Seasonal Variations in the Heat Stability of Concentrated Milk: Effect of Added Phosphates and pH Adjustment

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ABSTRACT

Natural variations in heat stability of 31% total solids concentrated milk have been surveyed over a 1-yr period. Very small variations occurred, and no distinctive instability period was observed. The stabilizing effect of pH adjustment with $NaH_2PO_4{\cdot}Na_2HPO_4$ or NaOH·HCl before sterilization was studied. The phosphates produced better stabilization than the acid-base combination at any pH between 6.0 and 7.0. The effectiveness of Na_2HPO_4 showed seasonal variations: the effects were marked on summer milks and smaller in winter milks. Conversely, seasonal variations were observed in the buffer capacity of the concentrates. The results emphasize the possibility of a specific stabilization mechanism by phosphate salts on concentrated milks.
(Key words: heat stability, concentrated milk, stabilizers)

Abbreviation key: HCT = heat coagulation time, TS = total solids.

INTRODUCTION

The manufacture of sterilized concentrated milk is subject to some technological problems arising from the instability of the product during the heat treatment. The heat stability of concentrated milk, referred to as the heat coagulation time (HCT) at 120°C, is an important processing parameter, but neither the destabilization phenomenon itself nor the factors affecting it are well understood (4). The addition of phosphate salts (mono- or disodium) prior to sterilization offers a possibility for overcoming this problem (12).

In Canada, the current practice in stabilization of 31% total solids (TS) concentrated milk is to add systematically a 3:1 mixture of $NaH_2PO_4{\cdot}HPO_4$ to a fixed level below the legal limit of .2% (or .1% calculated as P_2O_5). This practice is based on the assumptions that adding a mixture of mono- and diphosphates stabilizes the pH of concentrated milks during sterilization and that this is effective throughout the year.

However, it was observed in local dairies that the efficiency of these additives to stabilize concentrated milk was subject to seasonal changes. In fact, the amount of phosphate required for stabilization exceeded the legal limit of .2% for several weeks in succession. Therefore, an extensive survey of the seasonal changes in the heat stability of concentrated milk is needed to provide answers to this question.

It is known (2, 5, 6, 11) that unconcentrated skim milk exhibits a seasonal heat instability period between December and May. A significant correlation was found between the naturally occurring level of urea and the heat stability of milk (5, 7). However, there is little or no correlation between the heat stability of skim milk and that of its concentrate. Muir and Sweetsur (8) suggested that the mechanism of

Received October 26, 1989.
Accepted November 26, 1990.

coagulation in concentrated milk is similar to that which occurs within the minimum of the HCT-pH profile of unconcentrated skim milk.

Some seasonal variations have been observed in the heat stability of concentrated milk. Sweetsur and Muir (13) found low stability periods between February and April for homogenized concentrated milks, but the variations were less marked than for the corresponding unconcentrated milk. These authors also found the highest HCT values during May and June for concentrated milk. No significant correlation with any of the milk component was identified, and the variations observed in the HCT were attributed to shifts in the HCT-pH profile.

The use of stabilizers in the manufacture of concentrated milk has received some attention in the past decade. Sweetsur and Muir (12) studied the effect of ortho-, disodium, or trisodium phosphates, trisodium citrate, sodium hydrogen carbonate, and calcium chloride on the heat stability of concentrated skim milk (22.5% TS) and reconstituted milk powder. It was shown for concentrated milk that HCT-pH curves were only slightly affected by addition of Na_2HPO_4, Na_3 citrate, or $NaHCO_3$. However, when the milk was forewarmed, the use of Na_2HPO_4 increased the maximum coagulation time and enhanced the stability over the pH range 6.4 to 6.5, whereas the other stabilizers had little effect on the heat stability. These authors also tested the effect of pH adjustment of milk with a 3:1 mixture of $NaH_2PO_4 \cdot Na_2HPO_4$ on the heat stability of the concentrate. The addition of 80 mg of the mixture per 100 ml of forewarmed milk produced drastic increases in heat stability. It was suggested that the choice of the stabilizer should depend upon whether the natural pH of milk is on the acid (use Na_2HPO_4, Na_3PO_4, Na_3 citrate, or $NaHCO_3$) or on the alkaline (use NaH_2HPO_4 or $CaCl_2$) side of the maximum.

From these considerations, the stabilizing effect of the added salts likely is due to their ability to modify the pH of the concentrated milk before sterilization. Therefore, the nature (e.g., mono- or disodium phosphate) and the amount of salt needed for stabilization of a given concentrated milk should be determined in order to bring its pH closest to the value at which the heat stability is maximum.

In the present experiment, the HCT-pH profile of the concentrated milk has been established routinely, in order to identify the pH at which its HCT is maximum (optimum pH). The salts (Na_2HPO_4 or NaH_2PO_4) were added in order to adjust the pH of the concentrate towards its optimum value. The effect of the pH adjustment with the phosphates was compared with the effect of adjusting the pH to the same values with hydrochloric acid or sodium hydroxide. The experiment was conducted over a year in order to detect natural instability periods.

MATERIALS AND METHODS

Milk Supply

Fresh raw milk was collected from the bulk of a local dairy (Laiterie Cité, PQ). Approximately 160 L were used for each experiment scheduled, once every 2 wk over a 1-yr period.

Processing

The raw milk was converted to concentrated milk (31% TS) in our pilot plant, using semi-industrial equipments and following as closely as possible the local industrial process.

The milk was standardized to a 1:3.49 milk fat:TS ratio, using 35% cream prepared by separating a portion of the same milk on a Westfalia separator AG (Centrico Inc., NJ). The fat and TS determinations were done gravimetrically according to the Rose-Gotlieb method (AOAC Number 16.064). The standardized milk was preheated in batch at 88°C for 15 min in a 200-L jacketed tank. After heating, the product was pumped into the Mojonier vacuum evaporator (APV Co., England) operated at 63°C at 700 mm Hg. The evaporation was completed after approximately 90 min, after which the concentrate had reached 31% in TS. The final product contained 8.9% milk fat and 22.1% nonfat solids.

The determination of the amount of stabilizer (Na_2HPO_4 or NaH_2PO_4, HCl or NaOH) required for the concentrated milk was established after heat stability measurements in the laboratory.

The heat stability of the concentrated milks was determined at .2 pH intervals between 6.0 and 7.0, using the Davies and White procedure (1). Ten milliliters of concentrate were introduced in a stoppered glass vial and immersed in an oil bath at 121°C under a constant rocking rate of 6 cycles per minute. The HCT was defined as the time (min) at which the onset of coagulation is visually observable by the appearance of solid particles on the wall of the vial. Then pH curves were established for the concentrates, using HCl and NaOH or NaH_2PO_4 and Na_2PO_4 to modify the pH. The pH at maximum HCT value (between 6.0 and 7.0) was identified, and the amounts of stabilizer (m*M*) required to reach that pH value were chosen for the stabilization of the concentrated milk.

The concentrated milk was divided into three parts for stabilization: natural (not stabilized), stabilized with the optimum amount of phosphate, and with the optimum amount of acid or base. The stabilizer or the HCl·NaOH was added to each part, and the concentrate was stored at 4°C for 12 h. The sterilization was done in the can at 121°C in a Stork (Stork, Amsterdam B.V., Neth.) rotating simulator for 12 min (6 min heating and 6 min holding). A heat penetration curve was done as control.

RESULTS

The results presented in this report represent the entire study covering a 52-wk period starting from the 2nd wk of August (wk 1). Due to technical problems, some data are missing over the period between December and January (wk 15, 17, 21, and 23).

HCT-pH Curves from pH Adjustment and Phosphate Additions

The effect of NaOH·HCl or $NaH_2PO_4 \cdot Na_2HPO_4$ on the pH of concentrated milks was correlated with HCT or heat stability. For the purpose of this report, a representative set of results was chosen for each season and plotted in Figure 1 (a to d). Both NaOH and Na_2HPO_4 produced HCT-pH curves with the same maximum pH located on the alkaline

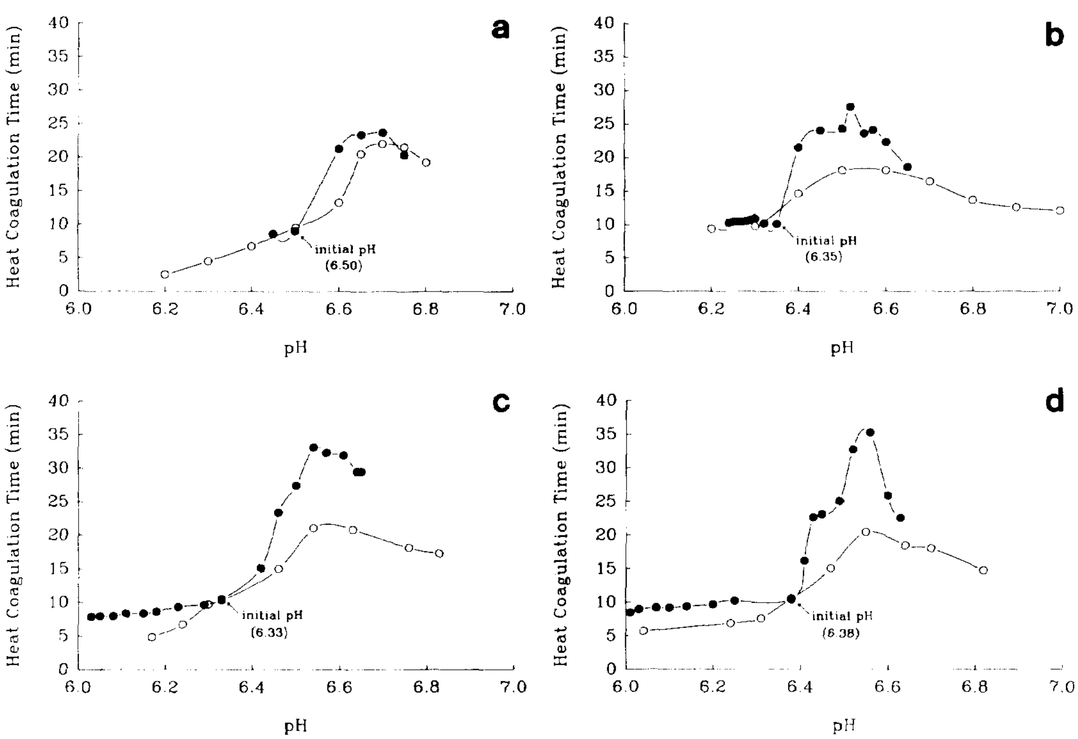

Figure 1. Heat coagulation-pH profiles for concentrated milk stabilized with HCl·NaOH (○), or $NaH_2PO_4 \cdot Na_2HPO_4$ (●): a) 2nd wk of November, b) 2nd wk of February, c) 3rd wk of May, d) 1st wk of August.

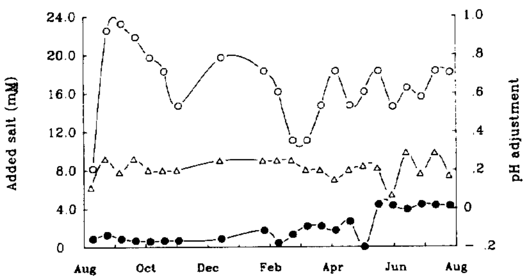

Figure 2. Seasonal variations in stabilization requirements in terms of Na_2HPO_4 (o), NaH_2PO_4 (●), or pH changes (Δ).

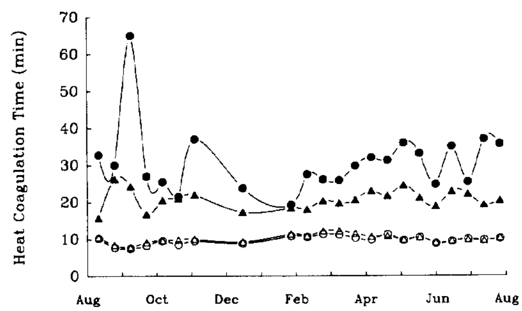

Figure 3. Heat stability of concentrated milk unadjusted (O), HCl·NaOH adjusted (▲), NaH_2PO_4 (Δ), or Na_2HPO_4 adjusted (●) over a 1-yr period starting from August.

side of the natural pH of the milks. At no time of the year was the natural pH of milk above the pH of maximum stability, so the addition of HCl always had a destabilizing effect. The general shape of the curves obtained changed slightly over the year period. During fall (Figure 1a), the effects observed were similar for the two additives: the pH at maximum HCT was located at 6.70, and the increase in heat stability was around 13 min. The only apparent difference was a slight upward shift of the HCT values for the Na_2HPO_4 curve with respect to the Na_2HPO_4 curve. During winter (Figure 1b), as the natural pH of the concentrated milks shifted to more acidic values (6.35), the pH at maximum HCT changed to values around 6.50. However, the stabilizing action of the phosphate salts was in the range of 15 min because the one for NaOH·HCl was in the range of 8 to 9 min. During spring (Figure 1c), the natural pH remained relatively unchanged, but the pH at maximum HCT shifted to values around 6.60. The stabilizing action of Na_2HPO_4 increased to 23 min as the action of HCl-NaOH

TABLE 1. Seasonal variations in the amount of Na_2HPO_4 required to adjust the pH of concentrated milks to maximum heat stability.

Season	n	Na_2HPO_4 per pH unit	
		(mg)	
		$\overline{X}$	SD
Fall (Sep to Dec)	4	647.2	84.9
Winter (Dec to Mar)	4	569.2	48.2
Spring (Mar to Jun)	7	621.1	63.3
Summer (Jun to Sep)	5	773.9	91.3

increased to 10 min. During summer (Figure 1d), as the natural pH of the milks shifted to 6.40, the optimum pH remained almost unchanged. The stabilizing effects observed were generally similar to those observed during spring, because the phosphates still gave higher stability values than HCl·NaOH at equivalent pH.

Figure 2 summarizes the seasonal variations in the extent of phosphate additions or of pH modification needed to produce the optimum stabilizing effect in concentrated milk. The requirements in Na_2HPO_4 fluctuated the most compared with those in NaH_2PO_4 or in pH modification. In fact, wide variations were observed in terms of Na_2HPO_4 requirements over the period between January and March.

The effectiveness of phosphates to modify the pH also showed some seasonal variations. When expressed in milligrams of Na_2HPO_4 needed to increase the pH of concentrated milk of one unit (Table 1), the buffer capacity of milk was maximum in summer (773.9 mg) and minimum in winter (569.2 mg). However, as seen from the standard deviations tabulated, considerable variations occurred (48.2 mg in winter and 84.9 mg in fall) during the experiment.

Heat Stability of the Concentrated Milks

Over the 1-yr period, the values of natural heat stability for the concentrated milks were between 7 and 10 min (Figure 3). Small natural variations were found during the experiment on the basis of the heat stability data. The adjust-

TABLE 2. Seasonal variations of natural pH and pH at maximum heat stability for concentrated milks.

		pH of concentrated milk					
Season	n	Natural		HCl-NaOH		Phosphates	
		$\bar{X}$	SD	$\bar{X}$	SD	$\bar{X}$	SD
Fall (Sep to Dec)	4	6.51	.06	6.74	.03	6.71	.05
Winter (Dec to Mar)	4	6.37	.02	6.60	.00	6.54	.04
Spring (Mar to Jun)	7	6.37	.02	6.57	.08	6.53	.04
Summer (Jun to Sep)	7	6.42	.06	6.63	.07	6.59	.08

ment of pH with acid or base improved the stability of the concentrates as the values reached the 15 to 25 min range at optimum pH. The stabilization obtained during fall and summer was better than for winter and spring. The addition of Na_2HPO_4 produced the best stabilization as the values reached 25 to 34 min, with greatest effects observed over the period between April and August. The stability curve obtained with NaH_2PO_4 overlaps the one for the unadjusted milk because this additive up to approximately 60 mg/100 ml never increased the heat stability of the concentrated milks.

The seasonal variations of both the natural and pH at maximum HCT of the concentrated milks are summarized in Table 2. The pH at maximum HCT was always on the alkaline side of the natural pH and slightly higher for NaOH·HCl stabilization than for the phosphates. All the pH values were highest during fall and lowest during spring.

DISCUSSION

Our stability data for the unstabilized concentrated milk (7.5 to 12 min) are lower than those generally reported in literature, but the TS contents were 26% in the experiments of Newstead et al. (10) and 22.5% in those of Sweetsur and Muir (12). The heat stability of concentrated milk is inversely related to its solids content (8, 15). Our low HCT values may also be a result of the higher temperature (63°C) used for concentrating the milk compared with the two other studies cited (45 to 50°C). The use of a higher temperature has undoubtedly accelerated some physicochemical changes such as salt balance shifts or pH decrease (4) and, in turn, may have decreased the heat stability of the concentrated product.

The results presented in this paper are derived from unhomogenized concentrated (31% TS) milks. However, a parallel experiment over a period from May to August showed that the homogenization process had very little effect on heat stability of the concentrated milks, in agreement with Sweetsur and Muir (14), who observed that summer milks can withstand homogenization but that winter milks cannot.

The seasonal variations in the natural heat stability of concentrated milk were surprisingly very small in contrast with the observations made by Sweetsur and Muir (13). According to our HCT data, no instability period could be clearly detected. Also, very small variations in natural pH were observed during the experiment. Because the observed seasonal behavior of concentrated milks in our study is very difficult to interpret on the basis of heat coagulation, we may consider the variations observed in phosphate requirements.

The Na_2HPO_4 additions exceeded the legal limit of .2% for most of the year. This suggests that because of the legal limitations in Canada, the stabilizing potential of phosphates is not fully exploited in concentrated milks.

The effectiveness of the Na_2HPO_4 showed marked seasonal variations. Its stabilizing effect was maximum in summer (June to August) and minimum in winter (January to March). This is in agreement with the observations from Sweetsur and Muir (13), who found a marked stabilizing effect of a $NaH_2PO_4 \cdot Na_2HPO_4$ mixture on homogenized concentrated milk during summer.

These seasonal variations in stabilization can be related to some changes in buffer capacity of the concentrate. Newstead (9) showed that reducing the salt content of concentrated milk increased its heat stability. In the present study, we have been unable to correlate the change in HCT values with the buffer capacity of the concentrated milks. We found the buffer capacity to be at its maximum in summer and at its minimum in winter, but very small variations in HCT were measured over the year. However, it appears that phosphates possess the greatest stabilizing effect when the buffer capacity of milk is at its highest. The relationship between buffer capacity and heat stability is not straightforward because the buffer capacity underlies the complex chemical equilibrium involving the salt balance and the proteins of milk.

It was expected that Na_2HPO_4 would give better stabilization than NaH_2PO_4 due to the presence of milk, the natural pH of which was on the acid side of the HCT-pH curve (13). The addition of NaH_2PO_4 produced decreases in pH and destabilization, but the destabilizing effect was smaller than that produced by a simple pH decrease with HCl. It appears that the specific phosphate effect observed at the optimum pH is also present on the acid side of the maximum, down to pH as low as 6.0.

The manipulation of pH with NaOH-HCl produced the same effects as the phosphates for the same purpose, but the stability was always better with the phosphates at a given pH. No other study can be found in which the addition of phosphates to concentrated milk has been done with the pH as a parameter. In the present study, there appears to be a specific stabilizing effect associated with the supplementation of concentrated milk with phosphate ions ($HPO_4^=$ or $H_2PO_4^-$), but the complex chemistry underlying this question has not been established yet. Deysher and Webb (3) reported that the addition of Na_2HPO_4 to concentrated milks can reduce tricalcium citrate precipitation, whereas simple pH adjustment cannot. This suggests that the added phosphate ions specifically affect the state of the salt balance. If this is true, the salt balance of concentrated milk would have to be considered as a major determinant of its heat stability. This hypothesis requires that more work be done on the changes in the milk salt balance induced by the stabilization and sterilization process.

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