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Original article

Skim milk powders with enhanced foaming and steam-frothing properties

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Abstract – The effects of citrate addition to milks on the stability of milk foams formed by two aeration processes, whipping at room temperature and by steam-frothing, were examined. Citrate addition (0.1–0.5 mol added citrate·kg^{-1} milk solids non-fat) improved the whipping properties of milks reconstituted from conventional low-heat (72 °C for 30 s) and high-heat (85 °C for 30 min) powders. This effect was attributed to the role of citrate in dissociating casein micelles. However, while citrate addition (0.1–0.2 mol added citrate·kg^{-1} milk solids non-fat) improved the steam-frothing properties of milks reconstituted from conventional low-heat milk powder it did not improve those of milks made from corresponding high-heat milk powders. Similar effects of citrate addition on foaming and stream-frothing properties were obtained when the salts were added to skim milk concentrate prior to drying. The citrated milk powders are alternatives to physical blends of conventional skim milk powders and citrate salts for enhancing the foaming properties of milks at both low and high application temperatures.

milk powder / foaming / stream-frothing / casein micelle / citrate

摘要 – 增强脱脂奶粉的发泡性和蒸汽发泡性的研究. 。本文研究了两个通风过程下, 即室温下的搅打和蒸汽发泡, 添加柠檬酸盐对牛奶泡沫稳定性的影响。 0.1–0.5 mol·kg^{-1} (占非脂固性物)柠檬酸盐添加量能够改善由常规低热处理 (72 °C、30 秒) 和高热处理 (85 °C 、 30 min) 奶粉制成还原奶的搅打特性。产生这种作用的原因是柠檬酸盐使酪蛋白胶束解离。然而, 当柠檬酸盐的添加量为 0.1–0.2 mol·kg^{-1} (占非脂固性物) 时, 仅能够改善由低热处理奶粉制成的还原奶的蒸汽发泡特性, 但是不能改善由高热处理奶粉制成的还原奶的蒸汽发泡性。如果在干燥之前的浓缩脱脂乳中加入柠檬酸盐则获得了与上述试验类似的结果。与采用物理方法将柠檬酸盐与低热或高热处理的脱脂粉混合相比较, 将柠檬酸盐加到干燥之前的浓缩乳中生产柠檬酸盐乳粉是提高还原奶发泡性能的首选方法。

乳粉 / 发泡性 / 蒸汽发泡性 / 酪蛋白胶束 / 柠檬酸盐

Résumé – Poudres de lait écrémé ayant des propriétés moussantes améliorées lors de leur reconstitution à froid et à chaud. Les effets de l'addition de citrate au lait sur la stabilité des mousses de lait obtenues par deux procédés d'aération, à température ambiante ou à la vapeur, ont été étudiés. L'addition de citrate (0,1–0,5 mol·kg^{-1} de matière sèche non grasse du lait) améliorait les propriétés moussantes des laits reconstitués à partir de poudres conventionnelles "low-heat" (72 °C-30 s) et "high-heat" (85 °C-30 min). Cet effet a été attribué au rôle du citrate dans la dissociation des micelles de caséine. Cependant, tandis que l'addition de citrate (à 0,1–0,2 mol·kg^{-1} de matière sèche non grasse du lait) améliorait les propriétés moussantes à la vapeur des laits

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reconstitués à partir de poudre conventionnelle de lait “low-heat”, elle n’améliorait pas celles des laits obtenus à partir des poudres “high-heat”. Des effets similaires de l’addition de citrate sur les propriétés moussantes à froid et à la vapeur ont été obtenus quand les sels étaient ajoutés au concentré de lait écrémé avant séchage. La fabrication de poudre de lait enrichie en citrate est une alternative au mélange de poudre de lait écrémé conventionnelle et de sel de citrate pour améliorer les propriétés moussantes des laits à froid et à chaud.

poudre de lait / propriété moussante / aptitude au moussage à la vapeur / micelle de caséine / citrate

1. INTRODUCTION

Foam formation is important in the development of the texture of foods such as ice-cream, mousse, whipped toppings and meringues. Food proteins are used in a number of these food applications because of their ability to move to an interface and stabilize it. Many studies have examined the stability and interfacial properties of milk proteins, used on their own, or in combination with low molecular weight surfactants, for the stabilization of foams. These have shown that intrinsic properties of proteins (i.e. inherent nature of the protein) as well as extrinsic factors (e.g. pH, ionic environment and heat) influence the formation and stability of a foam [10, 13, 14, 20–22].

Both caseins and whey proteins contribute to the foaming properties of milk. Caseins are adsorbed at interfaces in preference to whey proteins [8]. It has been shown that β-casein, α-lactalbumin and β-lactoglobulin are adsorbed at the air-serum interface and that casein micelles are secondarily attached in milk foams made from pasteurized milk [3]. Studies on single component systems as well as binary protein systems using surface dilatation and surface shear rheology have indicated that while both caseins and whey proteins stabilize foams, they exhibit different behavior at interfaces. Random coil proteins such as β-casein are more rapidly adsorbed and spread at the interface compared to globular proteins such as β-lactoglobulin [16]. Analysis of foams made by whipping skim milk showed that there was preferential adsorption of β-casein over casein micelles and whey proteins under conditions where there was β-casein in the supernatant. However, in milk solutions with added calcium chloride, which prevented dissociation of the casein micelle, the interface was comprised of casein micelles and whey proteins only [21]. These results suggest that the caseins had to be available in the supernatant for adsorption to the interface. Improvement in foaming properties of milk was obtained with the addition of chelating agents such as hexametaphosphate [12] or EDTA [20] to milk systems. These chelating agents are known to cause release of caseins into the serum by dissociating the colloidal calcium phosphate within the casein micelles.

Whilst most foams are formed at low temperature, there is also interest in the foaming properties of milk at high temperature, for example, in the foams produced by steam injection for hot milk-based beverages. Proteins have a major role in the stabilization of steam-frothed milks. Poor steam-frothing properties were obtained in milks with high levels of free fatty acids resulting from lipolysis of milk. The mono- and di-glycerides, formed along with free fatty acids during lipolysis of fat are considered to be responsible for the poor steam-frothing properties of milk containing fat [4, 7]. The risks associated with lipolysis are markedly reduced when skim milk is used for the preparation of cappuccinos.

In this work, we examine the effects of citrate addition to milk on the stability of milk foams formed by two aeration processes – whipping at room temperature and by steam-frothing. The feasibility of citrate addition during milk powder manufacture for the production of milk powder with enhanced foaming and steam-frothing properties was also tested.

2. MATERIALS AND METHODS

2.1. Materials

Skim milk was obtained from a local dairy company. Skim milk powders produced on several occasions were obtained from Tatura Milk Industries, Tatura, Victoria. Analytical grade chemicals were used in laboratory trials. These were trisodium citrate from BDH and citric acid, calcium chloride and disodium hydrogen phosphate from Ajax Chemicals. Food grade citric acid and tripotassium citrate used for the production of modified milk powders were from Proscience while citric acid and trisodium citrate (analytical grade) were from Unilab.

2.2. Manufacture of milk powders

For the production of conventional skim milk powders, the skim milk was preheated, concentrated to ~450 g solids·kg^{-1} in an APV pilot-scale double effect falling film evaporator and dried to ~960 g solids·kg^{-1} using a Niro Production Minor spray dryer (Niro A/S, Soborg, Denmark) [5]. Low-heat (72 °C/30 s) or high-heat (85 °C/30 min) preheat treatments were given to the skim milk for the production of low-heat and high-heat milk powders respectively.

Where modified milk powders (hereafter called citrated milk powders) were made, a mixture of citric acid and its trisodium/tripotassium salt was added to a skim milk concentrate (350–450 g solids·kg^{-1}) prior to drying. Levels of addition used were 0.1–0.5 mol added citric acid/citrate salt per kg milk solids non-fat (MSNF). These levels were chosen as preliminary trials carried out indicated that these amounts of citrate could improve foaming and steam-frothing properties of milk. From the preliminary trials, it was also estimated that molar ratios of 1:4, 1:5 and 1:10 of citric acid to trisodium/tripotassium citrate were required to maintain the natural pH (6.6 ± 0.1) of milk powder on reconstitution to milk to 100 g solids·kg^{-1} with 0.1, 0.2 and 0.5 mol·kg^{-1} MSNF respectively.

2.3. Preparation of milks

Milks at the required total solids were reconstituted by dispersion of milk powder in distilled water. When pH-adjustment was required, this was achieved by the addition of HCl or NaOH. When the preparation of milks with added salts (Na_2HPO_4 or citric acid/trisodium citrate mixtures or $CaCl_2$) was required, these were added at levels of 0.1–0.5 mol·kg^{-1} MSNF. All solutions were equilibrated at ~20 °C for 1 h prior to foaming experiments and 3–4 h at 4 °C prior to steam-frothing experiments.

2.4. Measurement of foaming properties

The method of Phillips et al. [15] was adapted. Foams were formed by whipping 100 mL of reconstituted milk in a Sunbeam Mixmaster (Model MX/AC) with a small bowl (MX18S18) (Sunbeam Corporation, Campsie, New South Wales, Australia). A setting of 12 was used. This setting corresponded to a beater speed of 1000 rpm and a bowl speed of 110 rpm. The bowl speed was kept constant by using a Parvalux Electric Motor (CMG Electric Motors, Ringwood, Victoria, Australia).

Milk solutions were whipped for 20 min. After whipping, foam samples were carefully scooped out with a spatula, placed into an open-ended cylindrical weighing vessel and weighed. Foam overrun was calculated as follows:

Foam overrun (%) =
[(Wt. 100 mL solution – Wt. 100 mL foam)/
Wt. 100 mL foam] × 100.

For the measurement of foam stability, a weighing vessel containing the foam which had been whipped for 20 min was allowed to drain into a measuring cylinder for a further 30 min. Foam stability was calculated as follows:

Foam stability (%) =
[(Wt. 100 mL foam – Wt. liquid drained)/
Wt. 100 mL foam] × 100.

For foaming experiments at room temperature where the foaming properties were measured as a function of pH and citrate level addition, there were single measurements done on each powder sample at each of the various pH's tested. Duplicate measurements of foam properties of powders previously carried out showed that the differences between measurements on the same sample were generally < 5%. Representative data from one data set has been given in the paper. Similar trends were obtained when replicate experiments were done on different occasions using milks produced at different times of the year.

2.5. Determination of steam-frothing properties

A Rancilio S10/CD Cappuccino machine was used for the assessment of steam-frothing properties of milks. The steam pressure was preset at 1.25 kPa. A four-holed steam nozzle (hole diameter 2 mm) was positioned so that the holes in the nozzle were below the surface of the milk. Steam was injected into 200 mL of milk in a 2 L stainless steel jug for 30 s. The steam pressure at the end of frothing was 1.1 kPa and the temperature of the milk was ~65 °C. After steam-frothing, the milk was decanted into a 500 mL measuring cylinder. After 5 min and 10 min from the start of the frothing, the volume of the milk at the liquid froth interface plus and the total volume (i.e. froth plus the liquid) was noted. The steam-frothing value (SFV), as previously defined by Deeth and Smith [7], was used except that measurements at 5 min were used. Foam volume was also measured at 10 min and taken as an indicator of stability.

Steam-frothing value ($SFV_{5\ min}$)=
(Total volume – Liquid volume)/
Liquid volume] × 100.

Foam value ($FV_{10\ min}$) = [Total volume
– Liquid volume].

For steam frothing experiments, triplicate measurements were done on each sample.

3. RESULTS AND DISCUSSION

3.1. Foaming properties of milks

The foaming properties of reconstituted milks were examined as a function of pH and the preheat treatment given during powder manufacture. The effects of addition of selected salts on the modification of foaming properties were also determined.

3.1.1. Effects of pH and preheat treatment of milk

The foaming properties of milk are given in Table I. The foam overrun at the natural pH of milks (pH 6.6 ± 0.1) reconstituted from low-heat powders and high-heat powders ranged from 760–860% and 790–920% respectively while the foam stability values were 55–60% and 55–80%.

The differences in the foaming properties of milks given different preheat treatments during powder manufacture were more marked at lower pH compared to that at natural pH. Lowering the pH from the natural pH of milk to pH 5.5 improved foaming properties of both milks although the improvements were more marked when a high-heat treatment was used. Increasing pH also improved foaming properties.

The variation in the foaming properties of milk obtained on three occasions was expected. It has been reported that foam volume produced from different samples of commercial skim milk varied by 15% and it was suggested that seasonal variation in protein content and composition do not by themselves significantly account for the fluctuations in the foaming properties of skim milk [1]. It has been postulated that the availability of β-casein and differences in the ionic composition of milk were responsible for differences observed [1]. It is also possible that low concentrations of surface-active peptides present in milk [8] were a contributory factor.

The effects of pH on foaming properties are in line with our previous work where milks of similar concentration (100 g solids·kg^{-1}) and conditions of foaming were used [20]. With decreasing pH, the major effect is an increase in foam overrun whereas foam stability is more improved at high pH. The foaming properties of milk is an interplay of many factors including the availability of surface active material that has the ability to lower the surface tension, the rheological properties of the interface due to interactions between the proteins at the interface and the viscosity of the solution. Depending on the pH, the relative importance of these factors can vary. The enhanced foaming properties observed on decreasing pH from the natural pH to pH 5.5 may be rationalized in terms of a change in the availability of individual caseins. As the pH is lowered, micellar calcium phosphate dissociates and individual caseins are liberated from casein micelles [6,19]. At lower pH's close to the isoelectric point, the charge on the proteins is reduced, hence protein-protein interactions are promoted and this stabilizes the film. The increase in foaming properties of milk as pH is increased above the natural pH of milk may also be attributed to an increased availability of caseins as pH is increased. Increasing levels of casein were found to solubilize as the pH was increased from 6.7 to 7.1 [2]. At high pH, it is probable that the viscosity effects have a major contributory effect on enhancing foam stability. When lower concentrations of skim milks (14 g solids·kg^{-1}) and a shorter whipping time were used, whippability was similar with increasing pH beyond pH 6.0 [21]. However, in these dilute milk systems where there was insufficient calcium in the serum to maintain caseins in the micellar state, reducing pH from pH 6 to pH 4.5 reduced whippability [21].

There are similar profiles in the trend of foaming-pH profiles of low-heat and high-heat milk powders. The foaming properties at corresponding pH's above and below the natural pH of the milks are marginally higher for high-heat treated milks. A major difference between high-heat and low-heat milk powder is the presence of denatured whey protein attached to the casein micelle, thus changing the nature of protein-protein interactions and the surface of the micelle. In addition it is well known that denaturation of whey protein increases its ability to hold water. These heat-induced changes in milk are expected to affect foaming properties but the relative contribution of various heat-induced changes to foaming properties is hard to know. Studies on the effects of heat treatments of caseinate and whey protein isolate solutions have shown that heat treatment improved foaming properties [17]. However, heat treatment of milk did not affect foaming capacity of milk [9]. Others have suggested that the effect of heat treatment was of

Table I. Effects of preheat treatment during milk powder manufacture on the foaming properties of reconstituted milk (96 g solids·kg^{-1}).

Low-heat milk powder			High-heat milk powder		
pH	**Foam overrun (%)**	**Foam stability (%)**	**pH**	**Foam overrun (%)**	**Foam stability (%)**
Batch 1					
5.6	1020	65	5.5	1150	70
6.2	810	55	6.2	840	55
6.4	780	50	6.4	850	55
6.6	760	55	6.6	820	55
6.9	760	55	6.9	850	60
7.3	760	60	7.3	870	65
7.8	780	75	7.8	850	80
Batch 2					
5.8	1080	65	5.7	1120	65
6.1	930	60	6.1	960	55
6.4	880	60	6.3	900	60
6.7	830	55	6.5	790	55
7.1	820	60	6.9	930	60
7.3	710	75	7.2	910	70
7.9	820	90	7.5	790	80
			7.9	870	90
Batch 3					
5.5	1090	75	5.5	1130	80
5.7	1000	70	5.8	1020	70
6.1	1000	60	6.1	890	65
6.7	860	60	6.3	790	60
6.9	770	60	6.7	920	80
7.3	750	65	7.2	880	80
7.7	820	90			

Low-heat and high-heat skim milk powders were made from the same batch of milk that was obtained on three different occasions. Foam overrun was measured after 20 min of whipping. Foam stability was that of the whipped foam after 30 min. These are single measurements for each pH from the 3 batches of milk.

secondary importance compared to conditions of aeration [11].

3.1.2. Effects of added salts

The effects of added citrate or phosphate (0.21 mol added salt·kg^{-1} MSNF) on the foaming properties of milk (960 g solids·kg^{-1}) reconstituted from high-heat milk powder are given in Figure 1. Similar trends were obtained when the effects of added salts were determined for another batch of milk powder. Both salts increased the foam overrun and foam stability although the addition of citrate was more effective for increasing foaming properties over the pH range examined. The addition of a lower concentration of salt (0.11 mol added phosphate or citrate·kg^{-1} MSNF) also produced better foams than milks without added salt but the effect was less pronounced (data not shown). The addition of $CaCl_2$ at a level of 0.21 mol added salt·kg^{-1} MSNF totally depressed

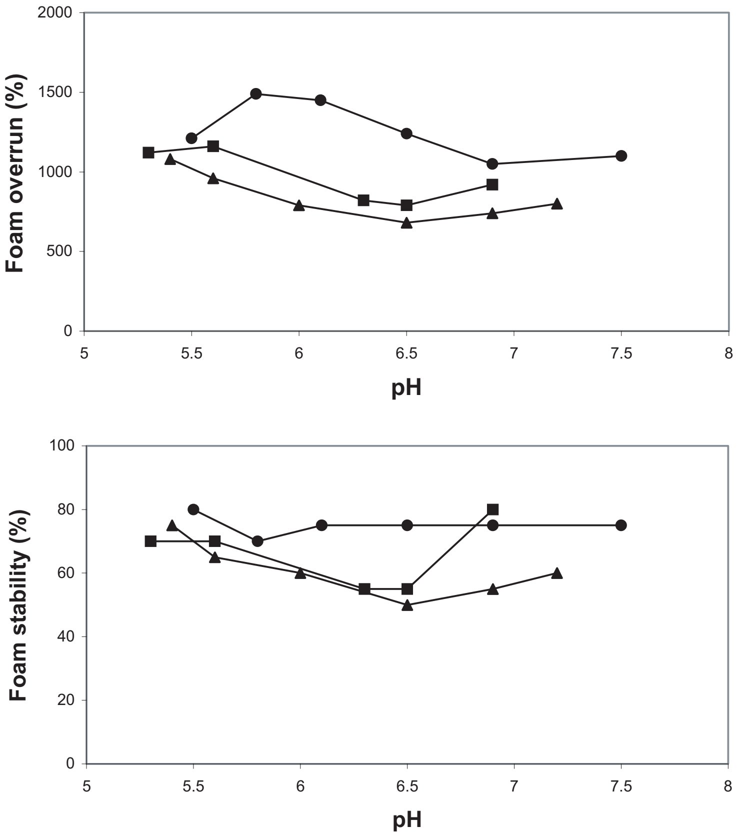

Figure 1. Effects of added salt (0.21 mol added phosphate or citrate·kg^{-1} MSNF) on the foaming properties of milks (96 g solids·kg^{-1}) reconstituted from high-heat skim milk powder. Foam overrun was measured after 20 min of whipping; foam stability was that of the whipped foam after 30 min standing (▲: milk with no additives; ■: milk with added phosphate; •: milk with added citrate).

foam formation in the range pH 5.5–7.8 and stable foam was only obtained at pH 5.2.

At the levels of salts used, it is known that added calcium decreases serum casein content whereas the addition of phosphate or citrate which complex calcium has the opposite effect [18]. The improved foaming properties of milks with added phosphate or citrate and the depression of foam formation with added calcium can be attributed to changes in the availability of soluble caseins. The observed effects of added calcium complexing salts on foaming properties of milk corroborate those observed previously [12, 20, 21].

3.2. Steam-frothing properties of milks

Figure 2 shows the effect of preheat treatment and citrate addition on the steam-frothing properties of milk (100 g solids·kg^{-1}). Low-heat milks had superior steam-frothing properties compared to high-heat milks and the addition of citrate was only effective for

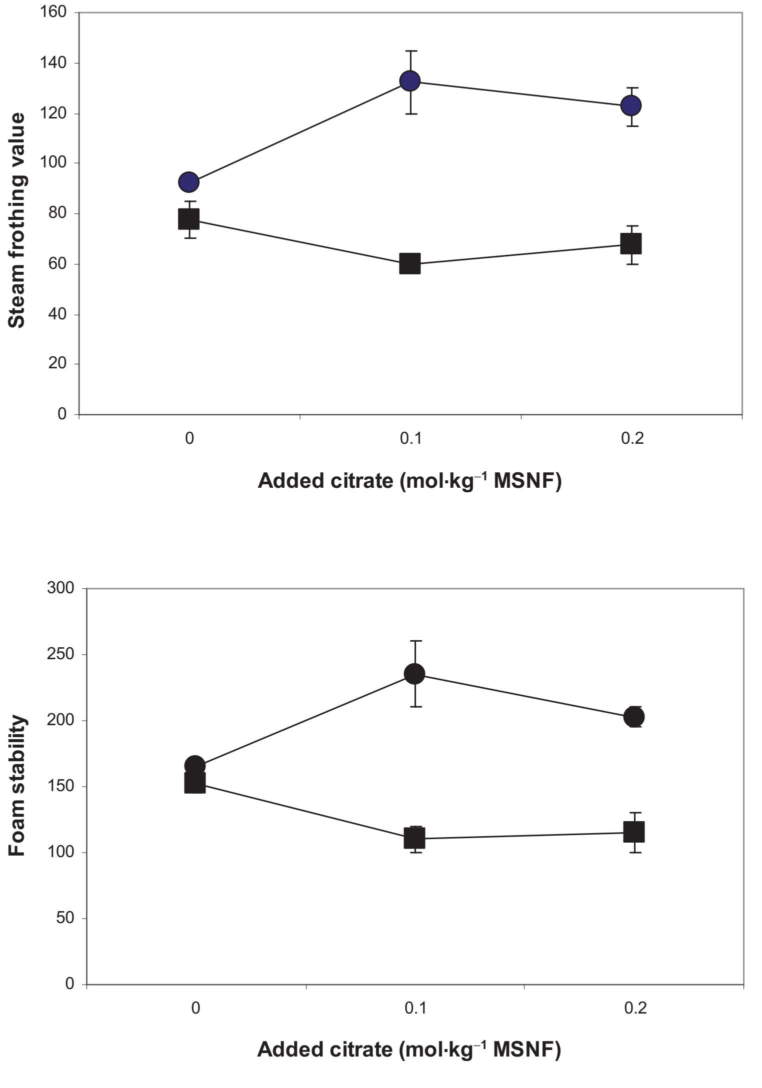

Figure 2. Effects of heat treatment and added citrate on the steam-frothing properties of milks (100 g solids·kg^{-1}, pH 6.7) reconstituted from skim milk powder. Steam-frothing value was measured after 5 min of frothing; foam stability was the foam volume of the frothed milk after 10 min standing (average data for 2 sets of powders; ●: milks made with low-heat milk powder; ■: milks made with high-heat milk powder).

improving the steam-frothing properties of low-heat milks. Others have found that while pasteurization of milk increased steam-frothing properties, the use of higher temperatures (> 72 °C) did not further enhance steam-frothing properties [7]. In this work, citrate addition at 0.1–0.2 mol added citrate·kg^{-1} MSNF improved steam-frothing properties of milks that were given a low-heat treatment. However, others have found that addition of lower levels of citrate to full-cream milk (1.5 g·kg^{-1} added trisodium citrate which corresponds to ~0.05 mol added citrate·kg^{-1} MSNF) did not produce a marked change in steam-frothing properties [4]. The difference could be due to the higher level of citrate used in this study.

The observation that the effects of added citrate on the steam-frothing properties were dependent on the pre-heat treatment given to milk may be attributed to differences in the protein states in the two milks. In the high-heat treated milk, the majority of the whey proteins are denatured and hence the air-water interface formed during frothing will be different from that formed when low-heat milk is steam-frothed. Previous work has shown that high-heat treatment causes ~70% whey protein denaturation [20]. It was also shown that although there was a similar degree of casein dissociation in low-heat and high-heat treated milks caused by the addition of a chelating agent (EDTA), the dissociation of the high-heat milk also caused dissociation of denatured whey protein from the micelle [4], leaving a micelle with different properties from a micelle in high-heat treated milk.

The fact that citrate addition improved the foaming properties of a high-heat treated milk at room temperature but not under conditions of stream-frothing suggests that the conditions used for foaming influence the functionality of the milk ingredients. Although the composition and speciation of the proteins in the high-heat treated milks with added citrate will be the same at the start of the low temperature foaming and steam-frothing experiments, the interfacial layer formed will be different under the different conditions used for foaming and steam-frothing. This could be due to the altered kinetics of adsorption of the surface-active material at the interface as well as changes to the milk proteins due to the exposure of the milk to increased temperature during steam-frothing. Differences in the interfacial properties will in turn influence the stability of the foams made at different temperatures.

3.3. Citrated powders

3.3.1. Manufacture

Milk powders with added citrate were prepared where citrate was added to the concentrate prior to drying. Citrated milk concentrates were dried immediately after addition of the citrate. It was apparent that the citrated concentrates were more prone to thickening and hence holding of concentrate should be avoided.

3.3.2. Foaming properties

The foam overrun and stability of milks reconstituted from conventional milk powders and citrated milk powders are shown in Figures 3–4. In separate experiments, when powders were made on different occasions, the trends in the data were the same although the absolute values varied due to the seasonal variation in the milk supply. The results indicate that milks reconstituted from citrated low-heat skim milk powders (0.2 and 0.5 mol added citrate·kg^{-1} MSNF) had higher overrun, compared to conventional milk powders over the range of pH studied. Foam stability was also improved over the pH range studied with citrate addition to low-heat milk. However, at pH > 7 citrated milk

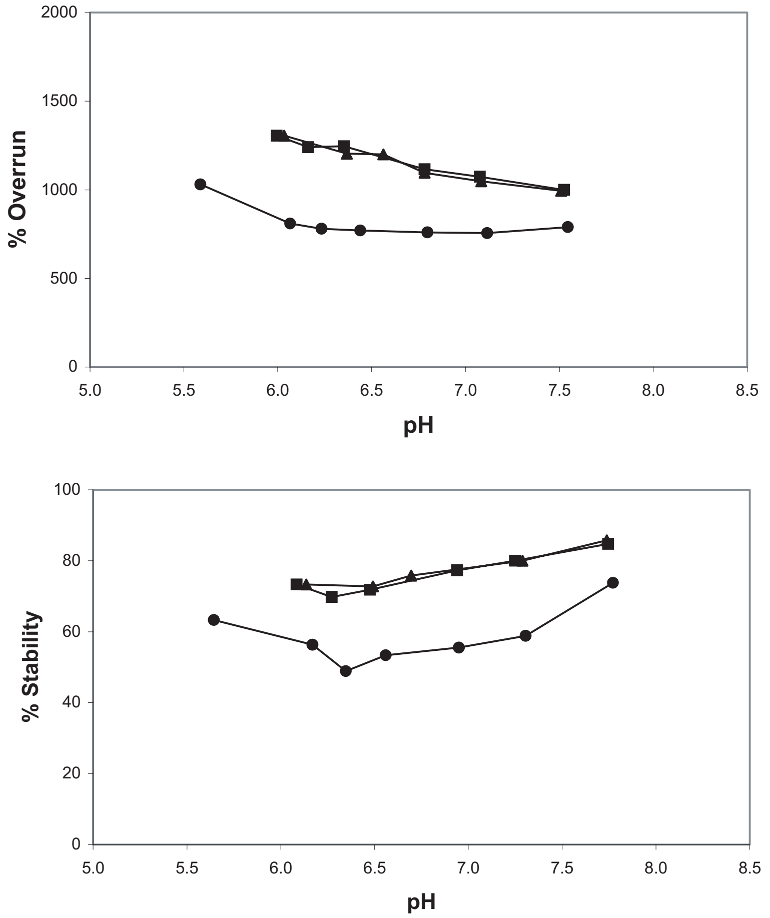

Figure 3. Effects of added salt (0.2 mol added citrate·kg^{-1} MSNF) on the foaming properties of milks (96 g solids·kg^{-1}) reconstituted from low-heat skim milk powder. Foam overrun was measured after 20 min of whipping; foam stability was that of the whipped foam after 30 min standing (●: low-heat skim milk powder; ■: citrated low-heat skim milk powder with 0.2 mol added citrate·kg^{-1} MSNF; ▲: low-heat skim milk powder with 0.2 mol added citrate·kg^{-1} MSNF added after reconstitution).

powder with high levels of added citrate (0.5 mol·kg^{-1} MSNF) were less stable than conventional low-heat milk powder. These trends in foaming properties of low-heat citrated milk powders with high levels of added citrate (0.5 mol·kg^{-1} MSNF) were similar to those for high-heat citrated milk powders (data not shown). These results demonstrate that citrated powder could be used as an alternative to adding citrate directly to milk, as the enhancement in foaming properties obtained by adding citrate to concentrate prior to spray-drying was of a similar magnitude to that obtained by the addition of citrate to skim milk after reconstitution.

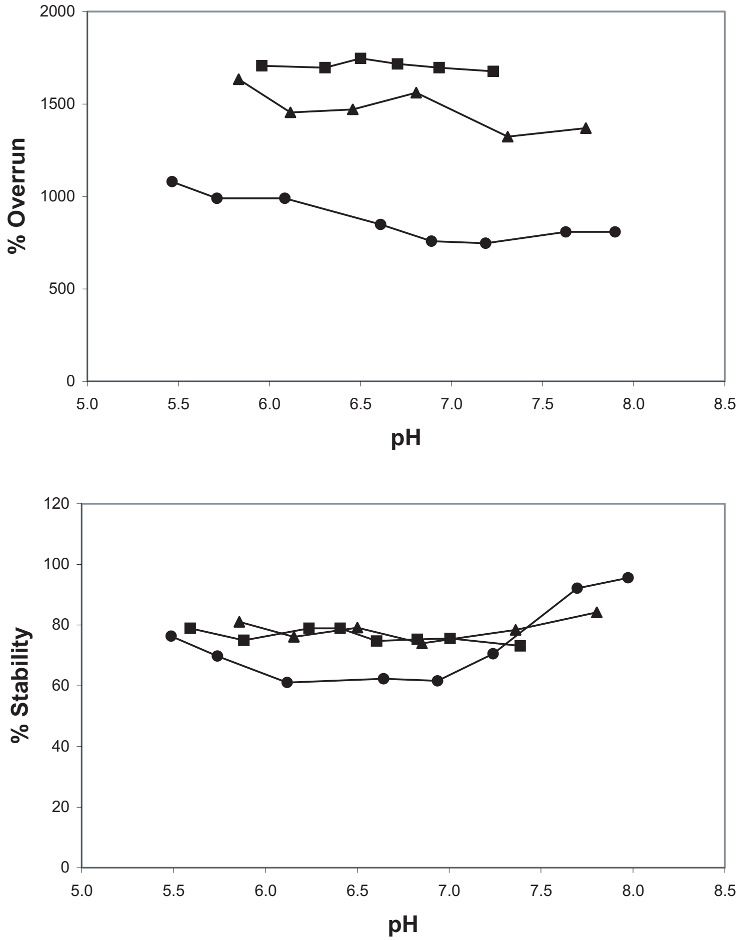

Figure 4. Effects of added salt (0.5 mol added citrate·kg^{-1} MSNF) on the foam overrun of milks (96 g solids·kg^{-1}) reconstituted from low-heat skim milk powder. Foam overrun were measured after 20 min of whipping; foam stability was that of the whipped foam after 30 min standing (●: low-heat skim milk powder; ■: citrated low-heat skim milk powder with 0.5 mol added citrate·kg^{-1} MSNF; ▲: low-heat skim milk powder with 0.5 mol added citrate·kg^{-1} MSNF added after reconstitution).

3.3.3. Steam-frothing properties

The addition of citrate at levels of 0.1 mol added citrate·kg^{-1} MSNF to milk concentrate during powder manufacture enhanced the steam-frothing properties of milk, as shown in Figure 5. This confirms that the citrate addition during powder manufacture produced similar effects to the addition of citrate to milk reconstituted from milk powders.

4. CONCLUSION

The improved foaming properties of citrated powders are attributed to the effects of added citrate on the dissociation of

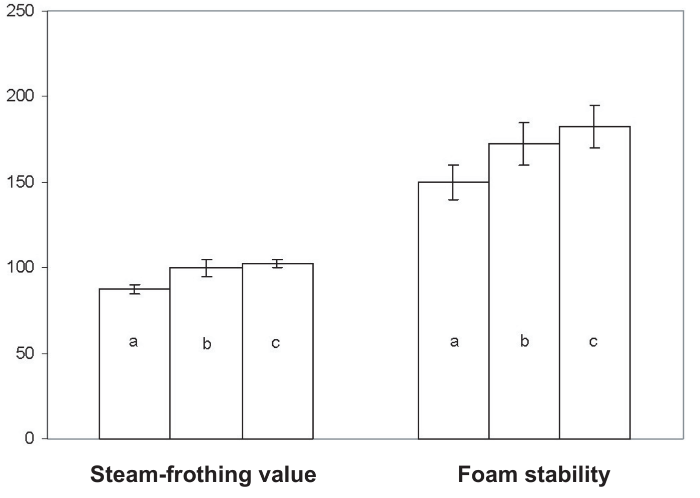

Figure 5. Comparison of the steam-frothing properties of milk (100 g solids·kg^{-1}, pH 6.7) reconstituted from conventional and citrated low-heat milk powders and milks to which citrate was added after reconstitution. Steam-frothing value was measured after 5 min of frothing; foam stability was the foam volume of the frothed milk after 10 min standing. a: skim milk powder (no additives); b: skim milk powder (citrate added after reconstitution); c: citrated skim milk powder. The level of citrate used was 0.1 mol added citrate·kg^{-1} MSNF. In citrated milk powders, citric acid/trisodium citrate was used. When citrate was added to milk, tripotassium citrate was used. Average of triplicate measurements of powders made on two occasions.

casein micelles. Citrated powders are an alternative to physical blends of conventional skim milk powders and citrate salts for enhancing the foaming properties at both low and high temperatures.

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