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FLOW AND STRUCTURAL CHARACTERISTICS OF CONCENTRATED FROZEN BUFFALO’S MILK

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ABSTRACT

The effects of freezing and heat temperature on the rheological behavior and structural of buffalo's milk samples were studied. Rheological properties of raw, pasteurized, whole and skim milk during freezing period of ١٢ weeks at (-٢٢ ºC ± ٢) were measured in a rotational viscometer at temperature (٣٠˚C). Differences between shear stress values of ascending and descending curves were negligible so, no remarkable hysteresis was observed. Obtained shear stress values were found to be dependent on type, treatment and fat content of the milk. The maximum obtained of shear stress values for pasteurized whole milk and raw whole milk were ٣٠,٩ and ٣٠,٧ dynes/cm^{٢} at shear rate ١٣١٢ s$^{-١}$ for pasteurized whole milk and raw whole milk, respectively. The obtained flow curves for the raw skim milk showed almost linear relationship between shear stress and shear rate values, which in turn express a Newtonian behaviour. Increasing the fat in milk did not greatly influence the obtained shear stress values as well as the linear characteristic of the obtained flow curves.

Pasteurized milk either whole milk or skim milk being frozen at (-٢٢ ºC ± ٢) gave the highest viscosity values, compared with that of the other tested raw milk samples. Freezing storage for ١٢ weeks caused an increase in the values of consistency coefficient of (k- values) of frozen milk concentrates, while the flow behaviour index (n-value) tended to be slightly lower than the unity indicating a shifting towards the non-Newtonian behaviour of the milk concentrates.

Transmission electron micrographs (TEM), of fresh and frozen whole concentrated milk obtained from ultrafiltration of whole milk caused changes in size, distribution, and average diameter of casein micelles. The fresh whole concentrated milk from UF showed a roughly spherical shape, in various sizes. The appearance of frozen whole concentrated milk from UF milk concentrated three times (٣X) also exhibited nearly spherical shapes with a wide range of sizes.

Keywords: Frozen buffalo's milk, Flow parameters, Viscosity, Microstructure

INTRODUCTION

Dairy industry in Egypt is facing a big problem in maintaining a constant supply with fresh buffalo's milk during the summer months due to lake of lactation during this period. Use of dried milk as alternative for fresh milk needs special technological solutions to make the reconstituted milk suitable for processing.

Freezing is an alternative preservation method, instead of the high energy cost drying, also for milk to extend shelf life Hekken *et al.,* (٢٠٠٥). The rheological behavior of milk products is important for the texture and stability of dairy products, process design, and fundamental research. It is complex and strongly dependent on temperature, concentration and physical status of the dispersed phases.

In freeze concentration, water is separated from liquid food by crystallizing ice at low temperatures, followed by a separation step to remove ice from the concentrate. Due to the low temperatures of operation, no heat-induced changes occur, resulting in high-quality products for many liquid foods. The application of freeze concentration to the dairy industry has been demonstrated in the past (Van Mil and Bouman, ١٩٩٠). However, only limited commercial success has been obtained. It has been claimed that reconstituted skim milk previously concentrated by freeze concentration has a smoother and creamier product texture than the original skim milk (Chang and Hartel, ١٩٩٧). No scientific evidence for this claim has been published, although physical changes in protein structure may cause some organoleptic changes. This physical change can be evaluated objectively by comparing the viscosities of the natural skim milk and the reconstituted skim milk from freeze concentration processes.

An important consideration in optimizing ice crystal growth in freeze concentration processes is the provision of rapid ice crystallization. (Shi *et al.,* ١٩٩٠). By varying the appropriate operating conditions, high rates of heat transfer can be maintained, resulting in these rapid rates of ice crystal growth (Hartel and Espinel, ١٩٩٣). A better understanding of the flow properties of freeze-concentrated skim milk is fundamental to the control of heat and mass transfer rates between the ice and the liquid interface, which is necessary for design of operations related to the freeze concentration process, in sensory analysis and in quality control.

The possibility of preserving milk by freezing has been of interest to food. One of the major obstacles to the successful marketing of frozen milk product has been the instability of milk proteins during freezing storage. Destabilization of proteins in milk during frozen storage is known to involve mainly the casein fraction and to depend on a number of factors including time and temperature of storage of milk concentration, lactose crystallization and pre freezing heat treatment (Dominic *et al.,* ١٩٩٦).

Therefore, the objective of the present investigation was to study the effect of frozen storage periods (١٢ weeks), of buffalo's milk and concentrated whole and skim buffalo's milk (-٢٢ ºC ± ٢) on their rheological behavior and changes in their structure.

MATERIALS AND METHODS

Fresh buffalo's milk (٦,٨٪ fat and ١٦,٥٪ total solids) was obtained from the herd of Shalakan Farm, Faculty of Agriculture, Ain Shams University. Fresh raw milk was divided into two portions; the first portion was treated as whole milk, and the second portion was skimmed using a laboratory milk fat separator to obtain skim milk. Both fresh whole and skim milk were pasteurized at ٧٥°C for ١٥ sec and homogenized at ٣٠٠٠ lb/in^{٢} .Ultra filtration of both different milk were carried out in a CARBOSEP pilot plant unit (type ٢S ١٥١ tubular, France) with Zirconium oxide membrane area of ٦,٨ m^{٢}. The inlet and outlet pressures were ٥ and ٣ bar, respectively. Milk was concentrated in a batch system to volume concentration factor ٣X. The resultant milk retentate was diluted using milk permeate to obtain concentration factor ٢X.

Retentate types (whole ٢٢-٣٣ %TS and skimmed ١٨-٢٨٪ TS) were packaged into PVC cups (٣٠٠ ml) and frozen at -٢٢ ± ٢°C for ١٢ weeks. The samples were taken when fresh and weekly till the end of freezing storage and physically analyzed.

The rheological properties of the milk samples were measured using rotational coaxial viscometer (Rheotest II, Medingen, Germany) at temperature ٣٠ºC. The rotating double space devise (N) was used with fixed cup (S) of the viscometer. Shear stress data were recorded for shear rate values between ٢٤٣ to ١٣١٢ sec$^{-١}$ .The Newtonian viscosity (µ) as well as the parameters of non- Newtonian behaviour, (consistency coefficient, k and flow behaviour index, n) were calculated as given by Dail & Steffe (١٩٩٠) and Toledo (١٩٩٧):

$$\tau = \mu \cdot \gamma \qquad (١)$$

and

$$\tau = \kappa \cdot \gamma^{n} \qquad (٢)$$

Where:

τ =Shear stress (Dynes/cm ^{٢}), γ = Shear rate (s$^{-١}$)

µ = Newtonian viscosity value (m Pa.s), n = Flow behaviour index (-)

k = consistency coefficient (Dynes/cm ^{٢} $\cdot$s ^{n}).

Whole milk and UF whole milk were prepared for transmission electron microscopy (TEM) by a slight modification of the method reported by Ali and Robinson (١٩٨٥). Two milliliters of samples were mixed with ٢ ml of ٦٪ glutaraldehyde in ٠,٢ M sodium cacodylate-HCl buffer (pH ٧,٢) and left for ١ h at room temperature. After this initial fixation, the mixture was blended with an equal volume of ٢,٥٪ molten agar at ٦٠º C, spread on a microscope slide, allowed to solidify, and sliced into small dices (١ mm^{٣}) The dices were washed with three changes of ٠,٢ M sodium cacodylate-HCl buffer (pH٧,٢), and post fixation was carried out using ١٪ (Mol) osmium tetroxide in the same buffer. The dices were washed in three changes of deionized water and then dehydrated in a graded series of water-ethanol mixtures (٥٠, ٧٠, and ٩٠٪ ethanol) followed by two washes with absolute ethanol. Finally, the dices were passed through a series of propylene oxide and Araldite mixtures before embedding in Araldite. Thin sections (٨٠ nm) were cut using ultramicrotome (Leica ultracut UCT). The sections were stained with lead acetate and then examined in an electron microscope (JEOL-TEM-١٠١٠).

Statistical analysis and correlation coefficient were carried out using applied SAS (٢٠٠٤).

RESULTS AND DISCUSSION

The rheological characteristics of the tested frozen buffalo's milk samples were discussed from the viewpoint of apparent viscosity values and flow parameters, as affected by freezing storage. These parameters are of importance for designing, handling and utilization of frozen milk.

Table (١) shows the shear data of whole milk stored for ١٢ weeks at -٢٢ ºC ± ٢. As seen, shear stress values were increased by ١٥٪ to ٤٧ % at the end of frozen storage period of whole milk indicating the occurrence of some aggregation in the milk components induced by freezing and frozen storage. Pasteurization of whole milk before freezing did not affect the pattern of flow curves even after freezing for ١٢ weeks (Table١), indicating a minimum effect of pasteurization on the flow behavior of whole milk. Separation of fat content from whole milk resulted in ٢٠-٢٥٪ reduction of the shear stress response of the skim milk (Table ١), compared with that of whole milk, at all tested shear rates. This means that fat content induced an increase in the viscosity values of milk. However, freezing and freezing storage of skim milk did not greatly influence the flow curves as did the whole milk, indicating the role of fat in aggregation changes of frozen milk. However, pasteurization of skim milk resulted in an average of ١٠٪ increase in the shear stress response indicating the role of fat in separation of milk aggregation during the heat treatment.

Concerning the effect of the heat treatment of milk on its flow behavior characteristic, it could be noticed that pasteurized samples showed higher shear stress response than those of raw milk samples, especially for pasteurized whole milk than skim milk. The obtained results agree with those reported by Marta, *et al.,* (٢٠١٠), who studied the rheological behaviour of commercial sodium caseinate at various temperatures.

Table (١): Shear stress values (Dynes/cm^{٢}) of frozen milk (-٢٢ºC) during storage periods at different shear rates.

Treatments	Shear rate Sec$^{-١}$	Frozen storage period (weeks)						
		Fresh	٢	٤	٦	٨	١٠	١٢
Raw whole milk	٢٤٣	٥,٨	٦,١	٦,٧	٧,٢	٧,٦	٧,٦	٧,٨
	٤٣٧	٧,٠	٧,٣	٨,١	٩,٠	٩,١	٩,٩	١٠,٤
	٧٢٩	١٦,٣	١٦,٧	١٧,٧	١٨,٠	١٨,٤	١٨,٦	١٨,٧
	١٣١٢	٢٩,٤	٢٩,٤	٢٩,٥	٢٩,٥	٣٠,٠	٣٠,٦	٣٠,٦
Pasteurized whole milk	٢٤٣	٥,٥	٦,١	٦,٩	٨,٠	٨,٧	٩,١	٩,٦
	٤٣٧	٩,٨	١٠,٤	١٠,٨	١١,٨	١٢,٣	١٢,٧	١٣,٠
	٧٢٩	١٤,٠	١٤,١	١٤,٦	١٥,٦	١٧,٠	١٧,٥	١٨,١
	١٣١٢	٢٨,٦	٢٨,٧	٣٠,٢	٣٠,٦	٣٠,٧	٣٠,٧	٣٠,٩
Raw skim milk	٢٤٣	٥,٨	٥,٨	٥,٩	٥,٩	٥,٩	٦,١	٦,٢
	٤٣٧	٧,٦	٨,١	٨,٧	٩,١	٩,٦	٩,٩	٩,٩
	٧٢٩	١٢,٣	١٣,٣	١٣,٦	١٣,٩	١٤,٥	١٤,٧	١٤,٨
	١٣١٢	٢٤,٢	٢٤,٤	٢٤,٤	٢٤,٧	٢٥,١	٢٥,٧	٢٦,٩
Pasteurized skim milk	٢٤٣	٦,٥	٦,٧	٦,٩	٧,٠	٧,٢	٧,٢	٧,٤
	٤٣٧	٨,٠	٨,٨	٩,١	٩,٦	٩,٧	٩,٨	٩,٩
	٧٢٩	١٣,٩	١٤,١	١٤,١	١٤,٦	١٥,٠	١٤,٦	١٥,١
	١٣١٢	٢٦,٨	٢٦,٩	٢٧,٤	٢٧,٥	٢٧,٥	٢٧,٥	٢٧,٥

The shear rate/shear stress data of the tested milk samples were subjected to flow pattern analysis according to the power model. (equation Nr.٢)

$$\tau = \kappa \cdot \gamma^{n}$$

The results of analysis are given in Table (٢). As seen the n-values of raw and pasteurized whole milk were very close to the unity (١,٠٤ and ٠,٩٩٣ respectively) indicating the Newtonian flow behaviour of raw and pasteurized milk. However, Freezing and feezing storage led to shifting the flow behaviour to the non- Newtonian shear thinning pattern, since the n-value decreased to ٠,٨٣٠ and ٠,٦٤٧ for raw and pasteurized whole milk, respectively. Such change in flow behaviour could be referred to structural changes and aggregation in the milk components during frozen storage. The flow behaviour of skim milk, whether raw or pasteurized, was characterized by a slight non- Newtonian behaviour before and after freezing storage, since the n-values were in the range of ٠,٨٢ - ٠,٩٠. It could be suggested that fat content greatly contribute to the pattern of flow. According to data in Table (٢), the values of consistency coefficient (*K-values*) increased by pasteurization and during frozen storage. Although it appears that fat separation resulted in an increase in the dynamic viscosity, the real apparent viscosity values, which relate viscosity to both shear rate γ and flow behaviour index (n) ($\eta_{app} = \kappa \,.\, \gamma^{n-١}$) reveal that the apparent viscosity values of skim milk were actually lower than those of whole milk. The obtained data on the rheological characteristics of milk could be confirmed with the data published in the literature. Most of the workers were carried out using cow's milk, and the data on buffalo's milk are rare. Mun *et al.,* (١٩٩٩) found that the viscosity of whole and skim milk was almost constant at a shear rate up to ١٠٠٠ $s^{-١}$ whitch value close to ١,٢ CP and n-value close to the unity. They also stated that casein is one of the major components in milk, that affected the fluid rheology, with viscosity increase with increasing casein content as well as with increasing fat content, as indicated by the difference between whole and skim milks, since casein micelles can be bound to fat globules readily.

On other side, Velez-Ruiz and Barbosa-Canovas (١٩٩٨) mentioned that dairy products rich in protein content behave rheologically different than those rich in fat. They also found that milk with ١٧,٢٪ total solids behaves as Newtonian fluid with k- value of ٠,٠٢ to ٠,٠٣ dynes.s^n/$cm^٢$ and it increased slightly upon ٤ weeks cold storage, which agree with the results obtained in the present work. In other work, Bienvenue *et al.,* (٢٠٠٣) found that the presence of minerals which mount high in milk, resulted in increase in its viscosity because of the relationship between minerals and casein aggregation. Furthermore, Velez-Ruiz and Barbosa-Canovas (٢٠٠٠) applied shear rates of ٥٠٠-١٠٠٠ $s^{-١}$ at room temperature for rheological determination of whole and concentrated milk. The flow behaviour index was close to the unity with k- value of ٠,٠١٨ to ٠,٠٢٣٣ dynes.s^n/$cm^٢$ for total solids of ١٢,٥ to ١٧,٢٢٪ indicating the Newtonian behaviour of whole milk. They also stated that casein micelles, fat globules, whey proteins, lactose and salts are capable of undergoing a variety of changes under the effect of heat. Published data of Chang and Hartel (١٩٩٧) revealed that average dynamic viscosity of skim milk (٩,٥٦٪ solids) was in the range of ٣,٧ CP being obtained by a capillary tube glass viscometer. In conclusion, the viscosity of milk, consistency coefficient and flow behaviour index were correlated as a function of total solid and affected either by skimming or heat treatment of milk.

Table (٢): Flow parameters of frozen milk during storage at -٢٢°C± ٢.

Treatments	Flow parameters	Frozen storage period (weeks)						
		Fresh	٢	٤	٦	٨	١٠	١٢
Raw whole milk	K	٠,٠١٦	٠,٠٢٢	٠,٠٤٥	٠,٠٤٨	٠,٠٦٧	٠,٠٧٤	٠,٠٩٠
	n	١.٠٤	١.٠٠	٠.٩٢٤	٠.٨٩٢	٠,٨٥٤	٠,٨٥٠	٠,٨٣٠
	$R^{٢}$	٠,٩٣٩٣	٠,٩٤٤٠	٠,٩٤٥٤	٠,٩٥١٢	٠,٩٥٨٠	٠,٩٧٠٨	٠,٩٧١٧
asteurized hole milk	K	٠,٠٢٢	٠,٠٣٧	٠,٠٥٧	٠,١٣٧	٠,١٥٥	٠,١٧٠	٠,٢٦١
	n	٠,٩٩٣	٠.٩٢٠	٠.٨٥٩	٠. ٧٣٣	٠.٧٢٣	٠.٧١٣	٠.٦٤٧
	$R^{٢}$	٠,٩٧٢٢	٠,٩٧٦٨	٠,٩٨١١	٠,٩٨١٤	٠,٩٨٣٧	٠,٩٨٥٠	٠,٩٩٠٢
Raw skim milk	K	٠,٠٤٠	٠,٠٤٨	٠,٠٤٩	٠,٠٤٩	٠,٠٥٠	٠,٠٥٨	٠,٠٦٧
	n	٠. ٩٠٠	٠. ٨٦٧	٠. ٨٦٧	٠. ٨٥٤	٠,٨٤٦	٠. ٨٣٣	٠. ٨٢٠
	$R^{٢}$	٠,٩٦١٢	٠,٩٧٩٣	٠,٩٨٧٦	٠,٩٩٦٢	٠,٩٩٧٨	٠,٩٩٧٩	٠,٩٩٨٨
steurized im milk	K	٠,٠٤٧	٠,٠٦٣	٠,٠٦٨	٠,٠٧٥	٠,٠٨٣	٠,٠٩٠	٠,٠٩٤
	n	٠. ٨٧١	٠. ٨٢٩	٠. ٨٢٠	٠. ٨١١	٠. ٧٨٤	٠. ٧٧٥	٠. ٧٥٧
	$R^{٢}$	٠,٩٥٠٧	٠,٩٦٣٠	٠,٩٦٦٥	٠,٩٧٧١	٠,٩٧٧٣	٠,٩٧٥٠	٠,٩٧٥٢

n = flow behavior index (-); K = consistency index dyne. s^n /$cm^{٢}$; $R^{٢}$ = correlation coefficient

Figure ١ show the dynamic viscosity of milk samples. As seen, the average viscosity value of whole milk was ٢,١٤ CP, and this value increased to ٢,٦ CP after ١٢ week of frozen storage. Viscosity values of whole milk were slightly affected by the applied shear rate, indicating the Newtoniaty of whole milk, even after١٢ week of feezing storage. Dynamic viscosity of whole milk was not remarkably influenced by pasteurization, since the average viscosity of pasteurized milk was ٢,١٩ CP and it increased to ٢,٨٩ CP after١٢ week of feezing storage.

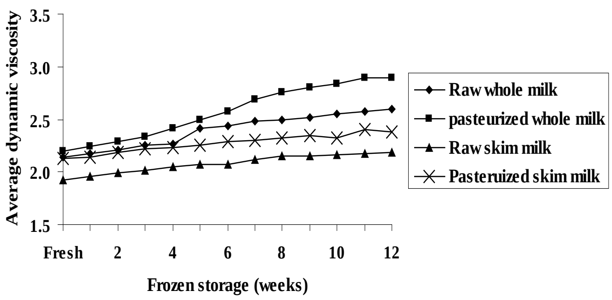

Fig. ١: Relationship between average dynamic viscosity and frozen storage at -٢٢°C± ٢.

Despite the linear relationship between the shear stress and shear rate, plots of dynamic viscosities versus shear rate were slightly shear thinning. According to Wayne and Shoemaker (١٩٨٨), the reason for such behaviour could be referred to the presence of small yield stress (I₀ -values) making the dynamic viscosity shear dependent to some extent. As expected, separation of fat resulted in a remarkable decrease in the dynamic viscosity, which reached a value of ١,٩١CP indicating that the fat content plays an important role in the viscosity of milk. However, viscosity of skim milk was increased to

٢,١٨ CP at the end of frozen storage. Pasteurization of skim milk led to an ١١٪ increase in the dynamic viscosity value.

Table (٣) show the shear data, i.e. the relationship between applied shear rates and obtained shear stress response, for the tested milk concentrates. For concentrated skim milk samples, the maximum shear stress response reached about ٣٠ dynes/cm^{٢} for fresh ٢X concentrated, and ٤٩ dynes/cm^{٢} for ٣X concentrates, respectively. The flow curves showed an almost linear relationship indicating the less deviation of the flow pattern from Newtonian behavior. According to Chang and Hartel (١٩٩٧), as well as the Mun *et al.,* (١٩٩٩), the flow behavior of ٣٠٪ concentrated skim milk exhibited a slight non- Newtonian behavior of pseudo plastic type. Wayne and shoemaker (١٩٨٨) gave a shear stress magnitude of ١٧ dynes/cm^{٢} (at ٥٠٠ s$^{-١}$) for ٢٠٪ concentrated skim milk, which agree with results given in Table (٣) of the present work. Velez- Ruiz and Barbosa- canovas (١٩٩٨) as well as Bienvenue *et al.,* (٢٠٠٣) referred such change in course of flow curves of concentrated milk to the removal of water, which causes an increase in volume fraction of dispersed particles and increase the micelle-micelle interactions as the distance between the micelles becomes smaller. Increasing the storage time of frozen concentrated skim milk led to an increase in the shear stress response of the concentrated milk at all shear rates. The increase reached an average of ٢,٢٪ and ٨٪ for ٢X and ٣X concentrated skim milk, respectively. As seen in Table (٣), the shear stress values at maximum shear rate (١٣١٢ s$^{-١}$) reached ٣٤ and ٥١ dynes/cm^{٢} for ٢X and ٣X buffalo's skim milk, respectively. According to Mun *et al.,* (١٩٩٩) there are other physicochemical changes taking place during storage time that are affecting the rheological behaviour of concentrated skim milk such as micellar aggregation, association of casein micelles with fat globules and whey protein change causing such change in the rheological properties of concentrated skim milk. The flow curves of concentrated whole milk were substantially different from those of concentrated skim milk. As seen in Fig (٣), the course of the flow curves is cleary non –linear and the magnitute of shear stress values is much higher. Also, the differences in the shear stress values between ٣X and ٢X concentrated whole milk are very clear. The shear stress values of ٣X concentrated whole milk increased above those of ٢X concentrated skim milk by an average of ٢٣ folds, while those of ٢X concentrated whole milk were, in average, ١,٦٨ folds those of ٢X concentrated skim milk. The whole milk concentrates behaved as non-Newtanion fluid. According to Velez- Ruiz and Barbosa-canovas (٢٠٠٠), the non-Newtanion behaviour of concentrated whole milk could be refered to decrease in the solubility of milk components, an increase in particle interactions, precipitation of denaturated whey proteins and aggregation of small particles. Additionaly, the fat globules in the milk concentrates are surrounded by a membrane which is thicker in the concentrated milk than in the fresh milk changes in the physical state of milk associated with processing are invariably reflected on the casein micelle surface whole milk during concentration. During frozen storage, the shear stress values of concentrated in contarary to concentrated skim milk were slightly increased by a ratio of ٢-٣٪. The storage- induced increase in magnitude of shear stress values may be due to rearrangement of the three-dimensional structure, resulting in increased number and strength of bonds between casein micelles and irreversible aggregation of the particles during frozen storage of concentrated milks.

According to Mun *et al.,* (١٩٩٩), the shear thinning behaviour of concentrated milk could be refered to alignment of asymmetric dispersed molecules with the shear planes by increasing shear rate so that frictional resistance is reduced.

Table (٣): Shear stress values (Dynes/cm^{٢}) of frozen buffalo's whole and skim concentrated milk during storage at different shear rates.

Treatments	Shear rate Sec$^{-١}$	Frozen storage period (weeks)						
		Fresh	٢	٤	٦	٨	١٠	١٢
Whole milk (٢X)	٢٤٣	٣١٢,٧	٣١٦,١	٣١٧,٣	٣١٨,٩	٣٢٥,١	٣٢٧,٥	٣٣٤,٣
	٤٣٧	٤٦٦,٩	٤٧١,٢	٤٧٢,٨	٤٧٥,٦	٤٧٧,١	٤٧٩,٣	٤٧٩,٠
	٧٢٩	٦١٨,٠	٦٢٢,٣	٦٢٤,٨	٦٢٦,٣	٦٣٠,٤	٦٣٢,٨	٦٣٥,٣
	١٣١٢	٧٧٩,٠	٧٨٢,٧	٧٨٣,٩	٧٨٦,١	٧٨٩,٥	٧٩١,٣	٧٩٢,٠
Whole milk (٣X)	٢٤٣	٥٥٩,٩	٥٦٤,٢	٥٦٧,٦	٥٧٢,٣	٥٧٥,٠	٥٧٧,٨	٥٧٨,٤
	٤٣٧	٧٤١,٦	٧٤٩,٠	٧٥١,٥	٧٥٤,٠	٧٥٥,٢	٧٥٧,٧	٧٥٧,١
	٧٢٩	٩٠٢,٣	٩٠٧,٥	٩٠٩,٧	٩١٤,٩	٩١٩,٩	٩١٩,٩	٩٢٣,٣
	١٣١٢	١١١٣,٦	١١٢٥,٤	١١٢٩,٤	١١٣٠,٩	١١٣٣,٧	١١٣٤,٣	١١٣٥,٣
Skim milk (٢X)	٢٤٣	٧,١١	٧,٨٨	٨,٤٧	٩,٠٥	٩,٧٠	٩,٩٥	١٠,٢٠
	٤٣٧	١٠,٣٢	١١,٤٠	١١,٩٩	١٢,٤٢	١٢,٩٢	١٣,٢٣	١٣,٤٧
	٧٢٩	١٥,٨٢	١٦,٨١	١٧,٨٩	١٨,٤٨	١٩,١٣	١٩,٥٦	٢٠,١٥
	١٣١٢	٢٩,٨٨	٣٠,٤٧	٣٠,٨٧	٣١,٤٦	٣٢,١٧	٣٢,٩٤	٣٣,٦٥
Skim milk (٣X)	٢٤٣	١٠,٣٢	١٠,٥٧	١٠,٩٧	١١,٢٥	١١,٤٦	١٢,٠٨	١٢,٤٢
	٤٣٧	١٧,٠٣	١٧,٣٠	١٧,٧٤	١٨,١٧	١٨,٢٣	١٨,٦٦	١٩,٠٧
	٧٢٩	٢٧,١٣	٢٧,٥٣	٢٧,٧٨	٢٨,١٨	٢٨,٥٨	٢٩,٤٢	٢٩,٩٧
	١٣١٢	٤٨,٧٣	٤٩,١٦	٤٩,٤١	٤٩,٩٧	٥٠,٤٣	٥٠,٨٣	٥١,١٤

To predict the type of the flow model dominating the flow behavior of the tested frozen concentrated whole and skim milk, the shear rate/shear stress data were evaluated according to the Newtonian (equation١) as well as the Oswald (Power law, equation ٢), and the obtained results are given in Table ١, for the tested concentrated whole and skim milk during freezing period of ١٢ weeks at (-٢٢ ºC ± ٢), respectively. In table ١, the flow parameters, consistency coefficient (*K-value*) and the flow behaviour index (n) were given as the result of the statistical analysis according to the applied flow models (eq.١ and eq.٢) using SAS statistical program. The $R^{٢}$-value was given to determine the best-fit model.

Table (٤) gives the calculated flow parameters for skim and whole concentrated milk, respectively. As seen, the flow behavior index (n- value) of fresh concentrated skim milk were in the range of ٠,٨٥٤ to ٠,٩٢ indicating the slight deviation of the concentrated skim milk from the ideal Newtonian behavior (n= ١). On other side, the values for consistency coefficient (k-value) were in the range of ٠,٠٦ Dynes. S^n/ cm^{٢}, indicating the low consistency of the concentrated skim milk. Calculations for yield stress ($ı_o$), i.e. the force required to initiate flow, of concentrated skim milk showed the presence of a negligible $ı_o$ value of ٠,١ to ٠,١٥ dynes/ cm^{٢}. Apparent viscosity values calculated at shear rate of ٤٣٧,٤ $S^{-١}$ were very close to those of dynamic viscosity measured at the same shear rate, indicating the slight deviation of the flow behavior from the Newtonian one.

However, freezing storage of concentrated skim milk for ١٢ weeks caused a substantial change in the flow parameters of concentrated skim milk. The flow behavior index (n-value) changed to the non-Newtonian side (٠,٧١٥ and ٠,٨٤٣ for ٢X and ٣X, respectively), and the consistency coefficient (k- values) increased by an average of ٢٤٠٪, indicating that the concentrate become more viscous at the end of frozen storage . Furthermore, the yield stress values increased by an average of ٦٠٠٪ and reached remarkable values of ٠,٥١٢ to ١,١٣ dynes / $cm^{٢}$.

The flow parameters of the concentrated whole milk were totally different from those of concentrated skim milk. The flow behavior index (n-value) were ٠,٥٤ and ٠,٤٠٦ for ٢X and ٣X, respectively, indicating the full non- Newtoniaty of the concentrated whole milk. Also , the consistency values (k- values) exceeded those of concentrated skim milk by ٢٧٠ to ١٠٠٠-folds and reached ١٦,٦١ and ٦١,٤٥ dynes.s^{n}/ $cm^{٢}$, for ٢X and ٣X ,respectively. Also, increasing the concentration degree from ٢X to ٣X caused an increase in k-value by ٤-folds. The concentrates possessed a remarkable yield stress value of ١٠٢,٥٣ and ١٦٥,٩٠ dynes/ $cm^{٢}$ indicating the paste character of the concentrated whole milk. Furthermore, the obtained apparent viscosity values were clearly different than those obtained by dynamic instrumental measurements. However, freezing storage of the concentrated whole milks resulted in low change in their flow parameters.

The obtained results agree with those reported in the literature. Hallstrom and Tragardh (١٩٨٨) as well as Chang and Hartel (١٩٩٧), who stated that the flow behavior index of concentrated skim milk decreased with increasing concentration and yield stress was equal to zero (٠ to ٠,٤) at all concentration up to ٤٠٪ TS. Also, they reported n-value of ٠,٩٣ for ٤٠٪ concentration. They described the non- Newtonian behavior of concentrated skim milk by protein concentration and hydration due to a compression of a "hairy" outer layer of the micelles making the concentrate close to the beginning of gross instability and gelation. On other side, Velez-Ruiz and Barbosa- Canovas (١٩٩٨) reported an n- value of ٠,٥٤ and k-value of ٢٠,٩ for ٤٨,٦٪ concentrated whole milk, which agree with n and k value given in the present work. They also observed a decrease in flow behavior index and an increase in the consistency coefficient with storage time of concentrated whole milk. They explained the increase in consistency of concentrated whole milk as the sum of the interaction effects caused by each of the individual milk particles suspended in a medium with less water content. Furthermore, Mun *et al.,* (١٩٩٩) explained the role of casein in the fluid rheology and indicated that viscosity increased with increasing volume fraction of casein in the fluid matrix. The particles come together; they adhere to each other, forming aggregates. The force is required to shear and possibly to break the aggregates. In other work, Velez-Ruiz and Barbosa- Canovas (٢٠٠٠) found that the consistency values of concentrated whole milk increased with increasing TS, being more noticeable at levels of ٢٢,٨٪ and higher. Bienvenue *et al.,* (٢٠٠٣) explained the mechanism of age thickening in concentrated milk by the loss of the tertiary and quaternary structure of the spherical casein micelles during storage. It could be noticed that the presence of fat beside casein, as it the case with concentrated whole milk, makes the problem of aggregation and lactose crystallization more complicated resulting in non-Newtonian flow behavior with high consistency values and remarkable yield stress values, which needs special consideration in mechanical handling and thermal processing of these milk concentrates.

Table (٤): Flow parameters of frozen buffalo whole and skim concentrated milk during storage at -٢٢ ºC ± ٢.

Treatment	Flow parameters	Frozen storage period (weeks)						
		Fresh	٢	٤	٦	٨	١٠	١٢
Whole milk (٢X)	K	١٦,٦١	١٧,١٥	١٧,٣٢	١٨,٠	١٨,٦١	١٩,٠٤	٢٠,٤
	n	٠,٥٤٢	٠,٥٣٨	٠,٥٣٧	٠,٥٣٥	٠,٥٢٨	٠,٥٢٥	٠,٥١٥
	I_o	١٠٩,٠	١١١,٥١	١١٢,٣٦	١١٣,٦٤	١١٨,٢٧	١٢٠,٢٥	١٢٥,٨٩
	η_{app}	١٠٢,٥٣	١٠٣,٣٢	١٠٣,٧١	١٠٦,٤٨	١٠٥,٥٠	١٠٥,٩٩	١٠٦,٨٦
Whole milk (٣X)	K	٦١,٤٥	٦١,٦٥	٦٢,٤٣	٦٤,٠٧	٦٤,٥٥	٦٥,٨٦	٦٥,٧٠
	n	٠,٤٠٦	٠,٤٠٦	٠,٤٠٥	٠,٤٠٢	٠,٤٠١	٠,٣٩٨	٠,٣٩٩
	I_o	٢٨٣,٤٢	٢٨٥,٠٣	٢٨٧,٥٧	٢٩٢,١٧	٢٩٣,٧٧	٢٩٧,٢٢	٢٩٦,٩٤
	η_{app}	١٦٥,٩٠	١٦٦,٤٤	١٦٧,٥٢	١٦٨,٨١	١٦٩,٠٦	١٦٩,٣٦	١٦٩,٣٨
Skim milk (٢X)	K	٠,٠٦٢٥	٠,٠٩٣	٠,١١٨	٠,١٤٥	٠,١٧٧	٠,١٨٤	٠,١٨٩
	n	٠,٨٥٤	٠,٧٩٩	٠,٧٦٨	٠,٧٤٢	٠,٧١٧	٠,٧١٦	٠,٧١٥
	I_o	٠,١٥٢	٠,٢٥١	٠,٦٤٥	٠,٨٣٧	١,٠٧	١,١٠	١,١٣
	η_{app}	٢.٥٧	٢,٧٤	٢,٨٨	٣,٠٢	٣,١٧	٣,٢٥	٣,٣٤
Skim milk (٣X)	K	٠,٠٦٤٦	٠,٠٦٩	٠,٠٨	٠,٠٨٧	٠,٠٨٩	٠,١٠٧	٠,١١٨
	n	٠,٩٢	٠,٩١١	٠,٨٩١	٠,٨٨٢	٠,٨٧٩	٠,٨٥٤	٠,٨٤٣
	I_o	٠,١٠٢	٠,١٣١	٠,٢٠٨	٠,٢٥٦	٠,٢٧١	٠,٤١١	٠,٥١٢
	η_{app}	٣,٩٧	٤,٠٢	٤,١٢	٤,٢٥	٤,٣١	٤,٤٢	٤,٥٤

n = flow behavior index (-); K = consistency index dyne. s^n /cm٢; I_o = yield stress (dynes/cm ٢), ηapp = Apparent viscosity (CPn) (mpa. sn/cm٢)

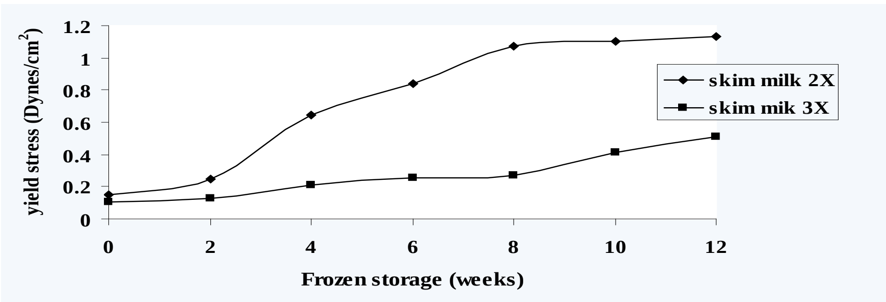

Fig. ٢: Changes in yield stress values of frozen skim concentrated milk during storage at -٢٢ ºC ± ٢.

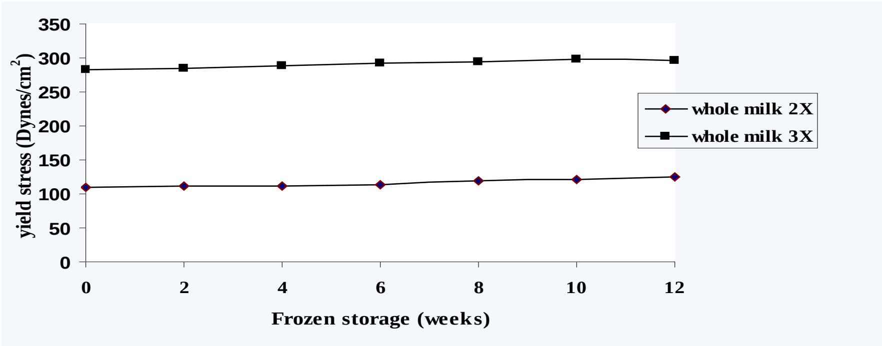

Fig. ٣: Changes in yield stress values of frozen whole concentrated milk during storage at -٢٢ ºC ± ٢.

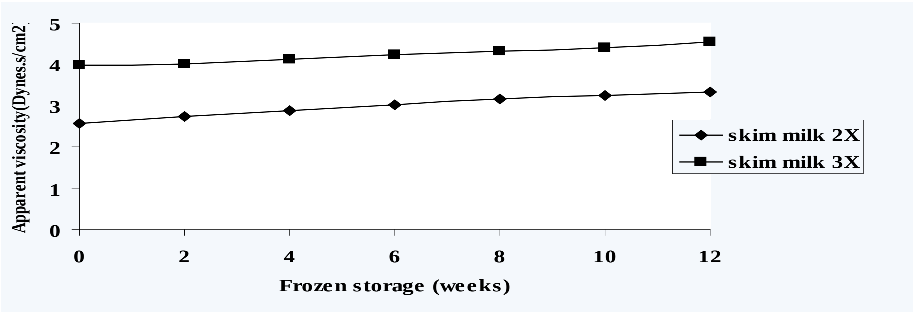

Fig. ٤: Changes in apparent viscosity (η_{app}) value of frozen skim concentrated milk during storage at -٢٢ ºC ± ٢.

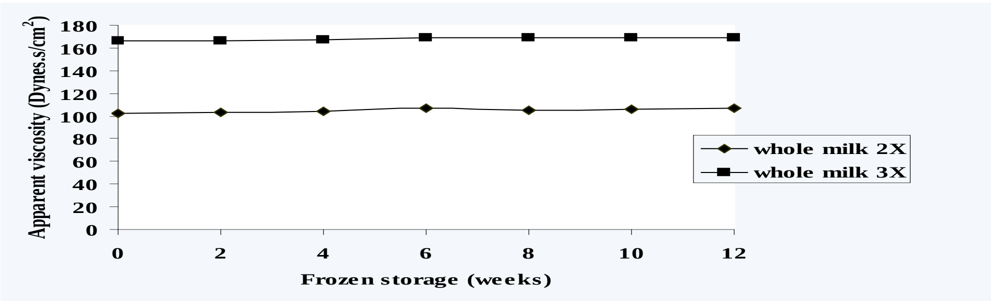

Fig.٥: Changes in apparent viscosity (η_{app}) values of frozen whole concentrated milk during storage at -٢٢ ºC ± ٢.

A B

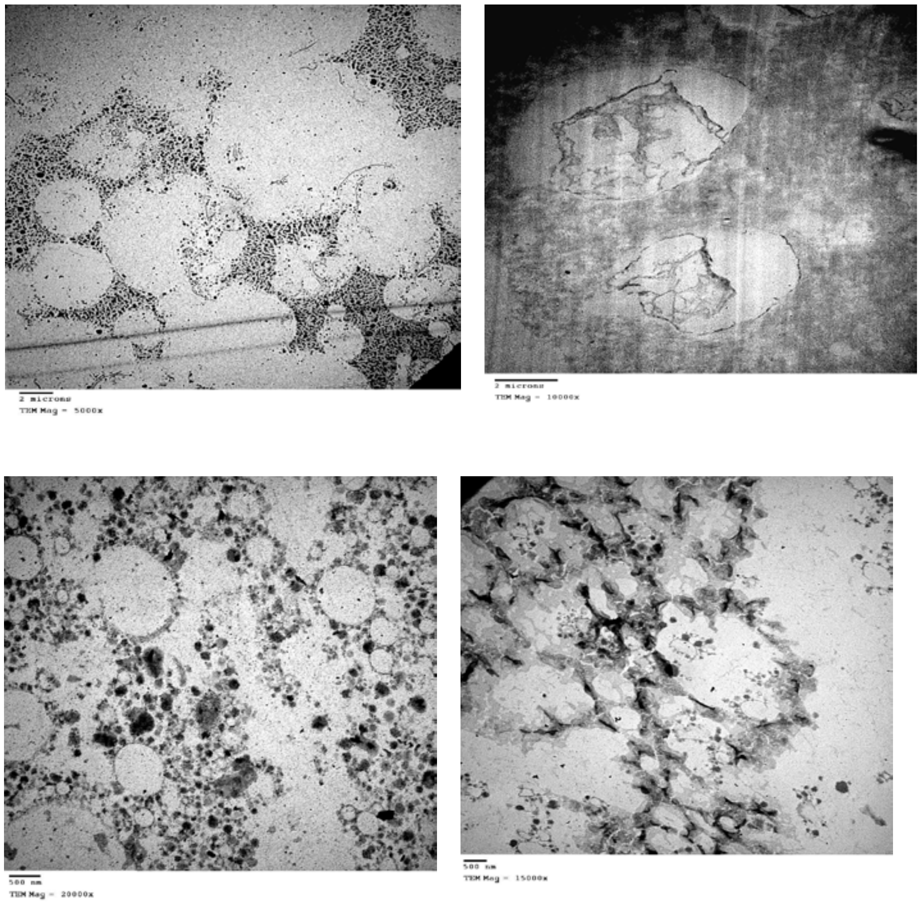

Fig. ٦: TEM micrographs of raw whole milk at fresh (A), concentrated whole milk (٣X) at fresh (C) and whole milk (B), frozen whole concentrated milk (D) after ١٢ weeks of storage at -٢٢ ºC ± ٢

During the study of microphotographs of all treatments by Transmission Electron Microscopy (TEM), it was observed that the fat in raw whole milk (Fig. ٦ A) had spherical shapes with a wide range of diameters. The milk fat naturally occurs as MFG. The presence of the milk fat globule membrane (MFGM) limits the impact of de-destabilization phenomena, such as flocculation, coalescence and creaming while protecting the milk fat from lipolysis. The MFGM surrounds the polar fat globule with a trilayer structure through association with the triglycerides in the liquid portion of the fat (Keenan & Mather, ٢٠٠٢). After freezing of buffalo's whole milk for a period of ١٢ weeks at (-٢٢ ºC ± ٢), an increase in the broken fat globules membrane was observed (Fig ٦ B). When milk is processed, changes occur in the

MFGM beginning with a ٢٠٪ loss of polar lipids during initial cooling. Additional processing increases the loss of phospholipids and results in a loss of the triple layer membrane, and in the production of lipid-protein vesicles and fat droplets surrounded by a monolayer membrane (Waninge *et al*., ٢٠٠٤). Transmission electron micrographs (TEM), of fresh and frozen whole concentrated milk obtained from UF whole milk concentrates are shown in Figure (٦ C &D). Ultrafiltration of whole milk caused changes in size, distribution, and average diameter of casein micelles. The fresh whole concentrated milk from UF showed a roughly spherical shape, in various sizes, as expected (Figure ٦ C). The appearance of frozen whole concentrated milk from UF milk concentrated three times (٣X) also exhibited nearly spherical shapes with a wide range of sizes (Figure ٦ D). In highly concentrated UF concentrate, the casein micelles are interacting over short distances and this can influence the size distribution of the micelles. In UF concentrate fixed by glutaraldehyde, only the size and not the surface structures nor the core of casein micelles could be observed. TEM micrographs revealed that MFG in (Fig. ٦ D) ranged in size from ٥٠٠ nm and that they were embedded in what appeared to be an aggregated protein matrix. The aggregated particles in the background material are believed to be artifacts formed during specimen preparation. Some MFG were irregularly shaped, whereas others were spherically shaped. Some of the MFG were well-defined with whole, intact membranes, whereas others exhibited ruptured and incomplete membrane layers. Srilaorkul *et al*., (١٩٩١).

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الخواص الانسيابية والتركيبية للبن الجاموسى المركز المجمد

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يهدف هذا البحث الى دراسة بعض الخواص الريولوجية لكل من اللبن الكامل والفرز المركزوالمجمد . تم تقدير الخواص الريولوجية لهذه العينات بإستخدام جهاز تقدير اللزوجة الاسطوانى الدورانى عند معدلات قص من ٢٤٣ الى ١٣١٢ لكل ثانية وعلى درجة حرارة ٣٠ °م. ولقد أوضحت النتائج الريولوجية أن الفروق بين قيم الإجهاد لمنحنى الصاعد والهابط (وهى قيم معبرة عن مقدار الإنهيار التركيبى نتيجة للقص) ليست ذات تأثير معنوى.

كما أظهرت النتائج أن قيم الإجهاد تعتمد على نوع اللبن و المعاملة الحرارية ومحتوى الدهن ووجد أن أعلى قيم قص (إنزلاق) للبن الكامل المبستر واللبن الكامل الخام كانت ٣٠.٩ و ٣٠.٧ داين/سم٢ .

كما وجد أن منحنيات السريان (التدفق) المتحصل عليها من اللبن الفرز الخام لها علاقة خطية لمعدلات القص والإجهاد، لذلك يمكن القول بأن اللبن الفرز الخام يسلك سلوك السوائل النيوتينية قبل عملية التجميد.

أدى تخزين عينات اللبن المركز المجمد لمدة ١٢ أسبوع الى زيادة ملحوظة فى قيم معامل القوام، كما أن قيم معامل السلوك انخفضت(عن الوحدة) ممايدل على حدوث تغير فى السلوك القوامى للبن المركز تجاه السلوك اللانيوتونى.

اظهر الميكرسكوب الالكترونى تغيرات في حجم وتوزيع ومتوسط قطر جسيمات الكازين فى كل من اللبن الطازج واللبن الكامل المركز بالترشيح الفوقى. كما اظهر تقريبا اشكال كروية في مختلف الأحجام للبن الطازج كامل الدسم المركزة بالترشيح الفوقى. وأضاف أن ظهور اللبن المجمد والمركز بتركيز ثلاث مرات ياخذ الشكل الكروى مع مجموعة واسعة من الأحجام.

قام بتحكيم البحث

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