Rheological Properties of Concentrated Skim Milk: Importance of Soluble Minerals in the Changes in Viscosity During Storage

A. Bienvenue, R. Jiménez-Flores, and H. Singh¹

Dairy Products Technology Centre, California Polytechnic State University,
San Luis Obispo, CA 93407

ABSTRACT

Properties of condensed milks prior to spray drying dictate to a large extent the functionality of the resulting milk powder. Rheological properties of concentrated skim milk, with total solids content of 45% but different mineral content, were studied as a function of shear rate and storage time at 50°C. These milks are proposed as a model to study the effects of minerals on rheology and age gellation of condensed milk prior to drying. During storage of the concentrated milk, the apparent viscosity, particularly after 4 h, increased markedly at all shear rates studied. The yield stress also increased steeply after 4 h of storage at 50°C. The changes in apparent viscosity of concentrated milk stored for up to 4 h were largely reversible under high shear, but irreversible in samples stored for longer time. The appearance of yield stress suggested the presence of reversible flocculation arising from weak attraction between casein micelles, with a transition from reversible to irreversible aggregation during storage. Particle size analysis confirmed irreversible aggregation and fusion of casein micelles during storage. Gradual reduction of mineral content of concentrated milks resulted in a marked decrease in the apparent viscosity and casein micelle aggregation during storage, while addition of minerals to milk had the opposite effect. The results demonstrated that the soluble mineral content is very important in controlling the storage-induced changes in the rheology of concentrated milks. (**Key words:** concentrated milk, yield stress, casein micelle aggregation, mineral environment)

Abbreviation key: PIDS = polarization intensity differential scattering.

INTRODUCTION

Milk can be considered as a colloidal dispersion consisting of fat globules and casein micelles dispersed in an aqueous solution containing whey proteins, lactose and minerals. Normal milk behaves as a Newtonian liquid and its viscosity is affected by temperature, fat content, protein content, total solids, and solid-to-liquid fat ratio (Fernandez-Martin, 1972; Randhahn, 1973; Bloore and Boag, 1981; Langley and Temple, 1985; Velez-Ruiz and Barbosa-Canovas, 1998, 2000). In skim milk, casein micelles are the main contributors to the viscosity of milk (Walstra and Jenness, 1984); any factors that alter the aggregation state of casein micelle, such as pH, salt balance and heat treatment, affect the viscosity of skim milk.

The viscosity of milk increases in a nonlinear fashion as the total solids concentration increases. At high concentrations (above 40% total solids), small additional changes in concentration lead to a very large increase in viscosity. There is a transition from Newtonian to non-Newtonian behavior as the concentration is increased (Walstra and Jenness, 1984; Prentice, 1992). This change occurs because the removal of water causes an increase in volume fraction of dispersed particles and increases the micelle-micelle interactions as the distance between the micelles becomes smaller. In milk processing, this could result in reduced flow rates, high pressure drops, and decreased turbulence and severe fouling in heating operations. In milk powder manufacture, the viscosity of the concentrated skim milk restricts the extent of concentration that can be attained by evaporation without adversely affecting the properties of milk powder (Bloore and Boag, 1981). The relationships between concentrate viscosity and the properties of milk powders have been investigated by Baldwin et al. (1980) and Snoeren et al. (1983).

A number of workers have studied the viscosity of concentrated milk prepared by heat evaporation (Fernandez-Martin, 1972; Bloore and Boag, 1981; Snoeren et al., 1982; Horne, 1993; Velez-Ruiz and Barbosa-Canovas, 1998). The viscosity of concentrated milk depends largely on total solids, temperature and holding time of the concentrate, the preheat treatment, and

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Corresponding author: R. Jiménez-Flores; e-mail: rjimenez@calpoly.edu.

¹Current address: Institute of Food, Nutrition and Human Health, Massey University, Palmerston North, New Zealand.

holding time and the milk composition. The viscosity of freshly concentrated milk decreases with increasing shear rate and follows a power law behavior (Fernandez-Martin, 1972; Velez-Ruiz and Barbosa-Canovas, 1998). Shear thinning increases with decreasing temperature and increasing total solids.

Previous work (Snoeren et al., 1984) has shown that the viscosity of concentrate increases upon storage, and this phenomenon is commonly referred to as "age-thickening." A so-called "structural" viscosity is developed during storage, which can be disrupted by agitation. However, the nature of physico-chemical changes involved in age thickening is largely unknown. Snoeren et al. (1984) proposed that age thickening in highly concentrated systems could be due to the loosening of casein micelles. As a consequence of concentration, the pH decreases and ionic strength increases, both of which reduce the amount of calcium bound to the micelles. This, in turn, increases the solubility of β -casein, resulting the loosening of casein micelle structure and consequent increase in voluminosity of casein micelles. Snoeren et al. (1984) pointed out that only a very small increase in casein micelle voluminosity would be required to cause a substantial increase in viscosity. No experimental evidence was presented to support this hypothesis.

The objective of the work reported in this paper was to further explore the physical and chemical changes that cause age thickening in skim milk concentrated to 45% total solids and to determine the importance of level of soluble minerals in this phenomenon.

MATERIALS AND METHODS

Experimental Protocol

Pasteurized skim milk was purchased from Producers Inc., San Luis Obispo, CA. The experimental protocol showing how the milk samples with altered levels of minerals were produced is given in Figure 1.

Skim milk samples with reduced levels of soluble minerals were prepared by ultrafiltration of skim milk (spiral wound UF membrane 10-kDa MW cutoff, GEA Technology, Hudson, WI) to remove 10, 20, or 30% of the original milk weight in the permeate. An equivalent amount (on a weight basis) of lactose solution (4.8% lactose in water) was then added to the retentate to normalize each sample to about 9% total solids.

Skim milk samples with increased levels of minerals were prepared by adding appropriate quantities of mother liquor after lactose crystallization (provided by Hilmar Cheese Inc., Hilmar, CA) into the skim milk. The composition of this material was: lactose (15%), Ca (0.3%), Mg (0.1%), P (0.5%), K (1.5%), Na (0.5%), and trace amounts of fat and protein. During cold storage,

lactose crystals were formed which were removed by centrifugation at $20,000 \times g$ for 20 min. The supernatant was removed and added to skim milk to increase the mineral content. Table 1 indicates the average total solids and ash content for the milk samples.

These experimental milks were kept overnight at 4°C. The next day, the milks were concentrated in a rising film single effect evaporator at 55°C with evaporative capacity 68 kg/h (Merriott Walker Corp., Birmingham, MI) to 45% total solids. The total solids content was determined by CEM microwave oven and adjusted to 45% by addition of water, if needed. Samples of the concentrated milk were poured into 250 ml bottles, 0.02% sodium azide was added to prevent bacterial growth, and then placed in a water bath thermostatically controlled at 50°C. The final pH of the concentrates was in the range 6.30 to 6.40. Samples were removed after different time intervals for rheological measurements. Subsamples were diluted with Milli-Q water to give 9% TS for particle size and polyacrylamide gel electrophoresis analysis.

Measurement of Viscosity

Flow curves of milk evaporated to 45% TS were obtained on a controlled stress rheometer (Rheometric SR-5000, Rheometric Instruments, Piscataway, NJ) equipped with cup and bob geometry and temperature control. All measurements were performed in a steady stress sweep mode at 50°C, after the samples had been stored in the water bath for different times. Samples were held for 5 min in the rheometer cup before starting the measurements. Steady stress sweep mode was normalized for each sample so that the shear rate was at least 1000 s^{-1} . The typical ranges were 0.06 to 50 Pa with increments of 1.0 Pa.

Measurement of Particle Size Distributions

Particle size distributions were determined using a laser diffraction particle size analyzer in the polarization intensity differential scattering (PIDS) optical mode (Beckman Coulter, model LS 230, Miami, FL). Diluted concentrated milks were added into the analysis chamber containing 1 L of UF milk permeate, until the required obscuration (about 50%) was achieved. The PIDS system uses three wavelengths of light (450, 600, and 900 nm) at 2 polarizations. Measurements are made at several scattering angles of the light polarized vertical to the scattering plane and the light polarized horizontal to the scattering plane. The difference in scattered intensity between the 2 polarizations is highly sensitive to particle size, wavelength, and angle of measurement. The PIDS system has the highest resolution

Figure 1. Experimental protocol for the manufacture of concentrated skim milks.

when the particle size is smaller than the wavelength, i.e., in the 100 to 400 nm range.

Polyacrylamide Gel Electrophoresis (PAGE)

The concentrated milks, diluted to 9% TS with Milli-Q water, were centrifuged at $53,000 \times g$ for 1 h and the supernatants were carefully removed. The diluted concentrates and the corresponding supernatants were examined by PAGE. Samples were dispersed in 0.5 M Tris-HCl buffer containing 10% glycerol, 10% (wt/vol) SDS (20 ml) and 0.05% bromophenol blue. For reducing conditions, 5% β -mercaptoethanol was added to the samples followed by heating at 95°C for 5 min in a boiling water bath. A 10- μ l sample was then loaded onto the SDS-gel and the gel was run in a Mini-Protean

system (Bio-Rad, Richmond, CA) at 200 V using a Bio-Rad power supply unit (model 1000/500, Bio-Rad, Richmond, CA). The SDS-PAGE systems have been described by Singh and Creamer (1991); the protein bands were fixed and stained using a solution of Coomassie blue R-250.

RESULTS AND DISCUSSION

Figure 2a shows the apparent viscosity of concentrated skim milk samples (45% TS) stored at 50°C as a function of shear rate. For all milk samples, the apparent viscosity decreased rapidly with increasing shear rate until about 50 s^{-1} and then decreased slowly with shear rate until the maximum shear rate of 1000 s^{-1} . Such behavior is called shear thinning and implies that the liquid has not true but an apparent viscosity. The apparent viscosity, particularly at low shear rates, began to increase significantly after storage of the concentrate for 4 h at 50°C. After 6 h, a marked increase in apparent viscosity was observed at all shear rates, although viscosity still decreased considerably with increasing shear rate. The concentrated milk held for about 19 h at 50°C showed about fivefold increase in viscosity, at a shear rate of 1000 s^{-1} .

Table 1. Average total solids and ash composition of samples.

Sample	Total solids	Ash
Control	9.58 ± 0.09	0.71 ± 0.01
+ 20% Salts	10.54 ± 0.04	1.02 ± 0.01
+ 10% Salts	10.03 ± 0.05	0.83 ± 0.01
10% UF	9.40 ± 0.07	0.59 ± 0.02
20% UF	9.02 ± 0.06	0.61 ± 0.02
30% UF	8.95 ± 0.09	0.67 ± 0.01

Figure 2.A. Apparent viscosity of concentrated skim milk (45% total solids), as a function of shear rate, that had been stored at 50°C for 0 (○), 1 (●), 2 (△), 4 (▲), 6 (◻), 8 (◼), 10 (▽), or 19 h (▼). **B.** Apparent viscosity of a 45% total solids concentrated skim milk during up/down shear sweep. The concentrate had been stored at 50°C for 0 (up ○, down ●), 8 (up △, down ▲), or 19 h (up ◻, down ◼).

Figure 3. Bingham yield stresses, extrapolated from flow curves, for three different concentrated skim milks (45% total solids) as a function of storage time at 50°C.

During the down sweep, the apparent viscosity increased with decrease in shear rate and up and down sweep curves for concentrated milks stored for up to 4 h were fairly similar. However, the concentrates, stored for ≥ 8 h produced hysteresis loops, indicating time-dependent shear thinning (Figure 2b).

To quantify these observations, each flow curve was analyzed in terms of the Bingham equation over the linear high-shear region of τ versus $\dot{\gamma}$ curves, as described by Horne (1993).

$$\tau = \tau_y + \eta_{PL} \dot{\gamma},$$

where η_{PL} is plastic viscosity (Pa s) and τ_y is Bingham yield stress (Pa). Yield stress were determined by extrapolating flow curves to $\dot{\gamma} = 0$. Good linear fits were obtained with correlation coefficients of about 0.98. Data from three separate experiments (Figure 3) clearly showed that the value of τ_B increased exponentially with increasing storage time at 50°C.

The shear thinning behavior of concentrated milks observed in this study is generally in agreement with the results of previous workers (Snoeren et al., 1983; Horne, 1993; Velez-Ruiz and Barbosa-Canovas, 1998). The presence of a yield stress indicates a three-dimensional structure that has sufficient strength to prevent flow when applied stress is very low. At high shear rates, the hydrodynamic forces cause disruption of weaker bonds such as ionic and hydrogen bonds and removal of hydration layers. Consequently, the structure collapses suddenly, resulting in lower apparent viscosity that is not subsequently affected by shear.

The time-dependence behavior was typical of a concentrated dispersion, with a rapid breakdown of structure on initial shearing and slower reformation of the structure once the shearing had been reduced again. At a structural level, this behavior can be attributed to combined effects of breakdown of weak linkages between the particles and reformation of linkages as a result of Brownian motion and molecular collisions (Tang et al., 1993).

The rheological behavior of fresh concentrated milk suggests that at high total solids, these milks behave as weakly flocculated suspensions (Buscall et al., 1991; Horne, 1993). The storage-induced increase in apparent viscosity may be due to rearrangement of the three-dimensional structure, resulting in increased number and/or strength of bonds between casein micelles. It appears that storage of the concentrates for long times (≥ 8 h) caused irreversible changes in the structure, as indicated by greatly enhanced apparent viscosity under high shear. Clearly, there was a transition from reversible to irreversible aggregation of the particles during aging of concentrated milks. This irreversible change in aggregation behavior during storage of concentrated milk has not been reported in the literature previously. In order to explore the nature of irreversible changes during storage, the concentrated milk samples after each storage time were diluted with water and mixed thoroughly by vigorous agitation to disrupt weak, reversible bonds. The samples were then analyzed for particle size distributions; the changes in particle size reflect irreversible aggregation and fusion of casein micelles.

The particle size distributions in the diluted skim milk concentrates as a function of storage time at 50°C are shown in Figure 4. The size distribution of casein micelles in the fresh concentrated milk was normal, with all the micelles in the size range 50 to 500 nm. The storage of the concentrate for up to 4 h had no effect on the size distribution of casein micelles, but thereafter the distribution shifted towards larger particle sizes. Concentrated milks stored for ≥ 8 h showed a bimodal size distribution, with a second peak between 1000 and 5000 nm.

To further explore the trends in the data, the apparent viscosity at 1000 s^{-1} was plotted against mean volume micelle diameter. Data from three separate experiments (Figure 5) showed that apparent viscosity increased in an exponential fashion with increase in casein micelle diameter, indicating that irreversible increase in viscosity during storage was probably related to the increase in casein micelle diameter, due to aggregation and fusion of casein micelles.

To determine the type of interactions that may be involved in causing micelle aggregation, samples stored

Figure 4. Particle size distributions of concentrated skim milks (45% TS) after storage at 50°C for 0 (○), 4 (●), 6 (△), 8 (▲), or 10 h (□).

for different times were subjected to gel electrophoresis in SDS-containing buffer systems. Samples of skim milk concentrates, diluted about 10% TS with deionized water, were centrifuged at $50,000 \times g$ for 60 min and the supernatants were carefully removed. Both the diluted concentrated milks and their corresponding supernatants were analyzed by reducing and nonreducing SDS-PAGE (Figure 6). Under reducing conditions, the milk samples showed no apparent changes in the intensities of casein bands with storage time (Figure 6). The β -lactoglobulin band, both in the milk and the supernatant samples, gradually decreased in mobility and became blurred (Figure 6). The intensity of casein bands

in the supernatants decreased slightly with increase in storage time. The SDS electrophoresis under nonreducing conditions on the above samples showed very similar patterns, except that the intensity of κ -casein was much lower, which is to be expected as κ -casein exists as disulphide-linked polymers in the micelles (results not shown). These results suggest that aggregation of casein micelles, as indicated by increase in micelle diameter, did not involve formation of new covalent (disulphide) bonds. Therefore aggregation of casein micelles during storage was probably the result of hydrophobic and ionic bonds. The blurring of β -

Figure 5. Relationship between mean volume diameter and apparent viscosity (at a shear rate of 1000 s^{-1}) for three different concentrated skim milks.

Figure 6. SDS PAGE patterns, under reducing conditions, of the concentrated milks stored at 50°C for the different times; 0 h (lane 2), 4 h (lane 3), 6 h (lane 4), 8 h (lane 5), or 10 h (lane 6). The original skim milk is shown in lane 1. The patterns of the supernatants ($50,000 \times g$ for 60 min) obtained from concentrated skim milk stored at 50°C for 0 h (lane 7), 4 h (lane 8), 6 h (lane 9), 8 h (lane 10), or 10 h (lane 11).

Figure 7. Influence of soluble mineral on apparent viscosity versus shear rate profile of concentrated skim milks containing (a) 70%, (b) 80%, (c) 110%, and (e) 120% of the original level of soluble minerals. The mineral-depleted concentrated milks were stored at 50°C for 0 (○), 1 (●), 2 (△), 4 (□), 6 (■), 8 (▽), 10 (▼), or 19 h (?). Concentrated milks with 110% of original soluble minerals were stored at 50°C for 0 (○), 2 (●), 4 (△), 6 (▲), or 7 h (□). Concentrated milks with 120% of original soluble minerals were stored at 50°C for 0 (○), 1 (●), 2 (△), 3 (▲), or 4 h (□).

lactoglobulin band during storage probably resulted from alteration of its molecular weight, due to the lactosylation reaction (Morgan et al., 1997).

The mechanism of age thickening in concentrated milk is not fully understood. Snoeren et al. (1984) that the casein micelles in the concentrate are spherical and that their tertiary and quaternary structures loosen during storage. It was assumed that some kind of hair-like protuberances were formed at the casein micelle surface, which were considered to be partly free-draining. At high shear rates, the periphery of the particle was thought to be drained, which reduced the effective micelle diameter. Concentration by evaporation of milk causes an increase in ionic strength and a decrease in

pH. These changes reduce the amount of calcium bound to caseins, resulting in an increased solubility of β -casein and a rise in voluminosity. Consequently, apparent viscosity increased during storage. However, we found no evidence of increased dissociation of β -casein or any other caseins, as seen on the gel patterns of ultracentrifugal supernatants. Moreover, this model does not explain the irreversible increase in apparent viscosity that occurs at relatively long storage times as observed in our study.

Based on the results of our study, we propose the following explanation for increased apparent viscosity during storage of concentrated milks. It is well known that removal of water by evaporation by itself causes

a number of physical and chemical changes in milk, including close packing of the casein micelles and higher concentrations of lactose, whey proteins and soluble and colloidal salts (Singh and Newstead, 1992). The pH of milk decreases and ionic strength increases with increased removal of water from milk. At 45% total solids concentration, the pH is about 0.5 to 0.6 units lower and the ionic strength would be almost five times higher compared with original skim milk. These 2 factors would reduce the net negative charge on the micelles, leading to decreased electrostatic repulsions between the micelles. As the milk is already saturated with calcium phosphate, a considerable proportion of soluble calcium and phosphate is transferred into a colloidal state during evaporation (Hardy et al., 1984; Nieuwenhuijse et al., 1988). This will lead to a greater amount of colloidal calcium phosphate/g casein in the concentrated milk as compared with normal milk. Because colloidal calcium phosphate is an essential component in the integrity of the micelles. This additional colloidal calcium phosphate is likely to contribute to destabilization of casein micelles (Mohammad and Fox, 1987). If this additional calcium phosphate is deposited on the micelle surface, shielding of charge may occur and hairy layer of κ -casein may be affected. In addition, there is a small increase in calcium ion activity during evaporation of milk (Nieuwenhuijse et al., 1988). Specific binding of calcium ions to the negatively charged casein micelle surface would further reduce electrostatic and steric repulsions, leading to flocculation of micelles in concentrated milk. Therefore it is likely that in the fresh skim milk concentrate, only small flocks, held together by relatively weak interactions, are formed, and that these flocks are broken down under high shear. With increasing storage time, these small flocks aggregate with each and with single micelles, resulting in the formation of large flocks with fairly open structures, resulting in an increase in viscosity. Simultaneously, the fusion of micelles occurs within these flocks causing irreversible changes in micelles size and apparent viscosity.

This hypothesis would predict that increase in pH and/or decrease in ionic strength and calcium ion activity would promote greater repulsion and reduce the extent of cross-linking and fusion of caseins, which would give rise to lower apparent viscosity. This prediction was tested by determining the rheological behavior of concentrated milks that had altered levels of soluble minerals.

The changes in apparent viscosity with storage time at 50°C were very sensitive to levels of soluble minerals. Reduction of soluble mineral content of the concentrate by $\geq 20\%$ resulted in a marked decrease in the apparent viscosity and pseudoplasticity (Figure 7a, b), while ad-

Figure 8. Bingham yield stresses, extrapolated from flow curves, as a function of storage time at 50°C for concentrated skim milks containing 70 (▲), 80 (△), 90 (●), 100 (○), 110 (■), or 120% (□) of original level of soluble minerals.

dition of minerals to milk had the opposite effect (Figure 7c, d). Mineral-depleted milks showed much slower increase in apparent viscosity with storage time; the effect being dependent on the extent of mineral removal. Mineral-enriched milks showed a faster rise in apparent viscosity with storage time.

The changes in yield stress with storage time for mineral-altered concentrated milks are shown in Figure 8. It is clear that the yield stress values, at each storage time, were inversely related to the concentrations of mineral content.

The mineral-altered concentrated milks were diluted with water and particle size determined by light scattering, as described earlier. A plot of volume average particle size versus storage time for different milks is shown in Figure 9. For the control sample, the reaction showed an initial lag phase, where casein micelle size remained fairly constant, after which the average size increased considerably. Decreasing the level of minerals gradually lengthened the lag phase, while addition of minerals shortened the lag phase. It is evident from these results that the level of soluble minerals affects the rate of aggregation of casein micelles in concentrated milk, which consequently influences the apparent viscosity of the system.

It appears therefore that the increased mineral content during evaporation of milk is primarily responsible for the observed changes in viscosity during storage of concentrated skim milk. Reduction of soluble minerals causes a decrease in the ionic strength and calcium ion activity, thus reducing the extent of micelle aggregation and fusion. Further studies will be useful to elucidate the role of individual mineral constituents on storage-

Figure 9. Changes in mean volume diameter as a function of storage time at 50°C for concentrated skim milks containing 70 (▲), 80 (△), 90 (●), 100 (○), or 120% (□) of original level of soluble minerals.

induced changes in rheological properties of concentrated milks.

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