfaces during the manufacture of sterilised or UHT liquid milk products is markedly reduced on the addition of calcium chelators (Burdett, 1974; Prakash, Datta, Lewis, & Deeth, 2007), with polyphosphates such as NaHMP being more effective than the monophosphates (Burdett, 1974).

The effect of NaHMP on the heat stability of milk is less clear cut. Abdulina (1975) and Abdulina, Kovalenko, and Alekseev (1970) reported improvements in the heat stability of milk of normal concentration on the addition of NaHMP, whereas Mittal, Hourigan, and Zadow (1990) reported that the addition of NaHMP to UHT recombined milk had a detrimental effect on heat stability, and this effect was more pronounced on the storage stability of the product. de Kort, Minor, Snoeren, van Hooijdonk, and van der Linden (2012) examined the effect of various calcium chelators on the heat stability of concentrated micellar casein solutions and found that

* Tel.: +64 6 350 4649.
E-mail address: skelte.anema@fonterra.com.

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NaHMP was the least effective in improving the heat stability, whereas weaker calcium chelators had the greatest effect on heat stability.

NaHMP addition is reported to improve the shelf life of UHT milk products by delaying the onset of age gelation. At least two mechanisms for age gelation exist (Datta & Deeth, 2001; Harwalkar, 1992). In one, there is an observed proteolysis during the storage of the UHT milk either by indigenous milk proteases such as plasmin, or through exogenous enzymes from bacterial contamination. In a second mechanism for age gelation, the gelation occurs on storage without obvious changes to proteins in the milk. McMahon (1996) has proposed a mechanism for this type of age gelation that involves the release of the heat-induced β-lactoglobulin–κ-casein complex from the casein micelles followed by a subsequent aggregation of this complex in the serum phase to form a gel network of cross-linked protein. NaHMP delays the onset of gelation by both mechanisms (Datta & Deeth, 2001; Harwalkar, 1992).

Although the effects of NaHMP on the mineral equilibria in milk, and in particular the soluble and ionic calcium activity under ambient conditions, are reasonably well understood, its effect on the mineral distribution over a wider temperature range has not been studied, In addition, the effect of NaHMP addition to milk on the casein micelles, in particular the dissociation of casein micelles has not received much attention. Although milk powders do not generally contain polyphosphates, there is provision in the Codex standards for milk powders for the addition of low levels of polyphosphates (Codex Alimentarius Commission, 2011). Therefore in this study, NaHMP was added to milk during milk powder manufacture. The properties of the milks reconstituted from these milk powders were studied. The serum phase mineral composition at a range of temperatures was monitored, and various properties of the casein micelles were determined, including the levels of casein dissociated from the micelles.

2. Materials and methods

2.1. Milk powder and reconstituted skim milk samples

Skim milk powders were manufactured with 0, 0.1, 0.5 and 1% added NaHMP (Innophos Cranbury, NJ, USA) on a dry basis. The appropriate quantity of NaHMP was added to chilled skim milk samples (~4 °C) and dispersed by stirring with an overhead stirrer for ~15 min. The powders were prepared from the skim milk samples using the techniques and equipment described previously (Baldwin & Truong, 2007). In brief, the powders were manufactured on a pilot scale spray dryer (Anhydro, Copenhagen, Denmark, nominal evaporative capacity 80 kg h^{-1}) using nozzle atomisation. Skim milk was pre-heated at 90 °C for 20 s by indirect heating and concentrated in a falling film vacuum evaporator with four effects to produce a concentrate of ~50% total solids. The concentrate was sprayed at ~125 bar pressure, with the inlet air temperature at 205 °C and the outlet air temperature at ~85 °C to produce a milk powder. Experimental powders were sealed in foil lined bags until use.

Experimental milk samples of 10% (w/w) total solids were prepared by adding the appropriate quantity of the skim milk powder to water and allowing samples to stir for at least 2 h before use. The levels of NaHMP in the four reconstituted milk samples were, therefore, 0, 0.01, 0.05 and 0.1% (w/w), respectively. These milk samples will be referred to as reconstituted skim milk (RSM).

2.2. Additional heat treatments of skim milk samples

Sub-samples (6 mL) of the reconstituted skim milk were placed in glass vials (8 mL total volume) and heated at 120 °C for 6 min (including the heat-up time of ~45 s) in a thermostatically controlled oil bath. After heating the samples were cooled in an ice/water bath until the temperature was below 30 °C. These milk samples will be referred to as heated reconstituted skim milk (HRSM).

2.3. Ultracentrifugation

RSM and HRSM samples were transferred to tubes and centrifuged at 101,000 × *g* for 1 h at 20 °C in a Beckman L8-40 ultracentrifuge and the associated Ti80 rotor (Beckman Instruments Inc., Palo Alto, CA, USA). The supernatants were carefully removed and used for analysis while the pellets were discarded.

2.4. Polyacrylamide gel electrophoresis and laser densitometry

The RSM and HRSM samples were analysed for native whey protein content and composition using native polyacrylamide gel electrophoresis techniques as has been described previously (Anema & McKenna, 1996). The skim milk samples and their respective ultracentrifugal supernatants were analysed for protein composition and concentration by reduced sodium dodecyl polyacrylamide gel electrophoresis (SDS-PAGE) as described in detail previously (Anema, 2009b). After staining and destaining procedures, the gels were scanned using a Molecular Dynamics scanning densitometer and the protein levels obtained by analysing the band intensities using the Imagequant integration software (Molecular Dynamics Inc., Sunnyvale, CA, USA).

2.5. Particle size measurements

RSM and HRSM samples were dispersed in calcium–imidazole buffer (5 mM $CaCl_2$, 20 mM imidazole and 30 mM NaCl at pH 7.0) and allowed to stand for 15 min. Casein micelle sizes were determined by photon correlation spectroscopy using a Malvern Zetasizer 4 instrument and the associated ZET5110 large bore sizing cell (Malvern Instruments Ltd, Malvern, UK). The correlation functions were collected at a scattering angle of 90° only. Each sample was measured 5 times and the average particle size was determined. In addition to the particle size, the intensity of the scattered radiation was recorded using the intensity function on the Zetasizer instrument. This involves the measurement of the scattered radiation, as photons per second, from the sample at an angle of 90°.

2.6. Zeta potential measurements

RSM samples were dispersed in the calcium–imidazole buffer and allowed to stand for 15 min. Zeta potentials were determined by laser Doppler electrophoresis using the Malvern Zetasizer 4 instrument and the associated ZET5104 electrophoresis cell. An applied voltage of 60 V was used in all experiments, and the temperature was maintained at 20 °C. A fresh sample was injected for each separate measurement as this provided more reproducible results. A total of 20 repeat measurements were made and the average determined.

2.7. Collection of permeate samples for determination of serum phase mineral levels

RSM samples were warmed to temperatures between 20 and 60 °C in a water bath and held for 1 h. Samples of milk ultrafiltrate were taken from the RSM at each temperature using an Amicon hollow fibre cartridge with a 10,000 Da cutoff membrane (Amicon, Inc., Beverly, MA, USA) as described previously (Anema, 2009a).