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Heat-induced changes in dairy products containing sucrose

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ABSTRACT

The aim of the present work was to analyse the influence of the variables reaction temperature, casein–sucrose ratio and pH, on the kinetic parameters of gelation reactions, the gelation time and the functionality of casein micelles in concentrated milk systems containing sucrose.

Global constant rate reaction order of gelation and were calculated, the first varying between four different orders of magnitude and the second between 1 and 7.

Mathematical models allowing the prediction of gelation time with a good fit ($r^2 > 0.94$) were obtained.

Activation energy (E_a) for gelation decreased as pH decreased. In presence of sucrose, E_a values showed a higher temperature dependence. Gel functionality showed to be pH independent. Although the kinetic aspects of the reactions were affected by pH, the thermodynamic ones remained almost unchanged. Aggregation and gelation were very fast at pH 6. When comparing gelation kinetics with those corresponding to fluorescence and colour development, gelation showed to be produced much earlier than the latter two phenomena.

1. Introduction

At temperatures above 100 °C, the thermal process of concentrated dairy systems containing sucrose induces thermal gelation of milk proteins (Pauletti, Castelao, & Seguro, 1996), which defines the texture of products such as milk jam (dulce de leche) and condensed milk, either during manufacture or sterilization (Moro & Hough, 1985).

Several authors have studied certain characteristics corresponding to this type of systems, such as density (Moro & Hough, 1985), rheological properties (Navarro, Ferrero, & Zaritzky, 1999) and colorimetric aspects (Rozycki, 1999, 2003). However, little research has been carried out on the influence of sucrose on gelation, fluorescence and colour development phenomena and on the comparison of the kinetics of these processes.

Comparatively, much more work has been performed on heat induced gelation of whey proteins, or on by acid and enzymatic induced gelation in milk, than on thermal gelation of milk proteins (Considine, Patel, Anema, Singh, & Creamer, 2007; Lucey, 2002). Moreover, various authors have studied heat-induced gelation of milk and dairy concentrates (Fox, 1981, 1982; McSweeney, Mulvihill, & O'Callaghan, 2004) but there has not been an in-depth investigation on sucrose effect yet. The knowledge of kinetic parameters corresponding to heat-induced gelation processes, such as the specific global constant of gelation reaction rate (k), its global pseudo-order of reaction (n) and its activation energy (E_a) are necessary to design continuous production equipments both for heat-gelified dairy products (milk jam – dulce de leche –, sterilized condensed milk) and those products in which this phenomenon is not desired (ice cream base, dairy desserts).

The most influential variables in the gelation processes of these systems are temperature (T), pH and protein concentration, which is determined by casein–sucrose ratio, here represented by R (the relative amounts whole milk powder (WMP)/sucrose (Rozycki, 1999).

Micellar hydration, related to zeta potential, is of great importance in gelation, its mechanism involving a kinetic scheme of controlled reaction where big particles react much faster than small ones. This leads to an "explosive" increase of aggregate size (Clark, 1992) where protein molecules, on hydration, increase their hydrodynamic volume and consequently the aggregation rate and gelation.

The main feature characterising the cascade mechanism applied to polymers is that each molecule or molecule aggregate has a number of reactive groups (f) which are able to join other molecules to form branched systems. As the process advances, cross-links between non-reacting branched groups take place, the relative average molecular mass tending faster and faster to infinity and reaching the gel point (Fox, 1982). The gel point was suggested to correspond to gelation time. For monodisperse systems, functionality f takes integer values: $f = 1$ for dimerization, $f = 2$ for linear polymerisation and $f = 3$ for branched polymerisation.

Under certain conditions, colour presents an induction period where colourless though fluorescent precursors occur, followed

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by intermediate steps with brown, and also fluorescent compounds. In the final steps of heating, when the system achieves an intense brown colour (as in dulce de leche), colour formation rate begins to decrease, which is not the case for fluorescence. Hence, the fluorescent compounds would be considered the promoters of brown compounds (Petriella, Resnik, Lozano, & Chirife, 1985) in the initial steps, colour and fluorescence following parallel paths (Matiacevich & Buera, 2006).

As regards colour and fluorescence, numerous sugar–aminoacid model systems have been investigated, mainly under accelerated storing conditions (55 °C), but few have been carried out in "real" food systems, at low water activity a_w = 0.83–0.87 and temperatures above 100 °C, as in this study.

In the present work, the influence of the initial system pH, reaction temperature and casein concentration (R) on the heat-induced gelation process and its governing kinetic parameters was studied, comparing the kinetic aspects corresponding to colour development and fluorescence.

2. Material and methods

2.1. Sample preparation

Table 1 shows each sample formulation. Whole milk powder composition was: 25.05% protein (21.30% casein), 26.45% fat, 40.02% lactose, 6.05% minerals and 2.43% water. Total solids percentage (70%) was kept constant. Casein concentration of each sample, calculated from the whole milk powder (WMP) content was: 3.41%, 4.90%, 5.96%, 6.92% and 7.67%.

R value was defined as the ratio WMP/sucrose. The samples were obtained by mixing whole milk powder, sucrose and distilled water at 45 °C during 4 min, using a magnetic stirrer. The pH was adjusted with calcium hydroxide p.a. and/or lactic acid 1:10, as necessary.

2.2. Experimental design

To evaluate the influence of temperature, pH and R on gelation time, a factorial experimental design (Montgomery, 1991) involving two variables (T and R) in five levels and three pH values (6, 7 and 8) was selected. Table 2 shows coded and uncoded variable values.

After adjusting the pH to the desired value, about 2 g of each sample were put in Pyrex glass flame-sealed tubes (150 mm length, 8 mm inner diameter and 1 mm wall thickness). Three samples (replicates) of each formulation were taken and their individual gelation times were determined (gel point) at the five design temperatures. The same procedure was applied for pH 6, 7 and 8 and every experience was carried out in duplicate. Gelation time was obtained from the average of the times corresponding to replicates of at least two determinations (α = 0.05).

2.3. Determination of gelation time (t_g)

Each sample tube was put in an oscillating system of 5 cycle/minute, inside a thermostatic bath of silicon oil (Haake DC3, Karlsruhe, Germany) at controlled temperature (+0.1 °C). To determine t_g, the Subjective Test of Heat stability (Fox, 1982), proposed by Hyslop and Fox (1981), was used. Each tube was subjected to a complete oscillation every 12 s, the originally liquid mix flowing from one tube end to the other at 10 times per minute and twice per cycle. Gelation time, which is the time ranging from sample introduction into the bath and the occurrence of fluidity loss due to gelation, was visually determined.

Table 1
Composition of the formulations employed.

Content (g)	Samples				
	A	B	C	D	E
Sucrose (%)	54	49	44	39	34
WMP[a] (%)	16	21	26	31	36
Water (%)	30	30	30	30	30
R [b]	0.296	0.429	0.591	0.795	1.059

[a] WMP = whole milk powder.
[b] R = ratio WMP/sucrose [% w/w].

2.4. Colorimetric evaluation

Colorimetric measurements of each sample were made using non-standard white and black cylindrical plastic cells (28 mm diameter, 4 mm high). The reflectance values for 450, 560, and 685 nm were determined to obtain the Kubelka–Munk index (K/S) using the SBRT software (Shelf Backing Reflectance Transformation software) appropriate for small samples (Rozycki, 1999). Measurements were made using a Minolta CM 508d spectrophotometer with illuminant C, 2 degrees standard observer angle and specular component excluded.

2.5. Fluorescence and optical density measurements

Three gram of each sample were exactly weighed, mixed with about 15 ml of 80% ethanol (Park & Kim, 1983) and shacked at 150 agitation cycles per minute, during 30 min. The samples were filtered twice through filter paper in order to obtain a clear solution. Optical density (OD) at 420 nm was measured in an aliquot of this solution with a Génesis 5 UV–Visible spectrophotometer (Spectronic Instruments, Inc., Rochester, NY, USA). Another aliquot (1 ml) was diluted 10-fold with bi-distilled water and fluorescence was determined in a Biorad Versafluor fluorimeter TM, excitation maximum at 380 nm and emission maximum at 465 nm, employing a standard solution of quinine sulphate quinina, of 1 μg/ml de SO_4H_2 0.1 N (Park & Kim, 1983), which fluorescence value was 1435 UF (fluorescence units), as an average of triplicate measurements. The fluorescence of each sample was referred to as a percent of this reference.

2.6. Chemical determinations

Casein concentration was determined in a reconstituted sample of whole milk powder (13% total solids) and water, using a FIL-IDF standard method (International Dairy Federation, 1964). To determine pH, an E516 pHmeter (Metrom Herisau, Switzerland) was used.

2.7. Water activity determination

Water activity (a_w) was measured at 25 °C, in coded samples ($X_2 = X_3 = 0$), and for $R = -1$, 0 and +1 (Table 2). The equipment used was AQUA Lab – CX-2T (Washington, USA).

2.8. Functionality determination

Average functionality of casein monomers (f) was determined from the kinetic equations below, in accordance with Pauletti et al. (1996):

$$\ln t_g = [\ln(B/k)] - [(n-1)\ln C_o] \quad (1)$$

$$\ln k = \ln A - E_a/RT \quad (2)$$

$$\ln k/B = \ln A/B - E_a/RT \quad (3)$$

where t_g = gelation time [min]; C_o = casein concentration [% w/w]; k = specific global reaction rate coefficient [g casein^{-1} min^{-1}];

Table 2
Values of coded and uncoded variables.

WMP (%)	Sucrose (%)	X_1[a]	X_1 (coded)	X_2[b]	X_2 (coded)	X_3[c]	X_3 (coded)
16	54	0.296	−1	378	−1	6	−1
21	49	0.429	−0.5	388	−0.429		
26	44	0.591	0	395.5	0	7	0
31	39	0.795	+0.5	403	+0.429		
36	34	1.059	+1	413	+1	8	+1

[a] $X_1 = R$ = ratio WMP/sucrose.
[b] $X_2 = T$ = temperature (K).
[c] X_3 = pH.

n = global pseudo-order of reaction (adimensional); E_a = activation energy [kJ/mol].

B parameter is defined according to the following equation:

$$B = \frac{\left[\frac{f-1}{f-2}\right]^{n-1} - 1}{(n-1)\cdot f^{n-1}} \quad (4)$$

If B/k and n are known for every temperature, functionality can be obtained from an iterative process, since f value satisfies Eqs. (2)–(4).

2.9. Statistical analysis

Results were subjected to a multiple regression and variance analysis (Statgraphics Plus 3.0, 1994), t Student tests being used to determine the coefficient significance and standard error ($p > 0.95$). To determine multiple correlations between t_g and the design variables, Table Curve 3D (1993) program was used.

3. Results and discussion

For any R and pH studied, gelation times decreased as heating temperature increased, as shown in Fig. 1a–c for the samples with the different R (0.291, 0.678, and 1.059), and at initial pH values 6, 7 and 8. Temperature increase encourages several chemical changes in casein micelles, which result in their irreversible aggregation. These changes are probably related to whey protein denaturation, casein complex formation, Ca^{++} saturation in the soluble phase, and the resulting pH decrease (Fox, 1982).

Casein accounts for approximately 80% of bovine milk proteins and casein micelles constitute the basic blocks conforming the milk gel. The position of κ-casein on the micelle surface has a fundamental meaning in the gelation process (Horne, 1998). When milk is treated at temperatures above 70 °C, the different whey proteins inter-react in a very complex way, and soluble complexes are formed in the first stages, which act as intermediates in the association of β-lactoglobulin the casein micelles (Corredig & Dalgleish, 1999; Anema, Lowe, & Li, 2004) and with α-lactalbumin, which then precipitate on the surface of the casein micelles. Heat treatment markedly affects the interactions among whey denatured proteins, and among them and with the casein micelles. As shown in Fig. 1, gelation times were very high at 105 °C (278 K), and, in the case of samples with the lowest protein and the highest sucrose proportions (lowest R values) studied, gelation was still not complete after 3 h of heating.

As R increased, the gelation times decreased, regardless of the pH or temperature. This is due to the fact that at higher R values, the casein percentage in the medium is higher, which in turn increases, by cross-linking, the proportion of reactive sites involved in the gelation process (Donato, Guyomarch, Amiot, & Dagleish, 2007). Also, an increase of sucrose proportion (R decrease) resulted in an increase of the gelation time, which could be partly explained by the capacity of sugars to delay heat-induced protein denaturation (Carpenter, Chang, Garzón Rodríguez, & Randolph, 2002; Passot, Fonseca, Alarcon-Lorca, Rolland, & Marin, 2005), which, as discussed before, is fundamental for the gel development. Thus, as the relative amount of sugar decreases (R increases) it is expected that proteins are more subjected to denaturation and consequently to develop the different stages leading to gel formation.

As previously discussed, denaturation of whey proteins, and, particularly of β-lactoglobulin is the necessary initial step which allows the formation of a tri-dimensional network in milk (Donato et al., 2007). However, the modifications occurring on the surface of the casein micelles are also of fundamental importance (Anema & Li, 2003). These modifications are manifested by changes in the micelle volume, which are sensitive to even slight pH modifications (Anema & Li, 2003).

When comparing samples with the same composition and treatment temperatures, gelation times were very low (usually below 1 min) for samples with initial pH 6 (Fig. 1), and the highest gelation times were obtained for samples with an initial pH 7, since this pH is very close to that of maximum casein thermal stability (Walstra & Jenness, 1987a, chap. 17). Gelation times of samples with initial pH 8 were higher than those obtained for pH 6, though lower than those for pH 7.

Anema and Li (2003) showed that at pH 6.5, about 70% of denatured whey proteins are associated to the casein micelle, and the degree of association decreases as increasing pH. Thus, it could be expected that at pH 8 the gelation times would be the highest. However, the low gelation times observed at pH 8 (compared to those at pH 7) could be a consequence of the fact that alkaline conditions promote the kinetics of browning reactions, which contribute to a marked and faster pH decrease (Buera, Chirife, Resnik, & Wetzler, 1987) than those obtained with samples of initial pH 7, and, consequently, to a shorter gelation time. Sugar hydrocarbon chain fragmentation and heat-induced acid generation from lactose were reported to occur during heating, contributing to the acid formation and pH decrease (Fox, 1982; Rozycki, 1999). The faster pH decrease at pH 8 than that occurring at pH 7, would lead to gelation in a shorter time. There seems to be a kind of competition between the rate of pH decrease, caused by Maillard reaction, and the narrowness of conditions for the point of highest micelle stability.

pH has also opposite effects on sucrose hydrolysis (which is favoured at acid pHs (Flink, 1983)) and on Maillard reaction (which is favoured at neutral pHs) and a compromise between both types of reactions was reported (Buera et al., 1987). The values of (B/k) from the ordinate to the origin, and of $(n-1)$ from the slope, were obtained for all casein concentrations, with good correlation coefficients ($r^2 > 0.94$) for the different heating temperatures and pH values under study. Table 3 shows the kinetic parameter values (n, k and B).

As discussed before, at pH values 7 and 8, the kinetic parameters for gelation, B and n, were very similar, probably by a partial compensation of the above-mentioned effects.

The high values of n (Table 3) show the complexity of the reactions involved and the diversity of the changes produced (Walstra

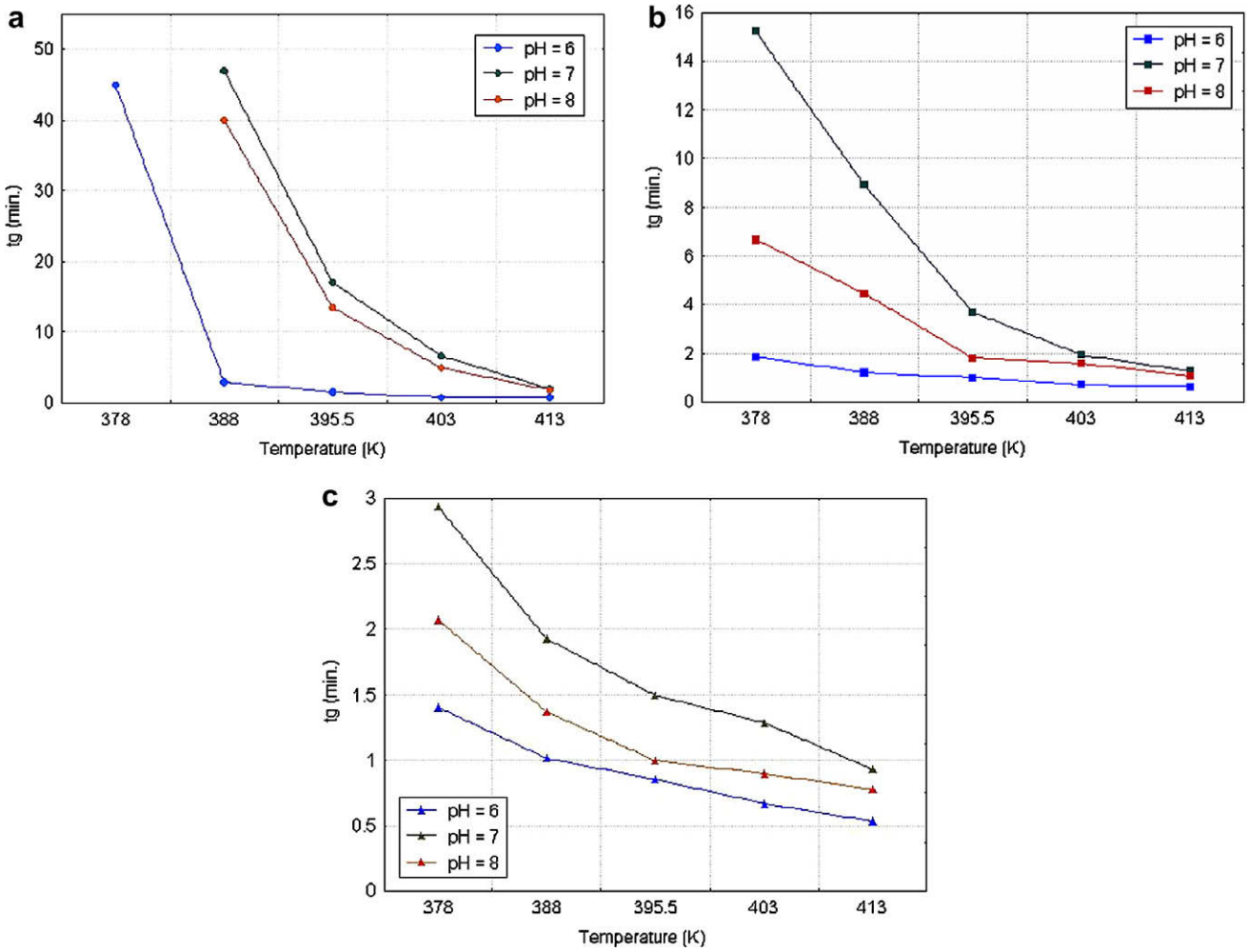

Fig. 1. Gelation time vs. temperature for samples with whole milk/sucrose ratios (R): $R = 0.291$ (a); $R = 0.678$ (b) and $R = 1.059$ (c), at different pH values.

Table 3
Kinetic parameters for the heat-induced gelation process, at different pH values.

pH	T (K)	n	B	k^a	P	s.e.	r^2
6.0	378	4.326	1.309	1.574E−03	0.014	1.099	0.947
	388	1.776	1.162	2.475E−01	0.019	0.282	0.948
	395.5	1.710	1.170	3.389E−01	0.001	0.103	0.979
	403	1.397	1.219	1.175	0.000	0.024	0.985
	413	1.241	1.250	1.235	0.007	0.060	0.949
7.0	378	6.214	0.983	8.529E−06	0.000	0.285	0.997
	388	5.180	0.882	8.792E−05	0.001	0.719	0.970
	395.5	4.092	0.833	1.212E−03	0.000	0.382	0.984
	403	3.089	0.847	1.115E−02	0.002	0.417	0.960
	413	1.981	0.960	1.444E−01	0.000	0.087	0.992
8.0	378	6.950	0.857	3.386E−06	0.002	0.935	0.975
	388	5.616	0.764	6.078E−06	0.002	0.703	0.976
	395.5	4.375	0.733	9.493E−04	0.003	0.631	0.965
	403	3.162	0.770	9.620E−03	0.000	0.210	0.989
	413	1.020	0.903	1.343E−01	0.001	0.149	0.978

s.e. = standard error.
[a] $(\text{g casein } 10^{-2}\ \text{g}^{-1})^{1-n}\ \text{min}^{-1}$.

& Jenness, 1987a, 1987b, chaps. 17, 10.2). Since thermal treatment at high temperatures can promote changes in the reaction mechanisms of the simultaneous reactions that take place, this could significantly influence n values (Villota & Hawkes, 1992, chap. 2).

The average casein micelle functionality (f), related to reactive sites in the casein micelles was calculated for all the samples by the method proposed by Pauletti et al. (1996). The f values obtained were the following: 2.37 (pH 6), 2.43 (pH 7) and 2.45 (pH 8), reflecting no significant changes on the average functionality of casein monomers when varying the mixture initial pH between 6 and 8. However, as shown in Table 3, k values at pH 6 were much higher than at pH 7 and 8. This could indicate that the pH 6 has a marked influence on the kinetic aspects of gelation reactions (k), but it does not significantly affect the thermodynamic aspects of gelation.

Consequently, the number of reactive (directly related to functionality f) sites per protein molecule is higher than 2 ($f > 2$) and it remains almost unchanged when varying pH between 6 and 8. It can be thus proposed that cross-linked branched polymers develop due to the thermal treatment, generating a three dimensional protein network involving the whole system, similar to other systems with whey and egg proteins (Rector, Matsudomi, & Kinsella, 1991).

The evolution of water activity (a_W) with reaction time was analysed in three samples, varying R between 0.296 and 1.059, keeping T (122.5°) and pH (7) constant and the results are shown in Table 4. At initial time (time = 0), as expected, a_W was lower as lower was the R value (higher the sucrose proportion). However, regardless of R, water activity decreased with increasing reaction time, which implies that as heating progresses, polymer–solvent interactions prevail over polymer–polymer one (Katsuta, Rector, & Kinsella, 1990). The solvation of the micelles, increases the hydrodynamic protein volume by increasing their "effective" radius which, according to the statistical gelation theory, would turn them more gelation reactive. Thus, the presence of sucrose limit

Table 4
a_W vs. reaction time, at $X_2 = X_3 = 0$.

t_g = 30–35 min[a]		t_g = 2.66 min		t_g = 1.3 min	
Time (min)	a_W ($R^b = -1$)	Time (min)	a_W ($R = 0$)	Time (min)	a_W ($R = +1$)
0	0.849	0	0.868	0	0.898
15	0.846	1.50	0.861	0.87	0.886
30	0.844	2.66	0.857	1.30	0.877
45	0.842	25	0.856	22	0.874
60	0.841	50	0.854	44	0.872

$X_2 = T$ (K).
X_3 = pH.
[a] Relatively noticeable gelation.
[b] R = LPE/sucrose (WMP = whole milk powder).

the water availability for micelle surface hydration, necessary for gelation to occur (Boye, Alli, Ramaswamy, & Raghavan, 1997). This would partly account for the fact that the higher the R (and the lower the S) values, the lower t_g and the more the amount of gelation reactive sites due to the increase in protein concentration.

By representing $\ln(k/B)$ for every pH as a function of $1/T$, straight lines were obtained (Fig. 2), and the obtained activation energy values resulting from their slopes are shown in Table 5.

The E_a values of the studied concentrated milk samples (Table 4) are more than twice higher than those corresponding to milk (100–120 kJ/mol), according to Pauletti et al. (1996). This effect can also be due to the sucrose–protein interaction, which increases micelle stability.

E_a values were significantly lower for the samples at pH 6 than for those at pH 7 and 8, which were similar. The little dependence on temperature for the samples at pH 6 may be associated to the fact that, at working temperature, there is a closer proximity in these samples to the optimum gelation pH for the concentrated milk. This could indicate that at pH 6 a different gelation mechanism could operate from that in the samples at PH 7 and 8.

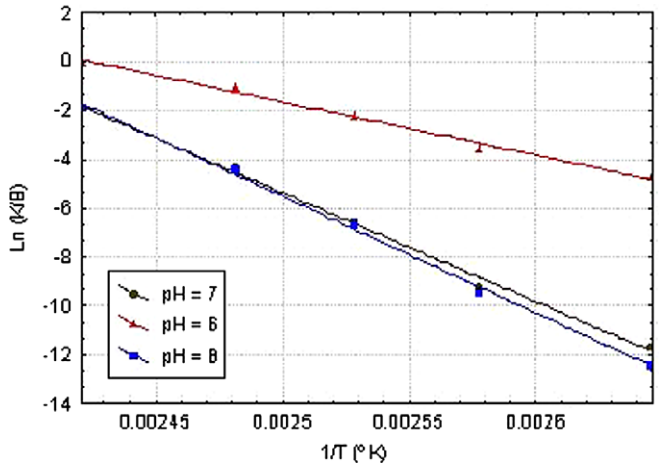

Fig. 2. Arrenhius plot for the gelation rate constants at different pH values.

Table 5
Activation energies and network formation energies values at different pH values.

pH	E_a[a] (kJ/mol)	r^{2b}	s.e.[c]	B^{*d}	r^{2b}	s.e.[c]
6.0	233.5	0.89	13.043	2,45,978	0.858	6953
7.0	371.3	0.996	4.274	3,69,285	0.995	1804
8.0	398.2	0.997	3.605	4,16,753	0.972	4883

[a] E_a = activation energy.
[b] r^2 = correlation coefficient.
[c] s.e = standard error.
[d] B^* = energy associated to network formation (kJ/mol).

Kim and Kinsella (1989) have defined the network formation energy, B^*, starting from a linear, Arrhenius-type, model

$$\ln k = \ln A - B^*(1/T) \quad (5)$$

where A = frequency factor; B^* = network formation energy.B^* is associated to the amount of consumed energy that is required for the network formation during gelation: as higher is B^* value, gelation is slower, thus favoring a wider micelle–micelle interaction and a denser network structure (Kim & Kinsella, 1989).

Using k values calculated above (Eqs. ((1)–(3)), and relating them with $(1/T)$ (Eq. (5)) by means of the linearisation method, B^* values are obtained from the slope of the straight lines, and are also shown in Table 5.

The analysis of these values shows that as the E_a values, the energy needed to form the network (B^*) increases with pH, being at pH 6 half the value of that at pH 8, and that energy is very similar for pHs 7 and 8.

By applying a multiple regression analysis (Statgraphics, 3.0) to the gel times and design variables (T, R and pH), the mathematical model represented by Eq. (6), which allows t_g value prediction, was obtained.

$$t_g = 4.681 - 11.255 \cdot X1 - 12.248 \cdot X2 + 3.510 \cdot X3 + 7.882 \cdot X12 + 9.755 \cdot X22 + 6.828 \cdot X32 + 17.481 \cdot X1 \cdot X2 - 4.870X1 \cdot X3 - 4.830 \cdot X2 \cdot X3 \quad (6)$$

($r^2 = 0.812$; standard error of estimation = 9.8515).

Linear regression coefficients show t_g to vary inversely with R and reaction temperature, gel time decreasing when casein proportion and temperature increase. Also, t_g is directly affected by initial pH, t_g decreasing when pH decreases.

When comparing linear and quadratic regression coefficients, it was observed that temperature was the most influential individual variable, though the influence of temperature–R interaction was also important.

In order to obtain simpler gel time prediction equations, and also a better fit, the regression analysis of experimental data (Table Curve 3D) as a function of two variables was carried out, at pH 6, 7 and 8, respectively. The following mathematical models were obtained ($r^2 > 0.94$):

$$\ln t_g = -3.661 + 1.356 \cdot e - X1 + 1.388 \cdot e - X2 \quad \text{pH6} \quad (7)$$

$$\ln t_g = 3.700 - 4.579 \cdot X1 - 1.936 \cdot e - X1 - 1.526 \cdot X2 \quad \text{pH7} \quad (8)$$

$$\ln t_g = 3.107 - 4.389 \cdot X1 - 1.705 \cdot e - X1 - 1.553 \cdot X2 \quad \text{pH8} \quad (9)$$

Heating affects the rate of two processes which mutually influence each other: gelation and non-enzymatic browning processes. The pH decrease promoted by non-enzymatic browning reactions affects system gelation. Gelation, in turn, causes variations in transport properties and sucrose hydrolysis kinetics, which influences directly and indirectly the kinetics of browning reactions.

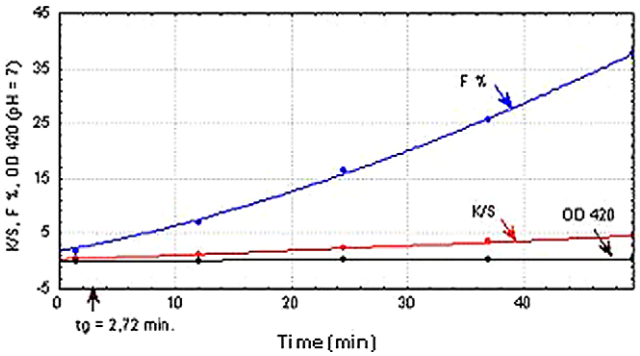

Fig. 3. Fluorescence, Kubelka–Munk index and optical density for the samples of $R = 0.591$, at pH 7, as a function of time. The arrow indicates the gelation time.

However, gelation and browning reactions have different kinetics, as activation energy and reaction pseudo-order values show (Rozycki, 1999).

In order to compare the kinetics of the gelation process in parallel to the non-enzymatic browning development, the browning indicators fluorescence (F), optical density at 420 nm (OD_{420}) and the Kubelka–Munk colour function K/S were measured and represented as a function of time. Fluorescence (F) presented higher sensitivity than the other colour functions or absorbance readings employed to follow browning development, as shown in Fig. 3, for the samples of $R = 0.591$, at pH 7. The corresponding gelation times (t_g), indicated as arrows noticeably show that the system gelation (at $T > 105$ °C) occurs much earlier than colour development can be appreciated, whereas fluorescence is clearly detected from the beginning of the reaction. It is concluded that both gelation and browning processes could be separated, as well as their individual design and control, which can be employed for the continuous production of concentrated and sucrose dairy products, whose organoleptic and texture characteristics would vary according to their future application.

4. Conclusions

The present work has shown temperature to be the most influential individual variable on the thermal-induced gelation of milk in the presence of sucrose. At temperatures close to the boiling point, at atmospheric pressure, both gelation and browning processes are slow and even below a certain proportion of milk solids there is no convenient system gelation. Also, the presence of sucrose increases gelation rate and its dependence on temperature.

At pHs 7 and 8, the system shows a similar behaviour, though sensibly different from that at pH 6, which shows the possibility of a change in the mechanism of the reactions involved in the gelation process.

The pH variation studied has no apparent influence on the thermodynamic aspects of gelation reactions and the average functionality of casein micelles, though it does influence the process kinetics, aggregation and gelation being fast at pH 6.

The mathematical models obtained were adequate to predict the system behaviour as far as its stability is concerned, combining technological variables commonly used in the industry.

pH was shown to noticeably affect the firmness and structural density of dairy gels obtained, these characteristics increasing at higher pHs (pH 8) since they produce a less fast (controlled) rate which allows a minimum heating time needed for establishing a higher number of bonds and the subsequent gel "reaffirmation".

System gelation occurs much earlier than the development of a noticeable brown colour.

These aspects are very useful for the development of continuous methods to obtain concentrated and sucrose products of different organoleptic and texture characteristics, for the optimisation of the designed processes, and the formulation of new products.

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