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Surface Tension and Foaming Properties as a Simple Index in Relation to Buffalo Milk Adulteration

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ABSTRACT

Surface tension and foaming properties were examined for buffalo milk samples either raw or adulterated in various ways. The results indicated some difference in surface tension and foaming properties of buffalo milk and its adulterated mixes. The data indicated that skim milk had higher surface tension than whole milk. Addition of water to either whole or skim milk decreased the foam ability compared to controls. Skim milk showed higher foam stability compared to whole milk. Surface tension significantly increased in all milk samples with increasing the added ratio of Skim Milk Powder (SMP). Additions of higher amounts up to 5% SMP into milk either whole or skim led to increase the foam ability and stability of all mixes. Surface tension values were increased with increasing percentage of sucrose added either whole or skim milk. The results indicted that sucrose greatly improved the foam stability of treatments. Addition of salt into whole or skim milk up to 11% led to decrease in foam ability values compared to control being the lowest in whole milk mixes. Surface tension of whole or skim milk mixes was increased with high ratio of added gum. On the other hand, incorporation of gelatin into whole or skim milk lead to decrease in foam ability of all mixes compared to controls. Addition of starch into whole or skim milk decreased foam ability of all mixes compared to controls. On the other hand, addition of starch with different ratios to whole or skim milk improved foam stability values. This improvement was increased with higher percentage of added starch into milk.

Key words: Surface tension, foam ability and stability, water, skim milk powder, sucrose, salt, stabilizers

INTRODUCTION

Surface tension is a fundamental physical property related to the stability of aerosols, foams, emulsions, bubbles, drops and films, as well as, affecting various industrial separation, fractionation and concentration processes. Surface tension can be considered as the work done per unit area in increasing the surface area under isothermal conditions. Surface or interfacial tension may change with time because surface-active amphiphiles in dispersion are in a dynamic equilibrium between the surface monolayer and the bulk monomeric or polymeric state. Alterations in temperature, pH, ionic environment (e.g., changes in soluble calcium to colloidal calcium ratio in milk), dielectric constant and denaturation of proteins contribute to this phenomenon which may influence film stability (Haque, 1993). Often, in designing a dairy or food processing system or in development of a food product, it would be beneficial to have a better understanding of the surface tension or the interfacial tension present in the system (Wittinger and Smith, 1987). Milk is one of several systems which might interact to its interfacial tension and foaming properties. Milk fat, some of milk proteins and free fatty acids are some surface-active constituents of milk which, undoubtedly, affect surface properties (Whitnah, 1959). Physicochemical properties of milk are influenced by chemical and structural characteristics of its constituents as well as the particular conditions prevailing in the system and interactions of proteins with other components (Kinsella, 1982). The variation in reported surface tensions of dairy fluids may be due to inherent variations in the compositions, concentrations, processing histories and sample handling (Roehl and Jelen, 1988). Several authors indicated that the surface activity or interfacial properties of protein solutions affect their foaming and emulsification properties (Waniska and Kinsella, 1985; Kitabatake and Doi, 1988; Roehl and Jelen, 1988; Wilson *et al.*, 1989; Wustneck *et al.*, 1996; Metwally, 2004).

Addition of several components (in purpose) to the milk for economical or extending shelf life reasons have been noticed since a long time ago which considered as forms of adulteration. Therefore, methods to detect the presence and ratio of these foreign components in relation to the milk constituents have been outlined. Adulterations of milk with different materials such as water, stabilizers or ionic solutions presumably lead to changes in surface activity and foaming properties. There has no data published on interfacial surface tension or foaming properties and its correlation to adulterated buffalo milk. The present study was, thus, undertaken to obtain data for surface tension and foaming properties of buffalo milk incorporated with mostly adulterated materials used in fluid milk.

MATERIALS AND METHODS

Materials: Fresh buffalo milk was obtained from the herd of Faculty of Agriculture, Ain Shams University. Skim buffalo milk was made by separating the cream from the whole milk using Alfa-Laval separator. Skim Milk Powder (SMP), product of Dairy Farmers of America, made in USA (3.98% moisture, 1.52% fat, 35.08% protein, 51.21% lactose and 8.17% ash) was obtained from Misr Milk and Food Co., Cairo, Egypt. Commercial grade cane sugar was purchased from Sugar and Integrated Industries Company, Giza, Egypt. Stabilizing agent, carboxymethyl cellulose (CMC), locust bean gum, gelatin and soluble starch, sigma products were obtained from local market. High purified commercial table salt (sodium chloride) was obtained from El-Nasr Company for salt, Alexandria, Egypt.

Surface tension determination: Buffalo milk samples (37 samples) for surface tension determination were collected from four Egyptian governorates and prepared by placing 100 mL of each freshly made milk sample in 150 mL plastic cup. Samples were warmed up to 25°C in a controlled water bath and stirred for 1/2 min just before measurement. A ring tensiometer (DuNouy ring Tensiometer, Krüss-Instrument, No. 8158, Germany) was used to measure the interfacial surface tension. The DuNouy ring used for determination was cleaned prior to each measurement by dipping the ring in dilute nitric acid, then flaming until the ring was "red" hot in the oxidizing portion of Bunsen burner flame to remove organic materials. After cooling, the ring was then hung from the load cell and lowered to the base of sample container. The ring was pulled from the surface of sample and the force required to do so was recorded as surface tension values which read directly from the instrument scale as N m^{-1}. Duplicate samples were prepared for measurements of each treatment which repeated at least 5 times.

Measurements of foaming properties: Foam ability and foam stability were measured as described by Closs *et al.* (1990). Samples of all fresh buffalo milk (200) either raw or adulterated in various ways were whipped at maximum speed for 5 min using blender (Germany). Foams were carefully transferred to a 1 L graduated glass measuring cylinder. The foaming capacity was measured according to Poole *et al.* (1984) and expressed as foam ability as follows:

$$\text{Volume increase(\%)} = \frac{\text{Foam volume-Initial volume}}{\text{Initial volume (200 mL)}} \times 100$$

The foam stability was expressed as time (min) required for the foam to breakdown (time required for return to initial sample volume, 200 mL).

Statistical analysis: All achieved data was statistically analyzed using the General Linear Models procedure of the Statistical Analysis System (SAS, 1998) and significance was defined at $p \leq 0.05$. All experiments, as well as the related analyses results, were repeated three times and all obtained data was expressed as averages.

RESULTS AND DISCUSSION

Effect of water adulteration: Surface tension and foaming properties of whole and skim buffalo milk adulterated with different water ratios are presented in Table 1. The data showed that skim milk possessed higher surface tension than whole milk even with added different water ratios. On the other hand, adding different ratios of water to the milk led to increase the surface tension values. The surface tension value increased with increasing the added percentage of water into whole or skim milk. This data agree with Whitnah (1959) who stated that surface tension of milk increased with decreasing concentration of fat. Dahlberg and Henning (1925) also reported that the surface tension of cream decreased with increasing fat percentage. The higher surface tension of milk resulted by adding the water could be due to the lowering concentration of surface active materials in the milk.

The data in Table 1 also indicated that the whole milk exhibited significantly lower foam ability and stability than that of skim milk. Foam Ability (FA) and stability (FS) values were significantly affected by adulterating milk (whole and skim) with different water ratios. Foam ability was gradually decreased by increasing the ratio of added water to whole milk. The foam ability of skim milk increased with adding the lower ratios of water up to 20% and then decreased with increasing the added water ratio. On the other hand, the foam stability (min) increased in whole milk with adding water up to 20% and then decreased with increasing the added ratio while the value decreased of skim milk from the beginning of added water. The changes occurred in foam ability and stability values of milk by adding water that could be attributed to the changes in surface tension of the mixes. Marshall *et al.* (2003) mentioned that ice cream mixes with higher surface tension values showed lower foam ability. The results agree with Kristensen *et al.* (1997) who stated that the measurements of surface tension indicated a high degree of instability which suggests that the milk fat globule was destabilized at the interface between air and water. The higher foam yield stress and drainage stability of foams appears due to forming smaller and more stable bubbles, that are packed together into structure that are more resistant to deformation.

Effect of adulteration with skim milk powder: The effect of milk adulteration with Skim Milk Powder (SMP) on surface tension and foam properties of fresh whole and skim milk is presented in Table 2. Addition of milk powder to fresh milk increased the surface tension values either in

Table 1: Surface tension and foaming properties of whole and skim buffalo milk adulterated with different ratios of water

	Surface tension (N m^{-1})		Foam ability (%)		Foam stability (min)	
Water addition (%)	Whole milk	Skim milk	Whole milk	Skim milk	Whole milk	Skim milk
Control	52.37	54.56	55	105	10.1	14.9
10	53.51	55.00	45	109	11.6	13.0
20	55.12	57.07	40	121	11.0	9.9
30	57.02	58.54	30	104	9.9	9.0
40	58.05	60.16	30	90	9.4	8.0
50	60.00	62.31	25	77	9.0	7.0

Table 2: Surface tension and foaming properties of whole and skim buffalo milk adulterated with different ratios of skim milk powder

	Surface tension (N m^{-1})		Foam ability (%)		Foam stability (min)	
Skim milk powder addition (%)	Whole milk	Skim milk	Whole milk	Skim milk	Whole milk	Skim milk
Control	52.37	54.56	55	105	10.1	14.9
1	55.75	56.00	67	181	33	38
2	56.62	57.00	76	139	27	31
3	57.00	58.66	82	126	21	26
4	58.25	59.25	90	120	15	19
5	58.85	59.50	95	112	14	17

whole or skim milk. The surface tension value increased with increasing the ratio added of milk powder being highest at 5% SMP. The surface tension values were higher in skim milk than that of whole milk when both adulterated with milk powder. Tornberg (1978) stated that interfacial tension-time curves indicated that soy proteins diffused more slowly to the interface than the other proteins which attributed to large particle size in soy protein. Addition of SMP to fresh buffalo milk has affected the foaming properties of the product. The foam ability increased gradually in whole milk by adding SMP. On the other hand, fresh skim milk adulterated with different ratio of SMP showed higher foam ability with dramatic increase at lower ratio being highest at 1% added SMP. Increasing the ratio over 1% resulted in lower foam ability but still higher than that of fresh milk and this trend continued up to 5%. Since foam ability is related to the rate of decrease of surface tension at the air/water interface by adsorbed protein, flexible proteins like β-casein which reduce surface tension rapidly, exhibit good foam ability with large air cells while highly structured proteins like lysozyme yield low over-run and small air cells because larger cells rupture since lysozyme fails to stabilize them quickly enough. The rheological properties of the film play dominant role in foam stability being lower with larger resistance to shear, lower dilatational modulus and lower thickness of the lamellae in foams. Since the rheological properties are maximal at the isoelectric point, protein stabilized foams tend to be most stable at this pH. The Foam Stability (FS) was highest in both, whole and skim milk, when SMP added at 1% but the stability decreased after that with increasing the added ratio of SMP. The FS of milk contained to be higher in the samples with added SMP than that of control. The changes in foaming properties (FA, FS) could be attributed to the differences in protein contents, types and characteristics. Sabharwal and Vakaleris (1972) mentioned that the emulsion stability (resistance to creaming) was decreased markedly at higher protein concentration, possibly due to the formation of bulky interfaces which cause fat globules to cluster, thereby increasing creaming rate. The solubility of proteins is highly pH dependent and thereby, it is expected that its surface activity would be

Table 3: Surface tension and foaming properties of whole and skim buffalo milk adulterated with different ratios of sucrose and table salt

	Surface tension (N m^{-1})		Foam ability (%)		Foam stability (min)	
Addition (%)	Whole milk	Skim milk	Whole milk	Skim milk	Whole milk	Skim milk
Control	52.37	54.50	55	105	10.1	14.9
Sucrose						
1	57.87	59.15	40	92	21.5	22.2
2	59.16	61.83	30	81	17.8	19.1
3	61.33	63.00	20	70	15.4	17
4	63.33	64.25	15	52	13.9	15.2
5	65.12	65.50	20	40	12.2	14
7	65.81	65.90	10	36	11.0	13
Table salt (NaCl)						
1	58.00	58.95	50	80	35	47
3	59.00	60.01	40	70	30	39
5	60.50	61.50	35	62	30	36
7	61.55	62.50	30	55	25	31
9	62.50	64.00	20	45	21	26
11	63.17	64.37	17	40	17	18

strongly influenced by pH (Mohanty *et al.*, 1988). Guo and Mu (2011) reported that increasing of protein concentration greatly increased foam stability values. Whitnah (1959) found an increase in foam stability of aqueous solution of purified milk protein with higher concentration of caseinate, albumin or lactoglobulin.

Effect of adulteration with sucrose and salt: The effect of milk adulteration with sucrose or table salt (sodium chloride, NaCl) is shown in Table 3. Addition of sucrose or salt to fresh whole or skim milk resulted in higher surface tension values being increased with increasing the ratio added of both. The surface tension values were slightly higher in skim milk than whole milk at any ratio added of sucrose or salt. This could be explained by the effect of sucrose or table salt in reduction of surfactant material effect such as proteins and triglycerides. Spyropoulos *et al.* (2008) observed an increase in the interfacial tension with increasing NaCl concentration of Pullulan-Sodium dodecyl sulphate aqueous two-phase systems. Belhomme *et al.* (2007) also stated that in the presence of higher NaCl concentration, egg yolk protein presents improved interfacial properties and the film formed was denser. The foaming properties of fresh milk were affected by adulteration with is sucrose and salt. Foam ability of fresh milk was decreased by adding both sucrose and salt and increasing the ratio added of either sucrose or salt resulted in lower FA values. These findings are in agreement with Marshall *et al.* (2003) who reported lower foam ability values with higher surface tension. Mohanty *et al.* (1988) stated that addition of salt up to 20 mM decreased foam capacity but increased foam stability. Foam ability of whole or skim milk was also affected by adulteration with sucrose or salt. From the data in Table 3, it could be noticed that adulteration of milk with sucrose or salt increased the FS in both whole and skim milk. These results are in agreement with Yang and Foegeding (2011) who stated that addition of sucrose decreased the initial bubble size which is corresponding to higher foam stability. Also, Berry *et al.* (2009) stated that incorporation of sucrose increased foam stability of egg white protein solution. Foam stability could be explained based on solution viscosity, interfacial characteristics and initial bubble size (Yang *et al.*, 2009).

Table 4: Surface tension and foaming properties of whole and skim buffalo milk adulterated with different stabilizing substances

Stabilizer addition (%)	Surface tension ($N m^{-1}$)		Foam ability (%)		Foam stability (min)	
	Whole milk	Skim milk	Whole milk	Skim milk	Whole milk	Skim milk
Control	52.37	54.50	55	105	10.1	14.9
CMC						
0.1	55.00	60.50	65	200	39	44
0.2	56.00	62.50	62	185	33	38
0.3	57.50	62.70	55	170	25	29
0.4	57.87	63.37	45	140	20	23
0.5	58.75	63.83	40	120	15	17
Locust bean gum						
0.1	57.31	59.13	99	210	30	35
0.2	59.37	61.25	85	180	26	29
0.3	62.50	63.15	74	160	21	24
0.4	63.24	64.50	59	130	16	19
0.5	65.11	65.33	45	110	13	17
Gelatin						
0.1	53.33	56.21	75	120	30	35
0.2	54.00	57.41	68	101	25	24
0.3	55.83	58.11	52	92	21	24
0.4	57.11	59.50	45	84	18	18
0.5	58.50	61.00	35	72	15	18
0.75	59.66	62.09	28	61	15	15
1.0	61.50	62.95	19	52	13	14
Starch						
0.1	54.33	55.50	60	110	25	27
0.2	56.33	57.00	31	96	20	28
0.3	57.50	58.50	25	82	17	24
0.4	58.83	59.18	22	71	15	21
0.5	59.16	60.16	19	60	11	17
0.75	60.66	61.66	15	51	9	14
1.0	61.50	63.00	15	44	7	12

Calibration of the surface tension apparatus: Surface tension of water =70.16 $N m^{-1}$, Surface tension of corn oil = 48.50 $N m^{-1}$

Effect of adulteration with stabilizing substances: One of the most used ways in milk adulteration is that of adding stabilizing substances to increase the milk viscosity. Therefore, the effect of adding different stabilizer materials to whole or skim milk on surface tension and foaming properties is shown in Table 4. Surface tension values were affected by adulterating the milk with stabilizing substances. Compared to milk without addition (control), the surface tension values were gradually increased with adding any of stabilizing materials used. This trend was noticed in all types of milk and stabilizers being with more pronounced effect in skim milk samples adulterated with CMC or locust bean gum. The presence of stabilizer material into the media would lead to a higher interfacial tension between different molecules. Miquelim *et al.* (2010) reported an increase in surface tension values when xanthan and guar gum were added into mix from egg albumin-polysaccharide in water. They also indicated that protein-polysaccharide coacervation at the air/water interface is an efficient process to increase foam stability. Redfers and Arbuckle (1949) stated also that the stabilizers increased surface tension values in ice cream mixes.

The foam ability of milk adulterated with different stabilizers was significantly affected. Foam ability was highly increased in the milk with adding the stabilizing substances being more noticeable in skim milk samples. The milk samples adulterated with stabilizing materials showed the highest foam ability at the lowest added ratio of stabilizers. Increasing the added ratio of stabilizers, resulted in lower foam ability with all types of stabilizers. The foam ability was highest in milk samples adulterated with locust bean gum and lowest in samples adulterated with starch. The foam value was significantly higher in adulterated skim milk samples than that of whole milk. The Foam Stability (FS) was also improved in milk adulterated with stabilizing materials. The data in Table 4 cleared that the foam stability was increased in all milk samples by adding the stabilizing agents being highest in milk samples with CMC and lowest in samples with starch. The foam stability data also stated that the stability was lowered by increasing the added ratio of stabilizing agents. Castellani *et al.* (2010) stated that all gums presented good oil in water emulsifying properties. The presence of stabilizing agents in the media would help in strengthen the membrane of created bubbliest which may help to improve the foam stability. Increasing the ratio added of stabilizing agents lead to a very high viscosity which may disrupt the bubbles formation and therefore lower foam ability and less foam stability in the media. High viscosity and at least moderate dispersibility were found to be important prerequisites for good foaming properties while, high charge density depressed foam stability.

Kinetics of changes: The kinetic of change in surface tension, foam ability and foam stability of whole and skim milk by addition of water, skim milk powder, sugar, salt and some food polymers was analyzed according to the zero-order reaction kinetics according to the following equation:

$$y = a \pm b\,x$$

Where:

- y = Value of corresponding physical property under study
- a = Estimated initial value
- b = Rate of change per one unit of added component
- x = Concentration of added component

The results of regression analysis are given in Table 5. The correlation coefficient (R^2) value of the obtained corresponding regression indicated a strong relationship between the change in physical properties and concentration of added component, since there R^2 values are higher than 0.9 in most cases. The highest rate of changes in surface tension for whole milk and skim milk were recorded for locust been gum (1.947) and water (1.771), respectively while the lowest effects on surface tension values were those of added skim milk (0.783) and CMC (0.753) into whole and skim buffalo milk, respectively. As seen in Table 5, the highest rate in change in physical properties of whole and skim buffalo milk was that of foam ability. The foam ability of whole and skim milk was negatively affected by all addition, except those of whole milk adulated by the addition of skim milk powder, where the foam ability was enhanced (Benboubetra *et al.*, 2004). The highest loss in foam ability (-13.4 and -15.7) were recorded for whole milk adulated with addition locust bean gum and skim milk powder, respectively. On other hand, the lowest effect on the loss of foam ability for whole buffalo milk was recorded with starch addition (-4.036) while that for skim buffalo milk was noticed with sucrose addition (-2.03). The pattern of foam stability was negatively affected by

Table 5: Rate of change in surface tension, foam ability and foam stability of milk as affected by type of component added

	Whole milk			Skim milk		
Parameters	Surface tension	Foam ability	Foam stability	Surface tension	Foam ability	Foam stability
Water						
Intercept initiation value	51.97	49.00	12.22	53.30	128.70	13.55
Rate of change	1.591	-5.00	-0.68	1.771	-9.50	-1.30
R^2	0.994	0.926	0.969	0.996	0.774	0.916
Skim milk powder						
Intercept initiation value	54.94	61.00	37.00	55.31	182.70	42.40
Rate of change	0.783	7.00	-5.00	0.925	-15.70	-5.40
R^2	0.979	0.992	0.962	0.929	0.831	0.976
Sucrose						
Intercept initiation value	56.15	41.00	22.38	58.67	103.93	18.39
Rate of change	1.702	-5.286	-2.023	1.315	-2.030	-0.946
R^2	0.984	0.832	0.958	0.946	0.979	0.164
Salt						
Intercept initiation value	57.05	55.00	38.53	57.88	86.87	51.73
Rate of change	1.069	-6.571	-3.486	1.145	-8.057	-5.4
R^2	0.987	0.981	0.969	0.984	0.994	0.904
CMC						
Intercept initiation value	54.21	73.50	44.77	60.32	224.5	50.9
Rate of change	0.973	-6.70	-6.10	0.753	-20.50	-6.90
R^2	0.968	0.973	0.992	0.868	0.982	0.994
Locust bean gum						
Intercept initiation value	55.67	112.60	34.40	57.98	223.00	38.6
Rate of change	1.947	-13.40	-4.40	1.565	-25.00	-4.60
R^2	0.968	0.998	0.994	0.972	0.995	0.976
Gelatin						
Intercept initiation value	51.63	83.86	30.57	54.97	126.57	33.57
Rate of change	1.375	-9.464	-2.750	1.159	-10.857	-3.107
R^2	0.993	0.989	0.929	0.993	0.988	0.853
Starch						
Intercept initiation value	53.78	40.00	26.57	54.50	117.71	31.86
Rate of change	1.137	-4.036	-2.929	1.196	-11.060	-2.857
R^2	0.975	0.918	0.981	0.991	0.988	0.962

all added components. The highest loss in foam stability of whole and skim buffalo milk (-6.1 and -6.9), respectively was recorded with addition of CMC while the lowest values (-0.68 and -0.946) were noticed with added water and sucrose, respectively.

CONCULUSION

The adulteration of whole and skim milk could be concluded with the help of values of the rate changes in the studied physical properties a control.

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