International Dairy Journal 97 (2019) 25–30

Contents lists available at ScienceDirect

International Dairy Journal

journal homepage: www.elsevier.com/locate/idairyj

Rheological methods to analyse the thermal aggregation of calcium enriched milks

Bárbara Erica Meza, Susana Elizabeth Zorrilla, María Laura Olivares*

Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional del Litoral (UNL), Güemes 3450, S3000GLN Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 23 November 2018
Received in revised form
2 May 2019
Accepted 3 May 2019
Available online 28 May 2019

ABSTRACT

The colloidal state of calcium enriched milks during heating and its microstructures were analysed through interpretation of rheometric data with the Brownian aggregation theory, which can be considered as complementary to the methods currently used. Viscosity was measured at 100 s^{-1} through temperature and time sweeps. It was observed that from 25 to 60 °C, viscosity slowly decreased as temperature increased; above 60 °C, viscosity sharply increased at different temperatures depending on the amount of $CaCl_2$. From time sweeps, the aggregation of casein micelles was described through the Smoluchowski theory. The addition of $CaCl_2$ at concentrations of 20–30 mmol kg^{-1} decreased the stability factor 5 to 6 orders of magnitude compared with non-enriched milk. Values of the fractal dimension indicated that aggregation yields disordered aggregates occluding high amounts of solvent. The methodology described may help to analyse colloidal stability and structures when different calcium salts are used for enrichment.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

The need for increasing population calcium intake has led to the development of a variety of calcium-enriched dairy products (Canabady-Rochelle et al., 2007; Janve & Singhal, 2018; Koutina, Knudsen, & Skibsted, 2015). However, when the delicate mineral equilibria in milk are modified, different changes can occur. Particularly, the addition of calcium salts reduces the pH and influences the level of colloidal calcium phosphate, the proportion of caseins in the micellar and serum phases, the activity of Ca^{2+} and the ionic strength of the milk. Also, the hydration of casein micelles (CM) and the zeta potential are reduced (Famelart, Le Graet, & Raulot, 1999; Koutina et al., 2015; Philippe, Gaucheron, Le Graet, Michel, & Garem, 2003; Philippe, Le Graët, & Gaucheron, 2005). As a consequence, these changes can affect the heat stability of milk (Omoarukhe, On-Nom, Grandison, & Lewis, 2010; On-Nom, Grandison, & Lewis, 2012; Sievanen, Huppertz, Kelly, & Fox, 2008; Singh, 2004).

On the one hand, heat processing of calcium enriched milk is challenging from a technological point of view (Koutina, Christensen, Bakman, Andersen, & Skibsted, 2016). For instance, the sediment deposition or film formation in heat exchangers (recognised as fouling) are increased by the addition of calcium in milk (Bansal & Chen, 2006; Boumpa, Tsioulpas, Grandison, & Lewis, 2008). Fouling reduces the process efficiency, can compromise the product by contamination, and needs a regular and more intensive cleaning (Hooper, Paterson, & Wilson, 2006; Sadeghinezhad et al., 2013). In this case, calcium addition has a negative impact on heat processing of enriched milk.

On the other hand, the heat treatment of calcium enriched milk was proposed as a novel process that leads to milk coagulation and to formation of the so called “calcium-milk coagulum” (Koutina et al., 2016; Ramasubramanian, D'Arcy, Deeth, & Oh, 2014). For instance, a fine gel network can be obtained by combining calcium addition to milk, pH adjustment and heat treatment (Koutina et al., 2016) or strong calcium-induced milk gels can be obtained using heat treatment at 70 °C (Ramasubramanian et al., 2014). In this case, calcium addition to milk can be advantageously used for making novel dairy products.

Therefore, there are many aspects that justify the study of the heat stability of milk as affected by calcium addition. The literature relating milk calcium supplementation, physicochemical changes and heat stability is vast and a wide variety of techniques has been used to fulfil this purpose (Dumpler & Kulozik, 2015; Jeurnink & de

* Corresponding author. Tel.: +54 342 4511595.
E-mail address: olivares@santafe-conicet.gov.ar (M.L. Olivares).

https://doi.org/10.1016/j.idairyj.2019.05.001
0958-6946/© 2019 Elsevier Ltd. All rights reserved.

Kruif, 1993; Kaushik, Sachdeva, & Arora, 2015; Koutina & Skibsted, 2015; Koutina et al., 2016; Lin, Kelly, O'Mahony, & Guinee, 2018; Omoaruke et al., 2010; On-Nom et al., 2012; Sievanen et al., 2008; Singh, 2004; Singh et al., 2007). However, the characterisation of calcium enriched milk during heating through rheological properties is still scarce and necessary. The aim of the present study was to analyse the rheological properties of calcium enriched milks during heating through the classical shear rate rheometry. Particularly, we intended to get additional information about the extent to which the stability of milks changes due to calcium enrichment and the microstructures obtained when the thermal aggregation begins after CM destabilisation and before gel formation.

2. Materials and methods

2.1. Preparation of milk samples

Skim milk powder (SanCor Cooperativas Unidas Ltda., Sunchales, Argentina: 4%, w/w, moisture; 1.5%, w/w, fat; 35%, w/w, protein; 8.5%, w/w, ash; 31 mmol kg^{-1} calcium) obtained with a low heat treatment that reduces the level of denatured whey proteins was used. Milk samples were prepared at a level of 10% (w/w), following the manufacturer's recommendations. The required amount of powder was gradually added to purified water at 25 °C while stirring at moderate speed. Samples were sealed and stirred for 4 h at 25 °C. To prevent microbial growth, sodium azide (0.02%, w/v) was added to the reconstituted milk samples before being stored overnight at 25 °C. The next day, milk samples with different added $CaCl_2$ concentrations (0, 10, 15, 20, 25 and 30 mmol kg^{-1}) were prepared under stirring at moderate speed for 5 min. Again, the samples were stored overnight at 25 °C to ensure the equilibration of mineral content. All samples were stored at 4 °C up to its analysis. Each sample preparation was carried out in duplicate.

2.2. Rheometry

Skim milks enriched with different amounts of $CaCl_2$ were evaluated with a speed controlled rheometer Brookfield DV3TLVCP (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA) with a cone-plate geometry (CPA-40Z, 0.8° angle and 48 mm diameter). The viscosity of the milk samples was measured for two rheometric tests, Test A and Test B.

In Test A (temperature sweep), the viscosity was measured as function of temperature in the range of 25–80 °C at a constant value of shear rate of 100 s^{-1}. The cell temperature increased linearly with a rate of heating of 2.4 °C min^{-1}.

In Test B (time sweep), the viscosity was measured as function of time at a constant value of shear rate of 100 s^{-1} while the temperature was kept constant.

All measurements were performed in duplicate.

3. Theory

3.1. Thermal aggregation of CM according to the Brownian aggregation theory

The heating of milk at high temperatures leads to coagulation, which is a consequence of the loss of CM stability. In this sense, the surface properties of CM rather than the interior ones are likely to be important (Singh, 2004). As a result, the CM surface characteristics provide electrostatic and steric stabilisation (Dalgleish & Corredig, 2012; de Kruif, 1999; Horne, 2006). Heat treatment markedly modifies the serum phase environment around the CM. pH decreases, calcium phosphate is deposited onto micelles, whey proteins associate with CM, caseins suffer dephosphorylation, dissociation and hydrolysis, zeta potential and hydration decrease, and covalent bonds are formed. All these changes modify colloidal interactions that allow micelles to approach each other and stay together long enough for aggregation (Singh, 2004).

In the aggregation problem of a suspension of colloidal particles, two limit cases are usually considered: perikinetic and orthokinetic aggregations. The relative importance of each mechanism can be measured by evaluating the number density flux of particles per unit area J (Russel, Saville, & Schowalter, 1989). For CM dispersions, $J_{Orth}/J_{Peri} = 4a^3\eta_s\dot{\gamma}/k_BT = 4Pe \approx 0.03$, where Pe is the Peclet number defined as the ratio of the Brownian time scale to shear rate time scale. The radius of CM a was assumed equal to 71.3 nm (de Kruif, Huppertz, Urban, & Petukhov, 2012), the dispersing fluid viscosity η_s is approximately 10^{-3} Pa s, the shear rate $\dot{\gamma}$ was experimentally set at 100 s^{-1}, the Boltzmann constant k_B is 1.3807×10^{-23} J K^{-1}, and a temperature T of 333 K was assumed for calculations. As a result $Pe < 10^{-2}$, indicating that the principal collision mechanism was due to Brownian aggregation.

In this context, the aggregation process of CM affected by temperature can be described through the Brownian aggregation theory (Walstra, Wouters, & Geurts, 2006). The rate of disappearance of primary CM particles in milk is (Eq. (1)):

$$-\frac{dn}{dt} = k_a n^2 \tag{1}$$

where n is the number density of particles (kinematic units) in the suspension at time t. $k_a = 4k_BT/3\eta_s = k_s$ is the Smoluchowski rate constant. When an energy barrier between particles is present, the collision frequency slows down and the rate constant becomes $k_a = k_s/W$, W being the corresponding colloid stability ratio (Russel et al., 1989).

Within the framework of the theory used here, it is assumed that CM during the aggregation process induced by heating form fractal structures. These aggregates constitute clusters occluding solvent. The average number of particles per aggregate N is defined as (Russel et al., 1989; Walstra et al., 2006) (Eq. (2)):

$$N = (R_a/a)^f \tag{2}$$

where R_a is the average radius of a cluster and f is the fractal dimension ($1 \leq f \leq 3$). f is a measure of the internal structure of the aggregates and it depends on the rate of aggregation (Russel et al., 1989). Thus, the volume fraction of aggregates φ_a as a function of the number of particles per aggregate N is (Eq. (3)):

$$\varphi_a = \varphi\, N^{(3-f)/f} \tag{3}$$

where φ is the volume fraction of CM in skim milk. In this study, $\varphi = 0.12$ was used (Walstra et al., 2006).

3.2. Viscosity of skim milks enriched with $CaCl_2$ during the thermal aggregation

When the aggregation process of CM begins, the viscosity of the suspensions increases. To describe the shear viscosity η of flowing suspensions, the modified Krieger–Dougherty equation can be used (Quemada, 1977) (Eq. (4)):

$$\frac{\eta}{\eta_m} = \left[1 - \frac{\varphi}{\varphi_{max}}\right]^{-2} \tag{4}$$

where φ_{max} is the maximum packing fraction and η_m is the dispersing fluid viscosity –i.e., the milk serum. In this study, $\varphi_{max} =$

0.637 (particles in random close packing) was adopted. Considering that the discrete phase is composed mainly by aggregates, φ is replaced by φ_a(Eq. (5)):

$$\frac{\eta}{\eta_m} = \left[1 - \frac{\varphi\, N^{(3-f)/f}}{\varphi_{\max}}\right]^{-2} \tag{5}$$

Eq. (1) can be solved at constant temperature. Considering that $N = n_0/n$, Eq. (6) can be obtained:

$$N = 1 + k_a^*(t - t_o) \tag{6}$$

where $k_a^* = n_o k_a$ and t_o is the initial time at which $N \approx 1$.

It is relevant to mention that skim milk is a dilute colloidal dispersion composed of casein micelles (≈0.1 μm; 2.8%, w/v) and whey proteins (≈0.01 μm; 1%, w/v). Smaller molecules (numbering more than 100,000 species in milk) are considered as part of continuous phase (Fox & McSweeney, 1998). Therefore, taking into account size and number of casein micelles, they can be considered as the primary aggregating particles. The effect of the other components on the aggregation process is taken into account mainly in k_a^*. In this study, the number of CM per m^3 is $n_o = 10^{20}$ (Walstra et al., 2006).

3.3. Calculation procedure

Rearranging Eq. (5), N is also obtained through the viscosity data (Eq. (7)).

$$N = \left\{\frac{\varphi_{\max}}{\varphi}\left[1 - \left(\frac{\eta_m}{\eta}\right)^{1/2}\right]\right\}^{f/(3-f)} \tag{7}$$

Combining Eqs. (6) and (7), the following equation can be obtained (Eq. (8)):

$$1 - \left(\frac{\eta_m}{\eta}\right)^{1/2} = \frac{\varphi}{\varphi_{\max}}\left[1 + k_a^*(t - t_o)\right]^{(3-f)/f} \tag{8}$$

Experimental data of η versus t can be used in Eq. (8) to obtain k_a^*, t_o and f as fitting parameters. N values can also be obtained through viscosity data using Eq. (7). Both equations were simultaneously used in the fitting procedure that was based on the minimisation of the differences between experimental and theoretical values.

4. Results and discussion

Fig. 1 shows experimental results obtained through Test A (temperature sweep). Two well differentiated temperature ranges were observed: (a) from 25 to 60 °C, where the viscosity slowly decreases as temperature increases; and (b) above 60 °C, where the viscosity sharply increases but at different temperatures depending on the amount of $CaCl_2$ added.

It is widely recognised that equilibria in milk are affected by temperature. For instance, between 4 and 40 °C, among the expected changes that affect viscosity, the amount of calcium in serum milk phase is reduced with increasing temperature due to the reduction in calcium phosphate solubility (Koutina et al., 2016; Walstra et al., 2006). In our case, the viscosity value increased as $CaCl_2$ content added increased, when a constant temperature is considered (Fig. 1, magnified insert). This behaviour indicates that the physicochemical changes related to the addition of $CaCl_2$ may modify the aqueous phase (serum) viscosity or the disperse phase (CM) structure, even at relatively low temperatures. Indeed, the expected change in pH due to the salt addition was observed

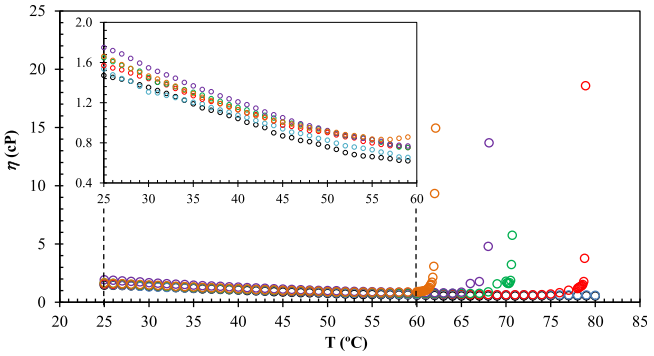

Fig. 1. Temperature sweeps (test A) for milk samples enriched with different $CaCl_2$ content: (○), 0 mmol kg^{-1}; (○), 10 mmol kg^{-1}; (○), 15 mmol kg^{-1}; (○), 20 mmol kg^{-1}; (○), 25 mmol kg^{-1}; (○), 30 mmol kg^{-1}.

(Table 1) as indicated in the literature (Bienvenue, Jiménez-Flores, & Singh, 2003; Philippe et al., 2003).

The Arrhenius-type equation can be used to represent the decrease of viscosity with temperature in the range of 25–60 °C (Rao, 1999) (Eq. (9)):

$$\eta = A_0 \exp\left(\frac{E_A}{RT}\right) \tag{9}$$

where A_0 is the pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the absolute temperature. The quantity E_A is the energy barrier that must be overcome before the elementary flow process can occur (viscous flow). The relevance of this data analysis is to focus that the viscosity scales exponentially to T^{-1}. The values of E_A were similar to data reported by Vélez-Ruiz and Barbosa-Cánovas (1998) for milk concentrate with 12.6% of solids (Table 1). It can also be observed that the addition of $CaCl_2$ did not notably modify the values of E_A, indicating that the viscosity change with heating is similar for all cases studied.

Above 60 °C, as $CaCl_2$ concentration increases, the viscosity divergence occurs at lower critical temperatures (Fig. 1). Numerous changes in milk can be caused by heating above 60 °C. The denaturation of whey proteins occurs at temperatures higher than 65 °C. At pH ≤ 6.5, denatured serum proteins partially cover CM via —S—S— linkages and also form serum protein aggregates (Koutina et al., 2016; Singh, 2004; Walstra et al., 2006). The pH of milk decreases during heating, the lower the initial pH, the lower the temperature at which coagulation occurs (Walstra et al., 2006).

In our case, the addition of $CaCl_2$ caused an expected pH decrease (Table 1), weakening electrostatic and steric repulsions of CM and leading to aggregation at a lower critical temperature. Moreover, an excess of calcium ions enhances the possibilities of —Ca— bridge formation between negatively charged groups of the overlapped hairy layers of two casein micelles. Additionally, at high temperature, covalent bonds between amino acid residues can be

Table 1
Values of pH, Arrhenius parameters and crossover temperature in the calcium enriched milks analysed.

Calcium concentration (mmol kg^{-1})	pH	E_A(kcal mol^{-1})	T_C(°C)
0	6.63 ± 0.03	5.72 ± 0.39	–
10	6.34 ± 0.01	4.85 ± 0.08	–
15	6.19 ± 0.00	4.41 ± 0.03	78.7 ± 0.1
20	6.11 ± 0.00	4.47 ± 0.09	70.0 ± 0.1
25	6.04 ± 0.02	4.95 ± 0.04	68.0 ± 0.0
30	5.94 ± 0.01	4.66 ± 0.09	61.7 ± 0.0

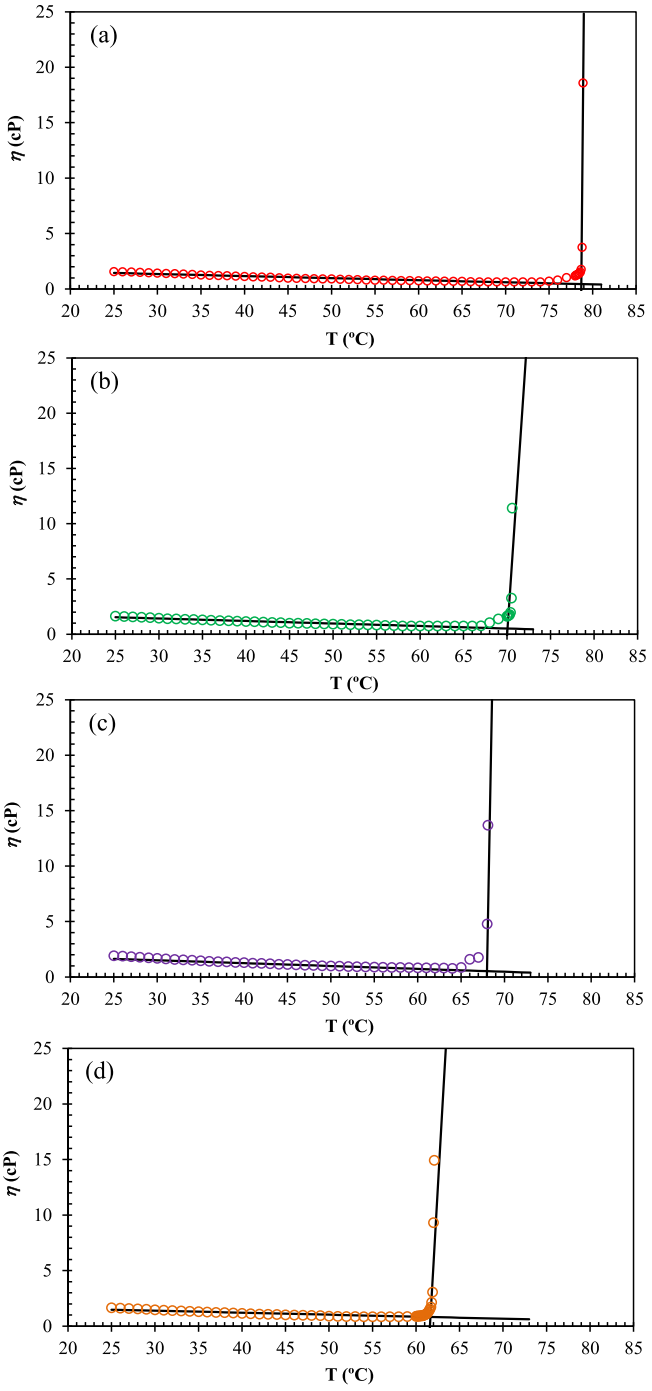

Fig. 2. Examples of the procedure used to obtain the crossover temperature T_C for milk samples enriched with different $CaCl_2$ content: (a), 15 mmol kg^{-1}; (b), 20 mmol kg^{-1}; (c), 25 mmol kg^{-1}; (d), 30 mmol kg^{-1}. Symbols are experimental values and lines represent the linear regressions.

formed, strengthening the junction (Walstra et al., 2006). Undoubtedly, there is a combined effect of calcium addition and pH reduction on coagulation phenomenon. In this sense, Horne (2016) reported some reworked milk heat stability data of Miller and Sommer (1940) and showed that when pH of calcium enriched milk is readjusted, the coagulation temperature is partially recovered to values of control milk.

To obtain representative critical temperatures when the aggregation process begins, the experimental data of viscosity versus temperature were analysed as follows. A linear regression of each linear segment was obtained. Then, the intersection between the two linear segments was used to determine a crossover temperature T_C, which can be considered as an estimation of a critical aggregation temperature (Fig. 2). Table 1 shows the values of T_C, which decrease linearly with the concentration of $CaCl_2$ (correlation coefficient $R^2 = 0.95$). Similar results were obtained by Ramasubramanian et al. (2014), who investigated the calcium-induced gelation of milk during heat treatment through oscillatory shear measurements. The authors found that the storage modulus (G') of calcium-added milk samples during heating from 20 °C to 70 °C increased for temperatures higher than 60 °C, particularly samples with 12.5, 15, 17.5 and 20 mM calcium chloride added. Samples with 0 and 10 mM calcium chloride added did not display gelation.

The values T_C are limit temperatures above which the aggregation process will vigorously occur. This information was used in the selection of the reference temperatures for Test B (time sweep). It is important to point out that the rheometric data for Test B should be obtained during the initial step of the aggregation process when a shear rate flow can be maintained (Berli, Deiber, & Añón, 1999). Additionally, at this stage the aggregation of CM is a second order reaction (Walstra et al., 2006).

From the cases studied, milk samples with 20, 25 and 30 mmol kg^{-1} $CaCl_2$ were selected for applying the aggregation theory of Smoluchowski. Milk samples with 15 mmol kg^{-1} $CaCl_2$ were not included in this analysis because the experimental thermal range was more difficult to handle in this case: i.e., at certain temperatures close to T_C, the aggregation process was practically undetectable and at a slight higher temperature the aggregation process occurred suddenly. Test B was carried out at 68, 65 and 60 °C for samples with 20, 25 and 30 mmol kg^{-1} $CaCl_2$, respectively (Fig. 3). At the beginning, a lag phase can be observed where viscosity remains constant. After that lag phase, viscosity increases with time. The viscosity evolution of milk samples with 20 or 25 mmol kg^{-1} $CaCl_2$ is similar, while the viscosity of the sample with 30 mmol kg^{-1} $CaCl_2$ evolves more rapidly.

As explained in section 3.3, the parameters k_a^*, t_o and f were obtained from experimental data of viscosity increasing with time. The values of the η_m were obtained from the viscosity data available for whey protein systems at different temperatures reported by Walstra et al. (2006). Fig. 4 shows examples of the calculation procedure carried out considering Eq. (8) to fit $1-\left(\frac{\eta_m}{\eta}\right)^{1/2}$ as function of t and Eq. (7) to simultaneously fit N as function of t for milk samples enriched with 20, 25 and 30 mmol kg^{-1} $CaCl_2$. Full lines represent the fitting curves (mean absolute percentage

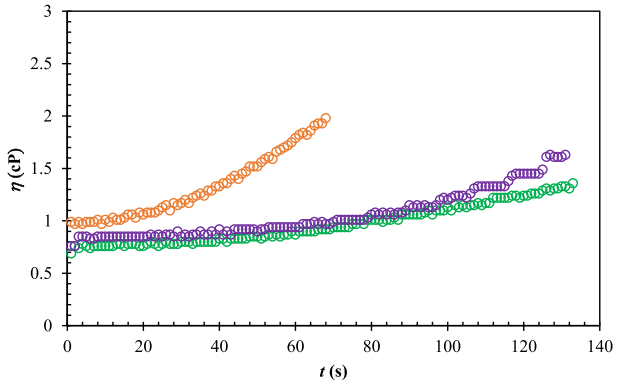

Fig. 3. Time sweeps (test B) for milk samples enriched with 20 (○), 25 (○) and 30 (○) mmol kg^{-1} $CaCl_2$ and evaluated at 68, 65 and 60 °C, respectively.

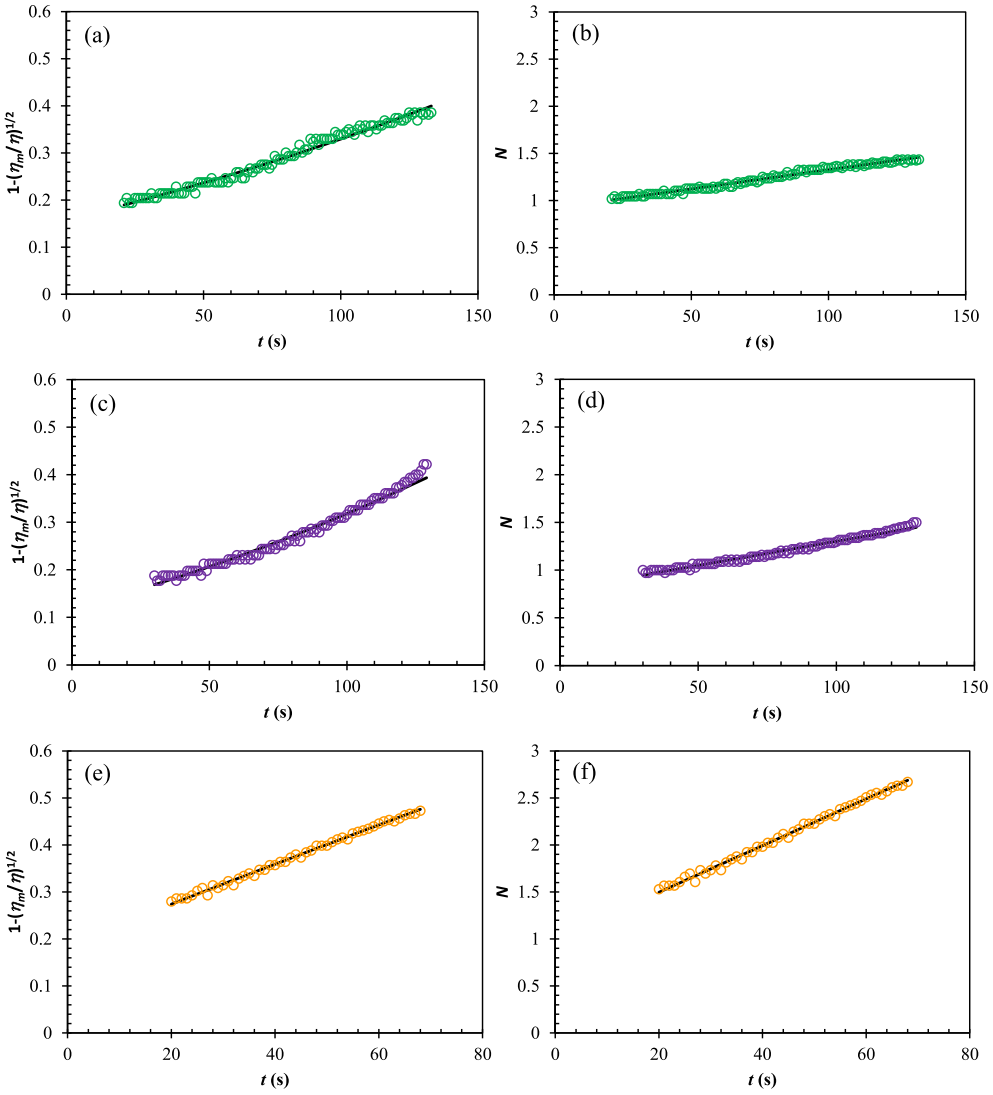

Fig. 4. Examples of the procedure used to obtain the parameters k_a^*, t_o and f through the simultaneous fitting of Eqs. (9) and (8) for milk samples. The $CaCl_2$ concentrations are: (a, b), 20 mmol kg^{-1}; (c, d), 25 mmol kg^{-1}; (e, f), 30 mmol kg^{-1}. Symbols are experimental values and lines represent the fitting curves.

deviation less than 0.2%). The average values of k_a, t_o and f are reported in Table 2. The values of k_a are similar for samples with 20 and 25 mmol kg^{-1} $CaCl_2$, while that parameter for sample with 30 mmol kg^{-1} had an aggregation rate one order of magnitude greater. Consistently, the stability factor W decreases one order of magnitude as $CaCl_2$ concentration increases to 30 mmol kg^{-1}. Walstra et al. (2006) estimated perikinetic aggregation of skim milk and determined that W would be approximately 10^{10}. Taking into account that W is the factor by which the aggregation is slowed down, through the present study it is possible to conclude that the addition of $CaCl_2$ at concentrations between 20 and 30 mmol kg^{-1}, W decreases 5 to 6 orders of magnitude.

All samples showed a low fractal dimension. These values probably indicate that the aggregation yields disordered aggregates occluding a high amount of solvent. For the case of the sample with 30 mmol kg^{-1} $CaCl_2$, it can be considered that a slightly more compact fractal structure was achieved. Koutina et al. (2016) showed CLSM micrographs of skim milk samples enriched and non-enriched with calcium chloride at different pH. The aggregate network of enriched milks had a more compact fractal structure than non-enriched samples. However, it is worth mentioning that in both cases the structure is disordered and occludes high amount of solvent.

When different calcium salts are used to increase calcium content in milk or milk products, the changes in the ion equilibrium can be different (Omoarukhe et al., 2010; Singh et al., 2007). Therefore, we consider that the methodology described in the present study may help to analyse the colloidal stability and the structure of aggregates in those cases.

Table 2
Aggregation parameters obtained from rheometric data using Eqs. (7) and (8) for milk samples enriched with 20, 25 and 30 mmol kg^{-1} $CaCl_2$.

Calcium concentration (mmol kg^{-1})	T(°C)	k_a(10^{-23} m^3 s^{-1})	k_s(10^{-17} m^3 s^{-1})	f	t_o(s)	W(10^5)
20	68	4.00 ± 0.08	1.27	1 ± 0	18.2 ± 1.9	3.18 ± 0.07
25	65	4.58 ± 0.66	1.21	1 ± 0	25.9 ± 20.1	2.67 ± 0.39
30	60	25.2 ± 0.38	1.11	1.552 ± 0.008	0 ± 0	0.44 ± 0.00

5. Conclusions

In this work, we explored some rheological properties of calcium enriched milks during heating through shear rate rheometry. When the viscosity of milks was measured as function of temperature, it was observed that between 25 and 60 °C, the viscosity of all milks slowly decreases. This decrease of viscosity was analysed by an Arrhenius-type equation and, from the values of E_A obtained, it was observed that the viscosity change with heating is similar for all cases studied. Also, the viscosity value increased as $CaCl_2$ content added increased, when a constant temperature is considered, indicating that the addition of $CaCl_2$ may modify the aqueous phase (serum) viscosity or the disperse phase (CM) structure.

Above 60 °C, the viscosity sharply increases but at different temperatures depending on the amount of $CaCl_2$ added. Crossover temperatures T_C were obtained and it was observed that as $CaCl_2$ concentration increases, the viscosity divergence occurs at lower critical temperatures. The denaturation of serum proteins and pH decrease (as consequence of calcium addition) destabilise CM and cause aggregation, while the added calcium ions enhances the possibilities of –Ca– bridge formation between negatively charged groups of CM.

Viscosity as function of time was measured and the aggregation process of CM was described through the Brownian aggregation theory. Two main conclusions were obtained from this analysis: (i) the addition of $CaCl_2$ at concentrations between 20 and 30 mmol kg^{-1} decreased W 5 to 6 orders of magnitude compared to non-enriched milk; (ii) f values indicated that the aggregation process induced by the addition of $CaCl_2$ yields disordered aggregates occluding high amounts of solvent.

Finally, it is concluded that the methodology described may help to analyse the colloidal stability and the structure of aggregates when different calcium salts are used for enrichment.

Acknowledgements

This study was conducted with the financial support of Universidad Nacional del Litoral (project CAI+D: 504 201501 00051 LI) (Santa Fe, Argentina), Consejo Nacional de Investigaciones Científicas y Técnicas (project CONICET: 11220150100606) (Argentina), and Agencia Nacional de Promoción Científica y Tecnológica (projects ANPCyT: PICT 2015-365 and 2016-249) (Argentina).

References

Bansal, B., & Chen, X. D. (2006). A critical review of milk fouling in heat exchangers. *Comprehensive Reviews in Food Science and Food Safety, 5*, 27–33.

Berli, C. L. A., Deiber, J. A., & Añón, M. C. (1999). Heat-induced phenomena in soy protein suspensions. Rheometric data and theoretical interpretation. *Journal of Agricultural and Food Chemistry, 47*, 893–900.

Bienvenue, A., Jiménez-Flores, R., & Singh, H. (2003). Rheological properties of concentrated skim milk: Importance of soluble minerals in the changes in viscosity during storage. *Journal of Dairy Science, 86*, 3813–3821.

Boumpa, T., Tsioulpas, A., Grandison, A. S., & Lewis, M. J. (2008). Effects of phosphates and citrates on sediment formation in UHT goats' milk. *Journal of Dairy Research, 75*, 160–166.

Canabady-Rochelle, L. S., Sánchez, C., Mellema, C. S., Bot, A., Desobry, S., & Banon, S. (2007). Influence of calcium salt supplementation on calcium equilibrium in skim milk during pH cycle. *Journal of Dairy Science, 90*, 2155–2162.

Dalgleish, D. G., & Corredig, M. (2012). The structure of the casein micelle of milk and its changes during processing. *Annual Review of Food Science and Technology, 3*, 449–467.

Dumpler, J., & Kulozik, U. (2015). Heat stability of concentrated skim milk as a function of heating time and temperature on a laboratory scale – improved methodology and kinetic relationship. *International Dairy Journal, 49*, 111–117.

Famelart, M. H., Le Graet, Y., & Raulot, K. (1999). Casein micelle dispersions into water, NaCl and $CaCl_2$: Physicochemical characteristics of micelles and rennet coagulation. *International Dairy Journal, 9*, 293–297.

Fox, P. F., & McSweeney, P. L. H. (1998). *Dairy chemistry and biochemistry*. New York, NY, USA: Blackie Academic & Professional.

Hooper, R. J., Paterson, W. R., & Wilson, D. I. (2006). Comparison of whey protein model foulants for studying cleaning of milk fouling deposits. *Food and Bioproducts Processing, 84*, 329–337.

Horne, D. S. (2006). Casein micelle structure: Models and muddles. *Current Opinion in Colloid & Interface Science, 11*, 148–153.

Horne, D. S. (2016). Ethanol stability and milk composition. In P. L. H. McSweeney, & J. A. O'Mahony (Eds.), *Advanced dairy chemistry. Vol. 1B. Proteins: Applied aspects* (p. 243). New York, NY, USA: Springer.

Janve, M., & Singhal, R. S. (2018). Fortification of puffed rice extrudates and rice noodles with different calcium salts: Physicochemical properties and calcium bioaccessibility. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology, 97*, 67–75.

Jeurnink, T. J. M., & de Kruif, K. G. (1993). Changes on milk on heating: Viscosity measurements. *Journal of Dairy Research, 60*, 139–150.

Kaushik, R., Sachdeva, B., & Arora, S. (2015). Heat stability and thermal properties of calcium fortified milk. *Journal of Food, 13*, 305–311.

Koutina, G., Christensen, M., Bakman, M., Andersen, U., & Skibsted, L. H. (2016). Calcium induced skim-milk gelation during heating as affected by pH. *Dairy Science & Technology, 96*, 79–93.

Koutina, G., Knudsen, J. C., & Skibsted, L. H. (2015). The effect of pH on calcium and phosphorus distribution between micellar and serum phase after enrichment of skim milk with calcium d-lactobionate. *Dairy Science & Technology, 95*, 63–74.

Koutina, G., & Skibsted, L. H. (2015). Calcium and phosphorus equilibria during acidification of skim milk at elevated temperature. *International Dairy Journal, 45*, 1–7.

de Kruif, C. G. (1999). Casein micelle interactions. *International Dairy Journal, 9*, 183–188.

de Kruif, C. G., Huppertz, T., Urban, V. S., & Petukhov, A. V. (2012). Casein micelles and their internal structure. *Advances in Colloid and Interface Science, 171/172*, 36–52.

Lin, Y., Kelly, A. L., O'Mahony, J. A., & Guinee, T. P. (2018). Altering the physicochemical and processing characteristics of high heat treated skim milk by increasing the pH prior to heating and restoring after heating. *Food Chemistry, 245*, 1079–1086.

Miller, P. G., & Sommer, H. H. (1940). The coagulation temperature of milk as affected by pH, salts, evaporation and previous heat treatment. *Journal of Dairy Science, 23*, 405–421.

Omoarukhe, E. D., On-Nom, N., Grandison, A. S., & Lewis, M. J. (2010). Effects of different calcium salts on properties of milk related to heat stability. *International Journal of Dairy Technology, 63*, 504–511.

On-Nom, N., Grandison, A. S., & Lewis, M. J. (2012). Heat stability of milk supplemented with calcium chloride. *Journal of Dairy Science, 95*, 1623–1631.

Philippe, M., Gaucheron, F., Le Graet, Y., Michel, F., & Garem, A. (2003). Physicochemical characterization of calcium-supplemented skim milk. *Le Lait, 83*, 45–59.

Philippe, M., Le Graët, Y., & Gaucheron, F. (2005). The effects of different cations on the physicochemical characteristics of casein micelles. *Food Chemistry, 90*, 673–683.

Quemada, D. (1977). Rheology of concentrated disperse systems and minimum energy dissipation principle. I. Viscosity – concentration relationship. *Rheological Acta, 16*, 82–94.

Ramasubramanian, L., D'Arcy, B. R., Deeth, H. C., & Oh, H. E. (2014). The rheological properties of calcium-induced milk gels. *Journal of Food Engineering, 130*, 45–51.

Rao, M. A. (1999). *Rheology of fluid and semisolid foods: Principles and applications*. Gaithersburg, MD, USA: Aspen Publishers, Inc.

Russel, W. B., Saville, D. A., & Schowalter, W. R. (1989). *Colloidal dispersions*. Cambridge, UK: Cambridge University Press.

Sadeghinezhad, E., Kazi, S. N., Badarudin, A., Zubair, M. N. M., Dehkordi, B. L., & Oon, C. S. (2013). A review of milk fouling on heat exchanger surfaces. *Reviews in Chemical Engineering, 29*, 169–188.

Sievanen, K., Huppertz, T., Kelly, A., & Fox, P. F. (2008). Influence of added calcium chloride on the heat stability of unconcentrated and concentrated bovine milk. *International Journal of Dairy Technology, 61*, 151–155.

Singh, H. (2004). Heat stability of milk. *International Journal of Dairy Technology, 57*, 111–119.

Singh, G., Arora, S., Sharma, G. S., Sindhu, J. S., Kansal, V. K., & Sangwan, R. B. (2007). Heat stability and calcium bioavailability of calcium-fortified milk. *Lebensmittel-Wissenschaft und -Technologie- Food Science and Technology, 40*, 625–631.

Vélez-Ruiz, J. F., & Barbosa-Cánovas, G. V. (1998). Rheological properties of concentrated milk as a function of concentration, temperature and storage time. *Journal of Food Engineering, 35*, 177–190.

Walstra, P., Wouters, J. T. M., & Geurts, T. J. (2006). *Dairy science and technology* (2nd ed.). Boca Raton, FL, USA: CRC Press.