Rheology and Surface Tension of Selected Processed Dairy Fluids: Influence of Temperature

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ABSTRACT

The effects of temperature on the rheological behavior and surface tension of commercial samples of skim milk, 3.5% milk, 38% cream, two different cultured buttermilk products, and buttermilk powder solution were studied using a controlled stress rheometer and the Wilhelmy plate method, respectively. The rheology of the dairy fluids was greatly influenced by temperature but to varying degrees depending on the product tested. The rheological data for skim milk, 3.5% milk, buttermilk powder solution, and 38% cream could be fitted to the Bingham model at all temperatures, and the cultured buttermilk products could be fitted to the power law model. For the uncultured products, viscosity and yield stress decreased as temperature increased. The dairy products exhibited great variation in surface tension, which also was strongly dependent on temperature. For 38% cream, the measurements of surface tension indicated a high degree of instability as temperatures varied, which suggests that the milk fat globule membrane was destabilized at the interface between air and water. This study demonstrates the effect of temperature on bulk and interfacial properties of dairy fluids as fat content and milk fat globule fragments vary.

(**Key words**: surface tension, viscosity, cream, buttermilk)

Abbreviation key: **CSR** = controlled stress rheometer, ***K*** = consistency coefficient, **n** = rate index.

INTRODUCTION

Dairy rheology is important for the texture and stability of dairy products, process design, and fundamental research (8, 20). The rheological behavior of milk products is complex and strongly dependent on temperature and on the concentration and physical state of the dispersed phases (26). Milk and cream usually exhibit Newtonian behavior when products are fresh, temperatures are above 40°C, fat content is below 40%, and shear rate is low (21, 32). The deviation from Newtonian behavior increases as fat and total solid contents increase and as temperature decreases at low shear rate (21).

In literature reports, variation in the reported flow properties of fluid dairy products is large. This variation can partly be ascribed to the different types of viscometers employed. Capillary tube viscometers have been used because of their good sensitivity for low viscosity fluids such as milk (5). Yamamoto et al. (32) used a low shear capillary viscometer with a continuous varying pressure head to investigate the flow properties of both human and bovine milks. These milks were found to have non-Newtonian behavior. However, such analysis can be complicated for heterogenous systems such as milk because of the variation in shear rates produced from capillary flow (20).

Cone and plate instruments traditionally have provided better uniformity of shear rate but at the expense of sensitivity. However, the development of more precise and sensitive instruments, combined with the development of sophisticated software packages for instrument control, data collection, and data analysis, have made rheological investigations of even complex fluids easier. Thus, cone and plate rheometers are now being used widely for food rheology. Studies using cone and plate have been carried out to examine the rheology of commercially processed milks (29) and to determine the viscosity parameters of ice cream mix at pasteurization temperatures (7). In the present study, a controlled stress rheometer has been applied to measure the rheological properties of various types of dairy fluids.

The surface tension of fluid dairy products is another fundamental physical property relating to the stability of foams, emulsions, and films as well as affecting industrial processes such as fractionation and concentration. Milk contains several surface-

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active components (e.g., proteins, free fatty acids, and derivatives of the milk fat globule membrane) that affect both the surface properties (e.g., surface tension) and bulk properties (e.g., micelle and globule formation) (30). Surface tension of dairy fluids has been reported in numerous studies involving the Wilhelmy plate method (9, 22, 31), Du Nouy ring method (4, 16, 28), drop number method (2, 13, 17), and oscillating jet method (10, 31). Analogous to the rheological properties, temperature has a large effect on the surface tension (13, 28). The surface tension data in the current study were obtained using the Wilhelmy-plate method (12).

The objective of this work is to investigate the rheological and interfacial properties of commercially processed dairy fluids with varying fat contents and milk fat globule membrane fragments at different temperatures.

MATERIALS AND METHODS

Materials

Commercially processed skim milk, 3.5% milk (HTST pasteurized, homogenized), 38% cream (HTST pasteurized), modern buttermilk (cultured, HTST pasteurized and homogenized 0.5% milk), and traditional buttermilk from butter production (made from cultured cream, containing 0.5% fat, unhomogenized, HTST pasteurized) were purchased in local supermarkets over a period of 10 wk. Three cartons of each type of product were analyzed in random order during this period. Hence, the tested samples were from different companies and had different production dates. The age of the milk samples were estimated to be between 1 to 5 d, on average 2 d, as judged from the container date of the samples. Each sample was tested on the day of purchase. Sweet buttermilk powder (Milex 500; MD Foods Ingredients amba, Nr. Vium, Denmark) was donated by the manufacturer.

Sweet buttermilk powder was reconstituted to 10% (wt/wt) by addition of deionized water and then stirred for 20 min at 20°C. This solution is referred to as buttermilk powder solution. The pH of the solution was determined to be 6.6.

Rheological Measurements

A rheometer (Carri-Med CSL^2 100 Rheometer; TA Instruments Ltd., Leatherhead, United Kingdom) was used to characterize the rheological properties of the dairy fluids at 10, 25, and 40°C. Measurements were conducted applying the controlled shear stress mode of the instrument. The following geometries were used: 6-cm acrylic cone, 1° (gap 43 μm) for skim milk, 3.5% milk, and buttermilk powder solution; 4-cm acrylic plate (gap 150 μm) for modern buttermilk and traditional buttermilk; and a 6-cm acrylic plate for 38% cream (150-μm gap). The gap was set automatically for each measurement. Prior to the flow experiments, the maximum shear stress was determined for each product that corresponded to the maximum measurable shear rate for the sample in question. This stress was determined manually and subsequently applied in the final experiments. The applied shear stress for the different products at 10, 25, and 40°C are listed in Table 1.

TABLE 1. Applied maximal shear stress for skim milk, 3.5% milk, 38% cream, modern buttermilk, traditional buttermilk, and buttermilk powder solution.

	Applied maximal shear stress		
Products	10°C	25°C	40°C
	(mPa)		
Skim milk	4000	4000	3000
3.5% Milk	8000	6000	4000
38% Cream	2000	2500	. . .
Buttermilk			
Modern	40,000	30,000	. . .
Traditional	30,000	20,000	. . .
Powder solution	6000	5000	3000

A preexperimental step (60 s) was carried out prior to the flow experiment. In the preexperimental step, the sample (2 ml) was equilibrated at the temperature in question (0.4% variation) and adjusted for zero velocity. The flow experiment was then conducted; the experiment consisted of an up curve shear stress sweep (300 s) to the set shear stress, a peak hold (60 s), and a down curve shear stress sweep (300 s). For 38% cream, the shear stress that was applied was lower because of churning. A minimum of three measurements per sample were performed.

Surface Tension Measurements

The surface tension measurements were performed by the Wilhelmy plate method (12) using a Sartorius Basic electrobalance (Sartorius, Göttingen, Germany)(sensitivity 0.5 mg) with automatic recording every 5 s. A platinum Wilhelmy plate (10 × 20 mm) was used. The platinum plate was flamed prior to each experiment.

The surface tension was measured at 10, 25, and 40°C (±0.5°C). Prior to each experiment, the samples were equilibrated at the corresponding temperature for 30 min. The sample (50 ml) was poured into a pyrex glass with a diameter of 66 mm in a temperature-controlled glass bath, the Wilhelmy plate was lowered immediately into the sample surface, and the surface tension was recorded for 1200 s. Measurements were conducted in triplicate per sample.

Data Analyses

The TA Instruments Rheology Solutions software Data Module version 1.1.3 for Windows™ (25) was used for conducting data analysis. The rheological parameters were estimated by model fitting using simplex analysis to minimize the standard error.

The data were fitted to the following models often applied in food rheology (7, 29):

Bingham,

$$\sigma = \sigma_y + \eta\dot{\gamma}; \qquad [1]$$

Power law,

$$\sigma = K^{n-1}\cdot\dot{\gamma}; \qquad [2]$$

and Herschel-Bulkley,

$$\sigma = \sigma_y + K^{n-1}\cdot\dot{\gamma} \qquad [3]$$

where σ = shear stress (millipascals), η = viscosity (millipascal·seconds), $\dot{\gamma}$ = shear rate (per second), σ_y = coefficient index yield stress (millipascals), $\boldsymbol{K}$ = consistency coefficient index (millipascal·seconds^{n-1}), and $\mathbf{n}$ = rate index (24).

The choice of a rheological flow model was based on the evaluation of standard error and regression values of the fits to these models, selecting the model that fit best at all temperatures tested. In the model fitting procedure, the Newton and Casson models also were also included, but were rejected because of the higher standard error of fit.

Statistical analyses of rheological and surface tension data were performed by ANOVA and Newman-Keuls multiple comparison test (23).

RESULTS AND DISCUSSION

In the present study, a controlled stress rheometer (**CSR**) was used for the rheological investigations. The CSR operates in a mode in which the stress is set, and the resulting shear rate is measured (25). In contrast, the method traditionally employed uses controlled shear rate instruments that preset the shear rate and determine the corresponding shear stress. The advantage of using the CSR is that it allows a direct determination of a yield point if such is present.

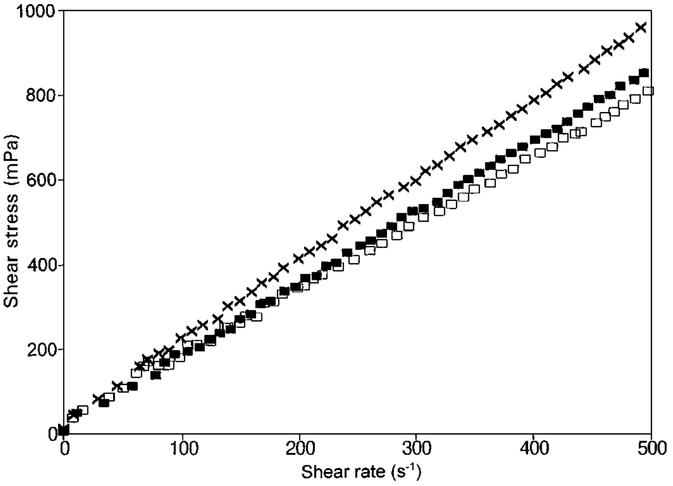

Figure 1. Shear stress versus shear rate of skim milk (□), 3.5% milk (**x**), and buttermilk powder solution (■) at 25°C. Geometry: 6-cm acrylic cone, 1°. Gap: 43 μm.

Preliminary experiments showed no difference between up and down shear stress sweeps of skim milk, 3.5% milk, and buttermilk powder solution. Hence, in the final experiments, only up curve sweeps were performed for these products.

The degree of non-Newtonian behavior at low shear rates was most pronounced with decreasing temperature for skim milk, 3.5% milk, and buttermilk powder solution, of which 3.5% milk exhibited the largest deviation from Newtonian flow. This trend is in accordance with results of previous reports (21, 29). The flow curves of the full shear stress range of skim milk and 3.5% milk produced the best fit applying the Herschel-Bulkley model. At 25 and 40°C, the flow curves exhibited shear thickening at the rate indices of 2.1 and 2.2, respectively, which indicated the occurrence of a centrifugation effect at high stresses leading to a heterogenous distribution of the particles. This result could be due to the high end stresses that were employed in the present study compared with the stresses obtained by Wayne and Shoemaker (29), who worked in a shear rate range of 121 to 485 s^{-1}. Hence, model fitting was repeated for data corresponding to shear rates between 0 and 500 s^{-1}, a shear rate range that is comparable with results of the latter report. The best fits based on R^2 values were obtained from the Bingham model for skim milk and 3.5% milk in accordance with results of a previous report (29) (Figure 1). The yield stress and viscosity for skim milk and 3.5% milk are listed in Table 2. The R^2 values of the Bingham model fits for skim milk between 0 to 500 s^{-1} were all greater than 0.99.

The estimated values for yield stress and viscosity were analyzed by two-way ANOVA testing for differences between the various temperatures and samples and a possible interaction between the two factors (Table 3). The differences between temperature and yield stress and between temperature and viscosity were significantly different ($P < 0.001$). Temperature had the largest influence on yield stress at lower temperatures, and the differences in yield stress of skim milk and 3.5% milk were significantly different ($P < 0.05$) between 10 and 25°C, but not between 25 and 40°C. The differences among samples were expected and were due to the natural variations of milks.

For 38% cream, great care was needed to pour the cream from the carton to the rheometer and to remove any clot from the sample. In the initial experiments, the maximum possible stress was applied during the shear stress sweeps. This stress resulted in churning of the cream. Hence, the maximum stress of 2 Pa, corresponding to an end shear rate of approximately 50 to 100 s^{-1}, was chosen. This rate was within the shear rate region that had been suggested as appropriate for the rheological evaluation of cream (20). The presence of clots in the cream made reproducible results difficult to attain. Samples of cream varied widely, especially in their tendencies toward the onset of churning, as has been previously reported (19). Reproducible results were not possible at 40°C, presumably because of the instability of the fat globules. The consistency of cream is influenced by several factors, including processing (e.g., temperature during separation and pasteurization and rebodying), age, and fat concentration (14, 20). During our experiments with 38% cream, it was observed that, as shear was initiated, stress built up almost linearly as the fat globules were being forced into a

TABLE 2. Fluid model behavior of skim milk, 3.5% milk, 38% cream, and buttermilk powder solution at 10, 25, and 40°C as estimated by the Bingham model.[1]

Product and temperature	Sample	Yield stress		Viscosity	
		(mPa)		(mPa·s)	
		$\bar{X}$	SD	$\bar{X}$	SD
Skim milk					
10°C	1	46.6	29.8	2.747	0.032
	2	67.7	21.4	2.523	0.057
	3	38.6	12.2	2.720	0.055
	$\bar{X}$	50.9	23.9	2.663	0.113
25°C	1	19.7	3.0	1.527	0.016
	2	17.4	10.7	1.501	0.035
	3	22.6	0.2	1.574	0.024
	$\bar{X}$	19.8	6.2	1.534	0.039
40°C	1	9.4	2.2	1.003	0.010
	2	5.8	3.2	0.903	0.101
	3	13.3	8.2	0.961	0.019
	$\bar{X}$	9.5	5.7	0.956	0.069
3.5% milk					
10°C	1	100.2	42.5	3.215	0.188
	2	284.4	84.2	3.862	0.079
	3	74.1	42.5	3.097	0.108
	$\bar{X}$	140.9	105.5	3.349	0.356
25°C	1	54.6	10.8	1.773	0.034
	2	42.2	25.6	1.871	0.053
	3	39.7	19.2	1.769	0.041
	$\bar{X}$	46.0	18.8	1.808	0.064
40°C	1	22.2	9.6	1.189	0.045
	2	19.2	8.4	1.157	0.018
	3	20.2	4.6	1.085	0.013
	$\bar{X}$	20.5	7.2	1.143	0.052
38% Cream					
10°C	1	499.6	54.6	32.17	0.92
	2	392.5	177.0	23.61	1.26
	3	221.1	68.0	20.27	5.97
	$\bar{X}$	329.7	146.7	26.64	4.93
25°C	1	436.6	49.4	10.23	0.34
	2	324.0	91.6	8.95	0.66
	3	385.0	85.1	9.69	0.89
	$\bar{X}$	381.0	91.22	9.44	0.78
Buttermilk powder solution					
10°C	1	35.4	8.4	2.831	0.033
25°C	1	20.46	2.6	1.679	0.011
40°C	1	19.5	8.4	1.136	0.015

[1] Estimation of flow model parameters for skim milk, 3.5% milk, and buttermilk powder solution is based on data corresponding to shear rates 0 to 500 s^{-1}.

TABLE 3. Results of two-way ANOVA tests of the influence of temperature (T) and sample (S) on the rheological parameters estimated for the tested products.[1]

Products	T	S	Interaction (T × S)
Skim milk			
Yield stress	***	NS	NS
Viscosity	***	***	**
3.5% Milk			
Yield stress	***	***	***
Viscosity	***	***	***
38% Cream			
Yield stress	NS	**	*
Viscosity	***	**	*
Buttermilk			
Modern			
Consistency index	***	***	***
Rate index	**	***	NS
Traditional			
Consistency index	NS	***	NS
Rate index	NS	NS	**

[1] Analyses of data for skim milk, 3.5% milk, and buttermilk are calculated from model fits based on data corresponding to shear rates between 0 and 500 s^{-1}.

*$P \le 0.05$.

**$P \le 0.01$.

***$P \le 0.001$.

new shape until the rate decreased; eventually, the stress dropped asymptotically to a steady value. This "overshoot phenomenon" has been reported to occur when cone and plate or concentric cylinder geometry viscometers are used to examine creams (20).

Cream of about 50% fat content at 20°C has been reported to exhibit non-Newtonian behavior (19). The flow curves were fitted to the power law with typical values of α of 0.7, where $\alpha = n - 1$. In the present study, the best fits were obtained using the Bingham model; the R^2 values for the flow curves were above 0.99 for 66 and 82% of the cases at 10 and 25°C, respectively. The rheological parameters for 38% cream are listed in Table 2. The results of the ANOVA testing are listed in Table 3. Viscosity was significantly different at 10 and 25°C, but no temperature effect on yield stress was observed.

Several reports (1, 3, 6, 15, 18, 26) have described the interrelationship between viscosity, fat content, and temperature. Bakshi and Smith (1) presented viscosity data of commercial dairy fluids in the temperature range of 0 to 30°C, these data had been obtained with a coaxial viscometer. Viscosity varied exponentially with temperature and linearly with fat content. Theoretical viscosities of skim milk, 3.5% milk, and 38% cream calculated from the equation proposed by Bakshi and Smith (1) are as follows: skim milk at 10 and 25°C, 2.05 and 1.26 mPa; 3.5% milk at 10 and 25°C, 2.89 and 1.78 mPa; and 38% cream at 10 and 25°C, 91.05 and 56.15 mPa. The viscosity values for skim milk and 3.5% milk that are given in Table 2 are higher than the calculated values; this difference is most pronounced for skim milk. This result may be related to differences in experimental technique. The values of yield stress and viscosity of skim milk and 3.5% milk at 25°C in the present study are in agreement with those given by Wayne and Shoemaker (29). However, the values obtained for 38% cream in the present study are significantly lower. It should be mentioned that the equation by Bakshi and Smith is based on measurements of samples with fat content of 0.1 to 30% fat. Hence, a direct comparison of the calculated value with the values obtained experimentally should be made with caution. Temperature has a marked effect on the viscosity of skim and 3.5% milks. Although water constitutes most of the continuous phase, the decrease in viscosity cannot solely be ascribed to the decrease in viscosity of water. Also, variation seems to be somewhat independent of the fat content, and the relative decrease in viscosity for the two products is similar. Thus, other ingredients in the milk contribute to the steep variation in viscosity. In the temperature range examined, the hydration of the casein micelles plays an important role (20). As the temperature is raised, the hydration shell of the casein micelles diminishes in size, and the volume occupied by the micelles is decreased. The contribution of micelles to the viscosity is therefore diminished, and, together with the decrease of the viscosity of water, the overall decrease in viscosity is more pronounced.

For the buttermilk powder solution, the high stresses also induced an apparent shear thickening, which was most pronounced at 40°C. Hence, model fitting was based on data that were obtained for shear rates between 0 and 500 s^{-1}. The Bingham model provided the best fits, and all R^2 were above 0.999. The shear stresses versus shear rates for skim milk, 3.5% milk, and buttermilk powder solution are illustrated in Figure 1. The apparent viscosity of buttermilk powder solution was similar to that of 3.5% milk at the temperatures tested (Table 2). This similarity may relate more to the higher content of fat in the buttermilk powder solution than in the skim milk. The fat content of a 10% solution of the sweet buttermilk powder is approximately 0.6% according to the data sheet from the manufacturer, but only 0.05% fat in skim milk. Pal and Malay (16) reported that the viscosity of sweet cream buttermilk was higher than that of skim milk and toned milk using buttermilk solids. In the same study, reconstituted buttermilk also had higher viscosity than did ordinary buttermilk as a result of denaturation of whey proteins during the condensing and drying stages. Viscosity data compared across temperatures differed ($P < 0.001$).

To obtain reproducible results for the cultured buttermilk products, large CO_2 bubbles had to be removed. No results were obtained at 40°C because of excessive syneresis. Shear thinning (pseudoplastic) behavior was observed for both cultured buttermilk products. The best models fits were the power law and Herschel-Bulkley models. For data fitted to the Herschel-Bulkley model, yield stress varied greatly within replicate samples of the same cartons. Furthermore, the estimated values for yield stress were not statistically significant from zero. Hence, the power law was used to describe the flow behavior of the cultured buttermilk products. Most pseudoplastic liquid foods have been reported to obey the power law, including sweetened condensed milk and ice cream mix (7, 24). The estimates of K and n for the two kinds of buttermilk are summarized in Table 4. The results suggested that traditional buttermilk samples were less viscous (lower K value) and showed less shear thinning (e.g., had larger values of n) than did

TABLE 4. Fluid model behavior of modern buttermilk and traditional buttermilk at 10, 25, and 40°C as estimated by the power law model.

Buttermilk product	Sample	Consistency index		Rate index	
		$(\mathrm{mPa \cdot s})^{n-1}$			
		$\bar{X}$	SD	$\bar{X}$	SD
Modern					
10°C	1	1784	267	1.40	0.01
	2	269	41	1.60	0.01
	3	671	31	1.50	0.01
	$\bar{X}$	906	686	1.50	0.09
25°C	1	1018	25	1.42	0.01
	2	183	18	1.60	0.01
	3	518	32	1.52	0.01
	$\bar{X}$	534	365	1.52	0.08
Traditional					
10°C	1	169	93	1.65	0.08
	2	273	110	1.60	0.05
	3	501	73	1.51	0.02
	$\bar{X}$	314	168	1.59	0.08
25°C	1	288	20	1.52	0.01
	2	257	125	1.56	0.06
	3	490	228	1.49	0.06
	$\bar{X}$	345	174	1.55	0.05

the modern buttermilk samples. This difference can be attributed to homogenization of milk prior to fermentation of the modern buttermilk, which results in higher water-binding capacity (27). The modern buttermilk exhibited thixotropy at 10°C at the given shear stress loop, but not at 25°C. No thixotropy was observed for the traditional buttermilk. The results from ANOVA testing of the effect of temperature on the values of *K* and n for the two cultured buttermilk products are listed in Table 3. For the modern buttermilk, a temperature effect was detected for n and *K*. This effect was most pronounced for *K*, which is often observed for liquid foods (24). For the traditional buttermilk, no significant temperature effect on *K* and n was detected. The influence of temperature on the flow behavior of modern and traditional buttermilks is shown in Figure 2. However, large variations in the consistency index are observed for different samples of modern and traditional buttermilk, and this variation is most pronounced for modern buttermilk. Thus, overall conclusions about the properties of the two kinds of buttermilk products are difficult to make. It is noteworthy that temperature apparently did not seem to have a large influence on the rheological parameters of the cultured buttermilk products. A possible explanation may be the combined result of stronger protein interactions with increase in temperature contributing in favor of higher viscosity, in opposition to the decrease in viscosity of water as temperature increased.

The results for the surface tension experiments of skim milk, 3.5% milk, and 38% cream are given in Table 5. No useful results could be obtained for 38% cream at 40°C because of the excessive formation of a slightly denser layer at the interface during the experiment that was possibly due to evaporation from the surface, aggregation of fat globules at the surface, or both.

The mean observed values of 3.5% milk and skim milk are in good agreement with data for homogenized milk that were obtained by Watson (28). In the study of Watson, a consistent difference in the surface tension of skim milk, whole milk, and homogenized milk was observed in temperature range of 16 to 39°C (60 to 102°F); divergence increased as temperature rose. The surface tension of homogenized milk averaged about 3 mN/m higher than that of raw milk over a temperature range about midway between the other two milks. The increase in surface tension of milk by homogenization can be attributed to the adsorption of caseins and whey proteins because of the increase in fat globule surface area during homogenization. A comparison of the value obtained in the present study for skim milk to 3.5% milk at 10 and 40°C suggests that the surface tension of these two products are not significantly different. At 25°C, however, the surface tension of 3.5% milk is significantly lower. This difference may be related to the effect of change in the condition of milk fat in the 3.5% milk, which is solid at 10°C and more liquid at 25°C.

The method for determination of surface tension has been reported to influence the results; that is, dynamic drop number method gives invariably higher

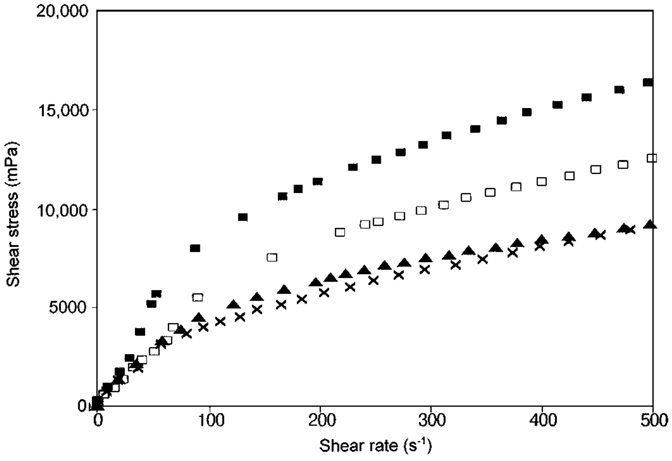

Figure 2. Effect of temperature on shear stress versus shear rate (up curve sweep) of modern buttermilk [10°C (■) and 25°C (□)] and traditional buttermilk [10°C (▲) and 25°C (**x**)]. Geometry: 4-cm acrylic plate. Gap: 150 μm.

TABLE 5. Surface tension of skim milk, 3.5% milk, and 38% cream at 10, 25, and 40°C for 300 s.

Product and temperature	Surface tension	
	(mN/m)	
	$\bar{X}$	SD
Skim milk		
10°C	49.72	0.86
25°C	47.29	1.21
40°C	42.22	2.87
3.5% Milk		
10°C	49.87	1.32
25°C	41.89	1.05
40°C	41.56	1.01
38% Cream		
10°C	42.43	1.76
25°C	31.39	2.15
40°C	NR[1]	NR

[1] No results obtained because of the formation of a slightly denser layer at the interface.

results than the static Du Nouy ring method because of the time dependency of diffusion of surface-active components to the interface (17). This result might also explain the results of Bertsch (2), which indicated significantly higher values for whole milk (4% fat) and skim milk in the temperature range 18 to 135°C by the drop number method.

For 38% cream, a large difference was observed in surface tension at 10 and 25°C for 300 s. Furthermore, the time dependency of surface tension was significantly different, as illustrated in Figures 3, 4, and 5. At 10°C, the surface tension dropped rapidly during the first 60 s, followed by a steady decrease, and did not reach a steady value after 1200 s. At 25°C, the initial decrease in surface tension was even faster and reached a final value of 31.05 ± 2.09 mN/m after approximately 600 s. The very low surface tension suggests a destabilization of the fat globules at the interface between air and liquid, which suggests that adsorption of the milk fat globule membrane fragments or components therefore (e.g., phospholipids or milk protein alone) cannot depress surface tension by that order of magnitude (9). Data for the surface tension of cream are scarce. Values of surface tension for cream obtained by the drop volume method or by the maximum pull on a straight horizontal wire (stirrup method) were significantly larger (13). However, the inherent difference between these methods and the method used in the present study may explain the discrepancies.

Table 6 lists surface tension data of the buttermilk products. The surface tension as a function of time for modern and traditional buttermilks is illustrated in Figures 4 and 5, respectively. At 10°C, the surface tension of modern buttermilk at 300 s was 61.10 ± 3.03 mN/m, dropping to 59.14 ± 2.92 mN/m at 1200 s. At 25°C, the drop in surface tension during the first 60 s was more pronounced. Surface tension at 300 and 1200 s was 56.68 ± 3.38 and 54.03 ± 3.49 mN/m, respectively. The surface tension for the modern buttermilk was unexpectedly high compared with the values of surface tension that were registered for skim milk and 3.5% milk with the same amount of fat and protein. The surface tension of traditional buttermilk was significantly lower, although higher than the values obtained for skim milk and for 3.5% milk. Surface tension dropped rapidly during the first 60 s at 10 and 25°C, followed by a steady decrease during the remainder of the experiment. The surface tension for this product was less influenced by temperature than was modern buttermilk. The high surface tensions of the cultured buttermilk products raise the question of whether the Wilhelmy plate method is suitable for these types of products. The contact angle θ may not be zero because of the presence of CO_2 bubbles or the very viscous nature of these products, but some viscous food products of paste and puree types (tomato puree and condensed acid whey) have fairly high surface tensions; for example, tomato puree with a dry matter of 5% had a surface tension of 62 m*M*/m at 20°C and 57 mN/m at 40°C (11). Hence, the results obtained in this study seem plausible. An indication of coherence between the viscosity and surface tension measured by Wilhelmy plate method is supported by the observed correspondence between low viscosity and low surface tension for modern buttermilk sample 2 and a slightly higher

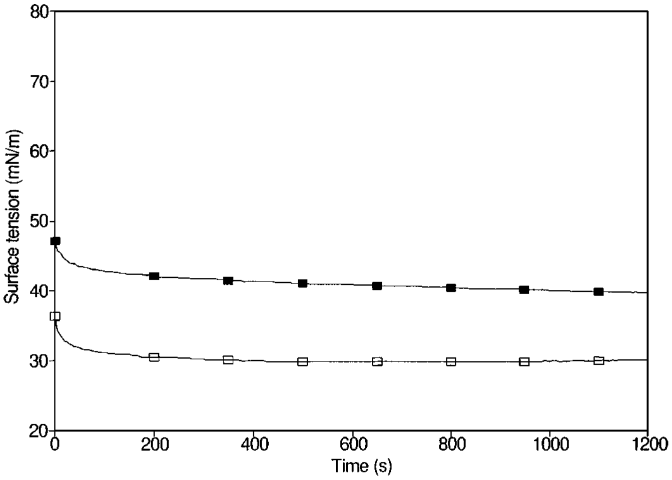

Figure 3. Surface tension as a function of time for 38% cream at 10°C (■) and 25°C (□).

TABLE 6. Surface tension of buttermilk products at 10, 25, and 40°C at 300 s.

Buttermilk product	Sample	Surface tension	
		(mN/m)	
		$\overline{X}$	SD
Modern			
10°C	1	62.99	0.96
	2	57.27	5.06
	3	63.05	3.01
25°C	1	58.16	1.14
	2	52.06	0.60
	3	59.83	0.63
Traditional			
10°C	1	51.33	1.62
	2	53.11	0.37
	3	51.72	0.90
25°C	1	50.99	2.07
	2	51.18	0.59
	3	50.77	0.42
Powder solution			
10°C	1	50.88	2.89
25°C	1	41.31	0.34
40°C	1	40.30	0.79

surface tension and viscosity for traditional buttermilk sample 2.

Surface tension at 300 s of the modern and traditional buttermilk products were statistically analyzed in two-way ANOVA tests between samples and temperature. Comparisons made on the modern buttermilk showed significant differences between surface tension at the different temperatures ($P < 0.001$) and between surface tension and samples ($P < 0.001$), but showed no statistically significant interaction between the two factors. Multiple comparison tests (Newman-Keuls test) showed that sample 2 was statistically different ($P < 0.05$) from samples 1 and 3. Comparisons made on traditional buttermilk showed no significant differences between surface tension and temperature and samples and no interactions between the two factors. The reason for the different temperature effect on the surface tension of the traditional buttermilk and the modern buttermilk is unknown. The rheological parameters of the two types of cultured buttermilk products exhibited the same differences in temperature sensitivity. It suggests that the two kinds of buttermilk have fundamentally different rheological and interfacial properties, which might be related to the presence of milk fat globule membrane fragments in traditional buttermilk as opposed to the modern buttermilk.

The surface tension value for the buttermilk powder solution at 25°C corresponds well with the observed value for uncultured buttermilk (buffalo) at 20°C (Du Nouy method), 44.27 ± 1.93 mN/m (16) and to the surface tension of 40.2 mN/m at 20°C of a buttermilk (0.8% fat) from churning of 22.5% uncultured cream from bovine milk (13). The values of surface tension of buttermilk powder solution at 10, 25, and 40°C closely resemble 3.5% milk, which was also observed for the rheological data. The presence of milk fat globule membrane fragments does not seem to lower surface tension substantially.

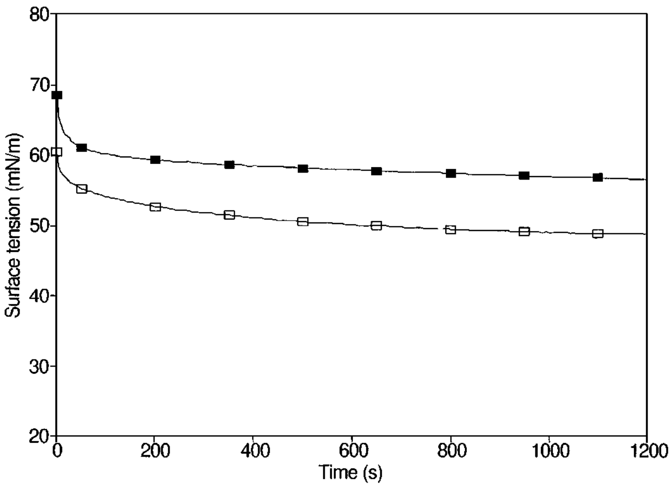

Figure 4. Surface tension as a function of time for modern buttermilk at 10°C (■) and 25°C (□).

CONCLUSIONS

The measurements for rheology and surface tension revealed differences in bulk properties and interfacial properties of the various dairy fluids. Tempera-

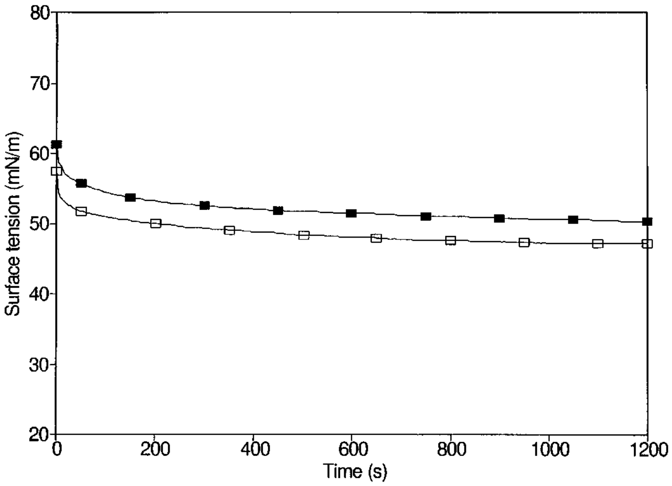

Figure 5. Surface tension as a function of time for traditional buttermilk at 10°C (■) and 25°C (□).

ture influenced the results differently, depending on fat content and on other factors such as the presence of milk fat globule membrane fragments and process parameters. Future studies include an investigation of the rheological behavior at low shear stress and low shear rate, which might allow a determination of whether the apparent yield stress determined for uncultured products in this study is a true yield point or whether it corresponds to a finite zero shear viscosity.

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