HAL
open science

Ionic strength dependence of skimmed milk microfiltration: Relations between filtration performance, deposit layer characteristics and colloidal properties of casein micelles

Anne Jimenez-Lopez, Nadine Leconte, Fabienne Lambrouin, Antoine Bouchoux, Florence Rousseau, Geneviève Gésan-Guiziou

To cite this version:

Anne Jimenez-Lopez, Nadine Leconte, Fabienne Lambrouin, Antoine Bouchoux, Florence Rousseau, et al.. Ionic strength dependence of skimmed milk microfiltration: Relations between filtration performance, deposit layer characteristics and colloidal properties of casein micelles. Journal of Membrane Science, 2011, 369 (1-2), pp.404-413. 10.1016/j.memsci.2010.12.026 . hal-01454151

HAL Id: hal-01454151

https://hal.science/hal-01454151v1

Submitted on 25 Sep 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ionic strength dependence of skimmed milk microfiltration: Relations between filtration performance, deposit layer characteristics and colloidal properties of casein micelles

A.J.E. Jimenez-Lopez[a,b], N. Leconte[a,b], F. Garnier-Lambrouin[a,b], A. Bouchoux[a,b], F. Rousseau[a,b], G. Gésan-Guiziou[a,b]

[a]INRA, UMR1253 Science et Technologie du Lait et de l'Œuf, F-35042 Rennes, France

[b]AGROCAMPUS OUEST, UMR1253 Science et Technologie du Lait et de l'Œuf, F-35042 Rennes, France

Abstract

Crossflow microfiltration (0.1 µm) of skimmed milk is largely used in the dairy industry. The overall performance of the process is governed by the accumulation of casein micelles at the membrane surface, which leads to the formation of an irreversible deposit (= a gel) in critical hydrodynamic conditions (CHC). To control the filtration performance, it is then necessary to understand how the micelles accumulate at the membrane and how they interact with each other during accumulation. In that aim, microfiltration of skimmed milks is performed at different ionic strengths (NaCl addition 0-0.3 M) and the properties of the casein micelles deposit are determined in each case in terms of structuration, transmission properties and fouling resistances. Upon addition of salt, our results indicate that the casein micelles turn into a gel at a lower "critical" casein concentration than with native milk. With the increase in ionic strength, the deposit is also more cohesive and harder to remove from the membrane. Finally, the addition of NaCl results in a change in the selectivity of the process, with a decrease in the overall protein transmission through the deposit layer. All these results are explained through a shift in the balance of interactions between and within the micelles as ionic strength is changed. They are also very consistent with the generic colloidal behavior of casein micelles as determined through osmotic stress experiments.

Keywords
Microfiltration, skimmed milk, ionic strength, fouling, colloidal interactions

Corresponding authors: anne.jimenez@rennes.inra.fr; genevieve.gesan-guiziou@rennes.inra.fr

1. Introduction

Skimmed milk is a complex mixture classically described as a suspension of casein micelles (association of α_{s1}, α_{s2}, β, and κ-caseins with an average radius of 100 nm, 26 g L^{-1}) in an aqueous phase containing soluble proteins (mostly β-lactoglobulin and α-lactalbumin, with an average radius of ~5 nm, 7 g L^{-1}), minerals (mostly calcium and phosphate, 8 g L^{-1}), and lactose (50 g L^{-1}). Casein micelles are negatively charged colloids in balance with the aqueous phase. Physico-chemical modifications of milk, such as changes in ionic strength which is classically performed in the dairy industry, induce direct changes in casein micelles characteristics in terms of average diameter, charge, hydration, mineral and protein composition [1]. This particular behavior makes it difficult to control the various operations used in dairy processing.

Crossflow microfiltration (0.1 μm) of skimmed milk is largely used in dairy industry to separate casein micelles from soluble proteins in order to produce a retentate enriched in casein micelles and a permeate enriched in soluble proteins, minerals and lactose [2,3]. The overall performance of the process, in terms of permeability and selectivity, is governed by the accumulation of the casein micelles at the membrane surface [4-6]. As in colloid filtration, the matter accumulated in the concentration polarization layer turns into an irreversible deposit (= a gel) under given operating conditions commonly named "critical hydrodynamic conditions" (CHC) [4,7-10]. In terms of performance, the CHC correspond to the transition between steady runs, i.e., high transmission of soluble proteins and low fouling resistance, and divergent runs, i.e., sharp decrease in transmission of soluble protein with high and irreversible fouling resistance [4,11]. The CHC can be defined through the critical ratio $(J/\tau_w)_{crit}$, corresponding to the ratio between convective mass transport towards the membrane, related to the permeation flux J, and the so-called "back-transport" from the membrane to the bulk, related to the wall shear stress τ_w [5,12].

To control the performance of skimmed milk microfiltration, it is necessary to determine the mechanisms behind the CHC and so to understand how the casein micelles accumulate at the membrane and how they interact with each other until forming a gel. To explore these questions, one approach consists in modifying the physico-chemical characteristics of the casein micelles and investigating the changes in the filtration performance. To this respect, interesting results have already been obtained by changing the composition of the milk and performing filtrations [13-16]. For instance, the addition of citrate to milk increases dramatically the total and irreversible fouling resistance in filtration. This is presumably because citrate induces a decrease in the casein micelles diameter and consequently leads to a deposit of lower porosity and membrane pore blocking [14,16]. Decreasing the milk pH down to 5.5-5.6 or adding high concentrations of NaCl up to 0.4-0.7 M is also known to decrease the "limiting" and "critical" flux during skimmed milk filtration [15,16] and to increase the fouling resistance remaining after filtration [13,14,16]. These results are mainly explained through the decrease in the average surface charge of the casein micelles (measured through the casein micelles zeta potential), leading to lower electrostatic repulsion forces between them. More recently, Kühnl *et al.*, [13] propose an explanation based on a shift in the balance between hydrophilic repulsion and hydrophobic attraction between the micelles as the pH is lowered.

In our opinion, the studies mentioned previously still fail in giving clear and unambiguous relationships between the physical properties of the casein micelles and the performance of milk filtration. A first important reason is that the characteristics of the deposit layer (cohesion, dynamic behavior during filtration, transmission properties) are poorly investigated in these works. Such information is crucial if one wants to accurately describe the mechanisms involved during filtration. A second reason is that the nature of the dispersions used in the quoted studies as well as the control of the performed physico-

chemical modifications, are often questionable. Indeed, the solutions used are either strongly heat-treated milks (Ultra High Temperature milks [15]) or milk powder suspended in water [16], i.e., solutions in which the casein micelles are not in their native solvent and/or are not strictly in their "native state". Moreover, in the studies in which the effects of NaCl or citrate are investigated [14,16], the variation of pH resulting from the addition of salts is generally not corrected. For example, the addition of 40 mM of citrate increases the pH from 6.6 to 7.1 which modifies the milk particle size distribution [16]. Also the addition of respectively 700 mM and 920 mM of NaCl to milk leads to a decrease in pH of 0.3 and 0.35 respectively and then results in partial solubilization of colloidal phosphate [15,16]. Then both effects of pH and salt addition on the characteristics of casein micelles cannot be dissociated, which makes uncertain some of the reported interpretations.

This paper focuses on the effect of ionic strength (through NaCl addition) on the performance of skimmed milk microfiltration. In that aim, fresh skimmed milk is used and ionic strength modifications are done with systematic pH adjustment. The properties of the casein micelles in terms of charge, average diameter and calcium content are measured as a function of the ionic strength. Filtrations of unmodified and modified milks are then performed and the properties of the casein micelles deposits are determined (setting up, structuration, transmission properties and fouling resistances). Some additional elements of understanding on the properties of the gel layer are also obtained through a careful treatment of the transmembrane pressures get during the CHC. The results are discussed with respect to the generic colloidal behavior of the casein micelle in concentrated regime as investigated through osmotic stress and rheological measurements [17,18]. Hence this work tends to connect and explain the relations between the physicochemical properties of the casein micelles and the microfiltration performance through a new and original approach.

2. Experimental

2.1. Fluids

2.1.1. Dairy fluids

The present work is performed with heat-treated (68 ± 1 °C, 25 s) skimmed milk obtained from raw milk provided by Entremont Alliance (Montauban de Bretagne, 35, France). After fresh milk is collected (one day before filtration), skimming (50 °C, 315 L h^{-1}, Elecrem type 125, Châtillon, 92, France) and thermal treatment (Actini, Evian les bains, 74, France) are performed at UMR1253. To prevent micro-organism growth, 0.2 g L^{-1} of sodium azide is added to the milk.

The ionic strength is increased by direct addition of NaCl (0 – 0.3 M, Fisher Scientific) at room temperature, under strong stirring. During the procedure, the pH variation is simultaneously corrected through the addition of small amounts of 2 M NaOH solution (the induced milk dilution is negligible with a dilution factor < 6 10^{-3}). The final ionic strength, after addition of 0, 0.085, 0.175 and 0.300 M of NaCl, is estimated to be 0.072, 0.157, 0.247 and 0.372 M in equivalent NaCl concentration (the estimation of ionic strength in equivalent NaCl has been checked through conductivity measurements [19]). All these physico-chemical modifications are performed the day before the microfiltration in order to reach the equilibrium state between the micellar and aqueous phases. The modified milk is then stirred one night at room temperature and the following day, the milk is warmed at 48°C (classic temperature used in the dairy industry for milk filtration) and then stirred for 1 hour before filling the microfiltration loop.

In all this work, unmodified milk and modified milks have comparable protein composition with a concentration in casein micelles of 26 ± 1 g L^{-1} and a concentration in total soluble proteins of 6.4 ± 0.3 g L^{-1}.

2.1.2. Water and cleaning solutions

The water used to warm up the installation to 48 °C before the experiment and to rinse the filtration rig after filtration is filtered on serial cartridges of 1.0 and 0.2 µm. The rinsing phase is performed in crossflow mode according to the method previously described by Jimenez-Lopez *et al.* [5].

Cleaning is performed at 50°C according to a procedure previously described [5]. Two detergent solutions are used: Ultrasil 25 F 1 % (v/v) (alkaline solution, Henkel-Ecolab SNC, Issy les Moulineaux, 92, France) and nitric acid (acid solution, HNO_3; 58% purity) at 1% (v/v) (Langlois Chimie, St Jacques de la Lande, 35, France). Permeation flux is systematically recovered (± 5 %) after cleaning.

2.2. Microfiltration set-up

2.2.1. Membrane

The membrane used is a 0.1 µm tubular ceramic Kerasep™ membrane with 7 channels (NOVASEP PROCESS, 01, France) and an active layer of ZrO_2 + TiO_2: membrane area = 0.0744 m^2, inner channel diameter = 4.13 ± 0.02 mm, length = 0.856 m. The hydraulic resistance of the clean membrane is $0.14 \pm 0.02 \times 10^{12}$ m^{-1}, as determined through Darcy's law.

2.2.2. Filtration rig

The experimental rig, previously described [5], is fitted out with a uniform transmembrane pressure system (circulation of the permeate co-current to the retentate) in order to avoid any transmembrane pressure (TMP) difference along the hydraulic path [20]. This allows performing experiments at high τ_w and low and homogeneous TMP, simultaneously.

Real time data are monitored and stored by a computer through a data acquisition card. The control software is specially developed with LabVIEW 7.1 (National Instruments, USA) for this filtration rig.

2.3. Operating procedure

The conditions of the deposit set-up and its characteristics are determined following a methodology previously described [5,12]: at constant permeation flux (J) and constant average retentate pressure (P_{AR}), the cross- flow velocity is decreased by steps and increased again by the same steps [6], thus performing successive filtrations at controlled wall shear stresses (τ_w). In these conditions, the TMP becomes a variable, directly related to the fouling phenomenon.

The experiments are performed at 48 °C. After concentration of the casein micelles at a volume reduction ratio (VRR) of 2, the parametric study (= run) is performed. The τ_w is decreased by steps of 30 minutes until reaching the critical hydrodynamic conditions (CHC, $\tau_w = \tau_{wcrit}$) at which a sharp increase in TMP is observed [5]. After ~1 hour at τ_{wcrit}, τ_w is then increased step-by-step in a similar way and using the same values of τ_w that at decreasing τ_w. From 120 to 80 Pa, τ_w is decreased by increments of 20 Pa at 6 Pa min^{-1}. From τ_w = 80 Pa to $\tau_w = \tau_{wcrit}$, in order to be more accurate in the determination of τ_{wcrit}, τ_w is decreased by increments of 5 Pa with a slope of 1 Pa min^{-1}.

The results reported are those obtained for one run with one given membrane. The experiments were repeated and similar results were obtained for the same given conditions (not shown). From the results obtained, the differences in TMP and protein transmission before and after the CHC are evaluated (what we call the "hysteresis" phenomenon in the rest of this work).

2.4. Physico-chemical analyses

2.4.1. Protein contents

The Kjeldahl method is used to determine the concentrations of casein micelles and total soluble proteins in milks, retentates and permeates after adapted preparations of samples. Casein micelles concentration is calculated after determination of total nitrogen (TN) on raw samples and non-casein nitrogen (NCN) after acid precipitation of caseins to their isoelectric point at pH 4.1- 4.6 (casein concentration = TN-NCN). Total soluble proteins are obtained by difference between non-casein nitrogen (NCN) and non-protein nitrogen (NPN) measured after the total protein precipitation with a trichloroacetic acid solution (15 % w/v). The serum proteins concentration obtained with the Kjeldahl method is compared to a chromatographic method of determination of the 5 major soluble milk proteins (RP-HPLC), adapted from Resmini *et al.* [21]. The RP-HPLC is performed using a PLRP-S column (gel of polystyrene divinylbenzene, 300 Å, 8 µm, 150×4.6 mm, Polymer Laboratories, Touzart et Matignon, 22, France). The sum of the concentrations of the 5 proteins obtained through HPLC and Kjeldahl gives similar results with a slight discrepancy (5 - 8 %).

2.4.2. Calcium content

The determination of total and soluble calcium (Ca_{total}, Ca_s) is performed using an atomic absorption spectrophotometer (AA300, Varian France, Les Ulis). The total calcium corresponds to the calcium contained in the casein micelles and in the aqueous phase, whereas the soluble calcium corresponds to the calcium contained in the aqueous phase only. Soluble calcium is measured in the permeate obtained after ultrafiltration of the milks at 48 °C with a laboratory pilot (Filtron GP 141, Pall Gelman Laboratoire, St Germain en Laye, 92, France) using a 5 kg mol^{-1} polyethersulfone plate membrane (Pall Gelman Laboratoire, St Germain en Laye, 92, France).

2.5. Casein micelles characteristics

The average diameter and the electrophoretic mobility (global charge) of the casein micelles are determined in milk at 48 °C prior to filtration. The measurements are performed using the Zetasizer 3000 HS (Malvern, UK) after dilution of the casein micelles fractions in their corresponding aqueous phase obtained through ultrafiltration (5 kg mol^{-1}) with the laboratory pilot described previously.

The turbidity of the microfiltration permeates is measured using a Turbidimeter Hach (2100AN IS, Hach, Namur, Belgium). This turbidity is attributed to a slight leak of casein micelles though the membrane, due to both distributions of membrane pore and micelle sizes [5]. In order to compare the turbidity data, and because there is a slight evolution in the membrane permeability with time, the turbidities are normalized with respect to that of the initial permeate turbidity obtained at $\tau_w = 120$ Pa.

3. Calculations

3.1 Wall shear stress and hydraulic resistances

The wall shear stress, τ_w, is calculated from the inner diameter of the membrane channels as proposed by Le Berre and Daufin [6].

The hydraulic resistances considered in these work are:

- R_m, the resistance of the cleaned membrane corrected by the irreversible fouling resistance which is assumed to be mainly attributed to protein adsorption phenomena that take place during the concentration phase. R_m is estimated from the water flux obtained at the end of an experiment performed in conditions where no deposit was formed. We find $R_m = 0.51\ 10^{12} m^{-1}$ and we assume this value is the same for all our experiments.

- R_p and R_f the polarization layer and the total fouling resistances, respectively. They are calculated from the Darcy's law at $\tau_w = 120$ Pa, at the beginning and at the end of the parametric study, respectively. Thus R_p corresponds to the polarization resistance in given

hydrodynamic conditions in which there is no deposit at the membrane surface. Conversely R_f corresponds to the resistance of the polarization layer (R_p) plus the resistance of the deposit (R_d) built during the run.

- R_d is the resistance of the deposit remaining at the membrane surface at the end of the parametric study. It is linked to R_p and R_d through:

$$R_d = R_f - R_p \quad \textbf{(1)}$$

- R_{id} is the irreversible part of the deposit as determined through Darcy's law [6] after a water flux at τ_w = 120 Pa at the end of the experiment.

- R_{rd} corresponds to the part of the deposit which is eliminated by water rinse after the experiment. It is calculated through:

$$R_{rd} = R_d - R_{id} \quad \textbf{(2)}$$

3.2. Soluble protein transmission (Tr)

The transmission of soluble proteins, Tr, is calculated according to:

$$Tr = \frac{C_P}{C_R} \quad \textbf{(3)}$$

with C_P and C_R (g L^{-1}), the protein concentrations in the permeate and in the retentate, respectively. The calculation of C_P is corrected by the dilution factor of the permeate loop, assuming a perfectly stirred reactor. C_P and C_R are smoothed using the 5 points adjacent averaging method implemented in Origin® 7.5 (OriginLab Corporation, USA). Tr_i and Tr_f are the average soluble protein transmissions for τ_w=120 Pa at the start and the end of the parametric study, respectively (Table 2).

3.3. Characterization of TMP evolution under critical conditions

At the CHC ($\tau_w = \tau_{wcrit}$), sharp TMP oscillations are observed [5], either during the whole period of this "critical" step or during a fraction of this step only. Those variations in TMP are first analyzed according to the two following parameters:

- the overall increase in TMP during the oscillation phase, which is characterized by the slope of the TMP signal versus time after linearization (Sl_{TMP} in Pa s^{-1}) (Fig 1 and 4).

- the ratio $\frac{\Delta t_{osc}}{\Delta t_{crit}}$, which gives the duration of the TMP oscillation phase in comparison with the total duration of the critical step (Δt_{crit}) (Fig 1).

We also characterize the TMP oscillations in terms of total number, frequency, and amplitude. Only the TMP oscillations with amplitudes that exceeded 0.5×10^5 Pa are considered in our calculations (all made using Origin® 7.5).

- the number of oscillations (N_{osc}) is calculated from the number of maxima and minima (N) in TMP values (Fig 1), according to:

$$N_{osc} = \frac{N}{2} \quad \textbf{(4)}$$

- the TMP oscillations frequency (Fr, in s^{-1}) is calculated according to:

$$Fr = \frac{N_{osc}}{\Delta t_{osc}} \quad \textbf{(5)}$$

with Δt_{osc} (s) the duration of the TMP oscillation phase (Fig 3).

- the amplitude of the TMP oscillations (Amp_{osc} in Pa, Fig 1) is calculated according to:

$$Amp_{osc} = \frac{A_{plot}}{\Delta t_{osc}} \quad \textbf{(6)}$$

Assuming that the TMP oscillations are symmetrical over and under the plot of the linear regression TMP = f (t) (Fig 4), A_{plot} corresponds to the filled area between the two plots (Fig 1) as:

$$A_{plot} = \int_{\Delta tosc} TMP(t)dt - \int_{\Delta tosc} (Sl_{TMP} \times t + a)dt \quad \textbf{(7)}$$

4. Results

4.1 Casein micelles characteristics versus ionic strength (I) at 48°C

The increase in ionic strength leads to changes in the characteristics of the casein micelles that are well documented at room temperature: at 20- 25°C, the addition of NaCl to milk leads to the decrease in the global charge of the casein micelle, and to the partial release of the colloidal calcium into the aqueous phase [1,22-25]. However, to our knowledge, the modifications of the casein micelles characteristics in milk are still poorly known in our experimental conditions, i.e., 48°C and NaCl addition with simultaneous pH correction. It is then necessary to characterize the casein micelle modifications in such conditions to make sure that no unexpected phenomenon is induced. The results are presented in Table 1. With the increase in ionic strength (I) from 0.072 to 0.372 M, the casein micelle electrophoretic mobility (which is related to its global electric charge) linearly decreases from 31±1 to 15±1 10^{-7} m^2 s^{-1} V^{-1}, while the concentration in soluble calcium (Ca_s) and the ratio Ca_s/Ca_{total} linearly increase. Regardless of I, the average diameter of the casein micelle is constant at 181 ± 6 nm (Table 1). These observed trends and values are pretty similar to those obtained at room temperature [16,22,24], indicating that no dramatic changes are induced by a 48°C temperature.

4.2 Microfiltration performance

4.2.1. Unmodified milk

Performance of the filtration of unmodified skimmed milk is presented in Fig 2 and Table 2. Before the CHC, in the range τ_w =120-80 Pa, the TMP is stable at 0.12 ± 0.01 × 10^5 Pa and the soluble protein transmission (Tr) is roughly constant at ~65 ± 4%. In the same time, the permeate turbidity increases, indicating a higher transmission of casein micelles through the

membrane. When the CHC are reached (τ_{wcrit} = 55 Pa, Table 2), the TMP quickly increases and starts to oscillate (Fig 2). This increase in TMP lasts all along the CHC phase ($\Delta t_{osc}/\Delta t_{crit}$ = 1, Table 3), with an average slope of 4.25 Pa s^{-1} (Table 3 and Fig 4). We count ~56 of these oscillations, with an average frequency of 0.036 s^{-1} and an average amplitude of 1.6×10^{-8} Pa (Table 3). Still in the CHC, the soluble protein transmission decreases from 65± 4 % down to 25 ± 3 % and the normalized turbidity also sharply decreases from 2.1 to 0.8, indicating a rapid decrease in casein micelles transmission.

After the CHC, the TMP oscillations stop immediately with the increase in τ_w. However, this increase does not fully restore the initial performance of the filtration. Indeed, TMP_f is increased by 66 % (TMP_f = 0.20 10^5 Pa, Table 2) compared to the average transmembrane pressure for τ_w = 120 Pa at the beginning of the parametric study (TMP_i, Table 2). The transmission of the serum proteins is also affected since it decreases from Tr_i = 66±1% to Tr_f = 53±1% at the end of the parametric study (Table 2). This "hysteresis" in TMP and protein transmission indicates that the deposit formed at the membrane surface during the CHC partially remains after the CHC, and this until the end of the parametric study. At this point, the resistance of the casein micelles deposit R_d is about 2 times the resistance of the membrane (Table 2) and R_{id} corresponds to 60 % of the deposit resistance.

After the CHC, the permeate turbidity shows a quite surprising behavior with a strong increase at τ_w = 80-100 Pa and then a global decrease until reaching its initial value (Fig 2). As it is already shown [5], the casein micelles are preferentially accumulated at the membrane surface. Hence, when the τ_w is increased again after the CHC, the sharp and quick decrease in TMP can lead to a “decompression” of the accumulated matter but the casein micelles accumulated do not returned instantaneously into the bulk. This phenomenon can result in a higher casein micelle concentration at the membrane surface and then in the increase in casein micelle transmission after the CHC for τ_w = 80- 100 Pa.

4.2.2. Modified milks

Impact of ionic strength on the overall filtration performance

The filtration performance obtained with modified milks is presented in Tables 2 and 3 and in Fig 3 for the three conditions of I investigated. Regardless of the ionic strength, the TMP is always low (TMP ≈ 0.1-0.2 × 10^5 Pa) and stable before the CHC (120-80 Pa). Also the resistance of the polarization layer (R_p) is pretty much the same at the beginning of each run (Table 2) and this irrespective of I. These results confirm that it is reasonable to compare the deposit resistance between the experiments performed at different I.

It is noticeable that for the higher ionic strength (I = 0.372 M), the TMP shows a quite significant increase (up to 0.5 × 10^5 Pa) at τ_w = 80 Pa (Fig 3 c). This increase is still small compared to what is usually observed at the CHC so that we decided to further decrease the τ_w. But this small increase in TMP suggests that the CHC are more probably located in between τ_w = 80 Pa and τ_w = 72 Pa (Table 2, Fig 3 c).

With the increase in I, and for a constant convective mass transport (J constant) and a similar polarization layer before CHC (Similar TMP), $(J/\tau_w)_{crit}$ decreases from 0.9 to 0.65 (Fig 5). As this critical ratio characterizes the formation of the irreversible deposit of casein micelles [4,5], this indicates that the deposit is formed at higher wall shear stress (τ_w) in high ionic strength conditions. Interestingly, the decrease in $(J/\tau_w)_{crit}$ is linearly correlated to I and then to the electrophoretic mobility of the casein micelles and to the release in soluble calcium (Table 1).

During the CHC, regardless of I, a sharp and quick increase in TMP is observed, as already described with unmodified skimmed milk. However the TMP behavior at the critical step is strongly different according to the level of ionic strength. For I = 0.072 M (unmodified milk) the TMP oscillations are observed all along the critical step ($\Delta t_{osc}/\ \Delta t_{crit}$ = 1), but for I = 0.157 and 0.247 M (Figs 3a and b) the TMP oscillations are observed only during the first part of

the critical step (named TMP oscillation phase, $\Delta t_{osc}/\ \Delta t_{crit}$ = 0.76 and 0.55 for I = 0.157 and 0.247, respectively); after the oscillation phase, the TMP reachs the value of 3.8 10^5 Pa, which corresponds to the maximum transmembrane pressure of the system (average retentate pressure set at 4.0 10^5 Pa and permeate compartment at atmospheric pressure). The TMP oscillations traduce a cyclic phenomenon of set-up/removal of the fouling layers accumulated at the membrane surface explained by a disengagement of the matter which returns into the bulk. A similar phenomenon has previously been observed with spikes of permeation flux during blood filtration [26]. For the highest I (0.372 M), no oscillations are observed ($\Delta t_{osc}/\Delta t_{crit}$ = 0); TMP increases regularly during the first part of the critical step and then finally stabilizes at 3.8 10^5 Pa (Table 3, Fig 3c).

With the increase in I, the number of TMP oscillations decreases from N_{osc} = 56 to 0, the oscillation frequency changes from Fr = 0.036 to 0 s^{-1} and the amplitude of oscillations, Amp_{osc} is multiplied by 10 from I= 0.157 to 0.247 M (Table 3). Moreover, the slope corresponding to the increase in TMP, $Sl_{TMP,}$ calculated before TMP stabilization, changes from 4 to 22 Pa s^{-1} as I increases from 0.072 to 0.372 M (Table 3, Fig 4). Then the higher the ionic strength, the sharper the increase in TMP (Sl_{TMP}), the shorter the TMP oscillations phase, the lower the frequency of pressure fluctuations (Fr) and the larger the amplitude of pressure oscillations (Amp_{osc}) at the critical step.

After the CHC, the TMP decreases as τ_w increases. Interestingly, the higher the I, the more pronounced the pressure hysteresis (Fig 3), indicating a more cohesive deposit. Indeed, the TMP hysteresis (TMP_f-TMP_i, Table 2) increases from 0.08 to 1.70 10^5 Pa for I increases from 0.072 M to 0.372 M (Table 2). This TMP hysteresis is directly correlated to the increase in the total resistance of the deposit that remains at the membrane surface at the end of the parametric study (R_d = 0.98 10^{12} m^{-1} for unmodified milk to 19.38 10^{12} m^{-1} for milk at I= 0.372 M, Table 2). The absolute values of both the irreversible (R_{id}) and the reversible (R_{rd})

parts of this total resistance increase with ionic strength. However, the increase in R_{rd} is much more pronounced as R_{id} and R_{rd} is multiplied by 4.9 and 43.2 respectively for I = 0.072 to 0.372 M. As a result, R_{rd} represents 40 % of the total resistance for the unmodified milk, versus 84-90 % for I = 0.157-0.372 M (Table 2).

Impact of the increase in I on protein transmission

Before and during the CHC, the normalized turbidities and soluble protein transmissions show similar evolutions at all the ionic strengths investigated. Before the CHC, the casein micelles transmission regularly increases with a maximum at the beginning of the critical step and then sharply decreases during the critical step. Before the CHC, the soluble protein transmission is constant around 65-70 % (Figs 3) and then sharply decreases when the CHC are reached. The higher I, the lower Tr at the critical step: the average Tr is 38 ± 11 % for the unmodified milk , 33 ± 3 % for the milk at 0.247 M and 25 ± 5 % for the milk at 0.372 M.

After the CHC, the turbidity evolutions are different between the unmodified milk and the modified ones. Indeed for the unmodified milk the turbidity increases with the re-increase in τ_w, while for the modified milks, the turbidity regularly decreases down to 0.1 NTU (casein micelles concentration in permeate < 0.6 10^{-3} g kg^{-1}), indicating an irreversible alteration of casein micelle transmission, as previously observed by Le Berre and Daufin (1998) [14]. Beyond CHC, Tr increases except for the milk at the highest I, for what Tr still continues to decrease (final Tr = 17 %). Regardless of I, the re-increase in τ_w does not restore the filtration performance: the higher the ionic strength, the lower the final soluble protein transmission (Tr_f), (Table 2).

5. Discussion

As shown previously, the increase in ionic strength through NaCl addition drastically modifies the performance of milk microfiltration when the casein micelles are sufficiently

concentrated at the membrane surface, i.e. near and at the CHC: lower critical ratio $(J/\tau_w)_{crit}$, sharper increase in TMP and higher alteration of protein transmission at high ionic strengths. In this discussion we show that those changes in behavior can be related to differences in the properties of the casein micelles deposit because of the different ionic strength conditions. We also explain our results based on previous observations done on the behavior of casein micelles in concentrated regime.

5.1 Deposit formation at lower casein micelle concentrations

A first important result in our experiments is that the CHC are located at a lower critical ratio $(J/\tau_w)_{crit}$ when ionic strength is increased . This indicates that the casein micelle deposit is formed at lower casein concentrations at the membrane when adding salt. Indeed and as it has been already shown by several authors [5,6], the casein micelles accumulated turn into a gel when their concentration exceeds a critical value at the membrane surface. Moreover, it seems reasonable to assume that the polarization phenomenon is not affected by a change in ionic strength: first the TMP values are pretty similar before the CHC, between the experiments performed at different I and in addition the casein micelle diameter being the same for each milk studied, hence its diffusivity is constant irrespective of the milk ionic strength. Hence, the fact that the CHC are located at higher τ_w (i.e., lower $(J/\tau_w)_{crit}$) for higher ionic strengths indicate that the deposit is formed in weaker conditions of polarization and consequently at a lower "critical" concentration. This result is fully consistent with the observations of Bouchoux *et al.* [18] who prepared casein micelle gels through osmotic compression and who found that an increase in ionic strength leads to a shift in the gel transition to lower osmotic pressures and volume fractions.

The formation of a gel layer at a lower concentration in casein micelle can be explained by a modification of the shift in the balance of interactions between the micelles. With the

increase in ionic strength, the liquid-gel transition is linearly correlated to the decrease in the global charge of the casein micelles (represented by electrophoretic mobility), and the increase in soluble calcium. The gel transition takes place when the distance between the micelles is small enough to induce changes in interactions: the attractive forces between the micelles become stronger than repulsive ones, thus coagulation of the accumulated micelles takes place and the deposit is formed [5,27]. With the increase in ionic strength, there is a decrease in the overall repulsions between casein micelles as:

- Steric repulsions become weaker because of the collapse of the κ-caseins brush, located at the surface of the casein micelles [28]
- Repulsive electrostatic interactions are affected through the screening of the surface charge of the casein micelle (represented by the electrophoretic mobility, Table 1). Note that some authors consider that, electrostatic interactions must be neglected at the natural ionic strength of milk [13]. Nevertheless, Tessier *et al.* [29] clearly show that electrostatic interactions still exist between proteins at 0.3 M of ionic strength.

As the overall repulsions decrease, the attractive interactions can take place and make easier the liquid-gel transition. Indeed, the hydrophobic forces are probably enforced at high ionic strength [30]. Moreover, as the soluble calcium concentration increases with I, the establishment of calcium bonds between the micelles [31] through the carboxylic acids or through sialic acids worn by the κ-caseins [32] can also take place.

5.2 A more cohesive deposit

Once the deposit is formed at the CHC, its characteristics clearly depend on the ionic strength. More particularly, the deposit appears to be more cohesive at higher ionic strengths. This increase in cohesiveness is visible through the TMP evolution (average value and oscillations) and the deposit irreversibility (R_{id}). At the CHC, the oscillations in TMP can be

seen as the result of a cyclic phenomenon of matter accumulation and removal at and from the membrane surface. With the increase in I, these TMP oscillations are larger in amplitude but decrease in number, frequency and duration; thus indicating that the deposit is "harder" to remove from the membrane and so more cohesive. Moreover, this increase in the cohesiveness is also shown through the delay observed (after the CHC) between the increase in τ_w and the decrease in TMP which is much more pronounced for the higher I. Finally, this assumption is strengthened through the more pronounced TMP hysteresis and the less reversible deposit, as seen through the value of R_{id} (Table 2). In accordance with these results, Bouchoux *et al*. [18] point out the fact that gels of casein micelles made through osmotic compression at high ionic strengths are more difficult to re-disperse, and consequently more cohesive. Once again, this phenomenon can be explained through a shift in the balance of attraction and repulsion forces between the micelles. Indeed, the hydrophobic groups that may be hidden by the κ-casein brush at milk ionic strength may become more accessible when this brush is partially collapsed at higher ionic strengths. So the micelles can stick to each other more efficiently as they come into direct contact. In addition, the casein network that constitutes the deposit may be strengthened by calcium bridges between the micelles and/or between the micelles and the membrane which can participate to the increase in the cohesiveness and the irreversibility.

5.3 A Deposit with modified selectivity

When the deposit is formed, the increase in ionic strength induces an irreversible alteration of the proteins transmission: the casein micelle transfer is immediately and irreversibly affected as the casein micelle transmission is close to zero (permeate turbidity < 0.1 NTU) at high ionic strengths while the transmission of soluble proteins decreases more gradually from 53 % to 17 % at I = 0.072 to 0.372 M, respectively. This change in the

selectivity of the casein deposit can be attributed to several phenomena. First, a deposit more cohesive is probably less porous, i. e., made of a “tighter” casein network. This would result in some stronger size exclusion effects that partly explain the alteration of the protein transfer, which is much more pronounced for the larger proteins (average casein micelle diameter ≈ 100 nm VS soluble protein average diameter < 10 nm).

Second, the deposit is made of a quantity of matter accumulated that is more important at higher ionic strength (increase in R_{rd} with I, Table 2). This high density of negative charges possibly generates strong repulsive electrostatic interactions between the casein deposit and the proteins in solution in the bulk. Some authors already showed that significant electrostatic interactions still exist between proteins even for I=0.372 M [29]. Hence, the casein micelle deposit could constitute a material with a high negative charge density at the membrane surface which could repel other negatively-charged proteins (casein micelles, major soluble proteins such as α-lactalbumin and β-lactaglobulin) and consequently alter their transfer. To investigate these two hypotheses, size exclusion phenomena and/or electrostatic repulsions, further experiments aiming at the transmission of individual soluble proteins as a function of their diameter and charge properties will be carried out.

6. Conclusions

The microfiltration 0.1 µm of skimmed milk at various ionic strengths allows a better understanding in the structuration of the casein micelle deposit which rules the performance (permeation flux, transmembrane pressure and protein transmission) of the operation. The experiments performed in this study, allow to put in light the role of the interactions between casein micelles in the set-up and in the properties of the deposit. With the increase in ionic strength, the global charge of the casein micelles is reduced and the concentration of soluble calcium is increased. These physico-chemical modifications lead to a decrease in repulsive

interactions between micelles by the screening of the casein micelle charge and by the collapse of the κ-casein. The hydrophobic interactions between micelles are then favored and are possibly strengthened by calcium bonds between micelles. As a consequence, the micelles can come into direct contact more easily and can form stronger intermolecular links. Hence, with the increase in ionic strength, the deposit is set-up for a lower casein micelle concentration at the membrane surface and it is harder to remove by the increase in its cohesiveness. Finally, the higher the ionic strength, the more pronounced is the decrease in protein transmission. This can be related to both an increase in steric repulsion mechanism and an increase in electrostatic repulsion. The deposit appears less porous possibly because of the reduction of the interstitial spaces inside the casein network. Additionally, some repulsive electrostatic interactions between the deposit and the proteins can still exist even at high ionic strength; hence the negative charged proteins in suspension in the bulk are possibly rejected when they approach the deposit. All these results are very consistent with previous studies of the casein micelle behavior in concentrated regime (osmotic compression).

Acknowledgements

The authors wish to thank L. Fromont and C. Geneste for technical support and precious advices.

Nomenclature

A_{plot} :	Filled area under two plots (Pa s)
Amp_{osc} :	Amplitude of oscillation at CHC (Pa)
CHC :	Critical Hydrodynamic Conditions
Ca_{total} :	Total calcium (g L^{-1})
Ca_s :	Soluble calcium (g L^{-1})
C_P :	Soluble protein concentration in the permeate (g L^{-1})
C_R :	Soluble protein concentration in the retentate (g L^{-1})
Fr :	Oscillations frequency (s^{-1})
I :	Ionic strength (M)
J :	Permeation flux (L h^{-1} m^{-2})
NCN :	Non casein nitrogen
NPN:	Non protein nitrogen
N :	Number of maxima and minima of TMP during the oscillation period
N_{osc} :	Number of TMP oscillations
P_{AR} :	Average retentate pressure (Pa)
R_d :	Deposit resistance (m^{-1})
R_{id} :	Irreversible deposit resistance (m^{-1})
R_{rp} :	Reversible deposit resistance (m^{-1})
R_f :	Total fouling resistance (m^{-1})
R_m :	Membrane resistance (m^{-1})
R_p :	Polarization layer resistance (m^{-1})
Sl_{TMP} :	Slope of the linear regression of the increase in the TMP oscillation phase (Pa s^{-1})
TMP :	Transmembrane pressure (Pa)
TMP_i :	Transmembrane pressure at the beginning of the parametric study for τ_w = 120 Pa
TMP_f :	Transmembrane pressure at the end of the parametric study for τ_w = 120 Pa
Tr :	Soluble protein transmission (%)
Tr_i :	Soluble protein transmission (%) at the beginning of the parametric study for τ_w = 120 Pa
Tr_f :	Soluble protein transmission (%) at the end of the parametric study for τ_w = 120 Pa
VRR :	Volume reduction ratio

Greek symbols:

τ_w :	Wall shear stress (Pa)
τ_{wcrit} :	Critical wall shear stress (Pa)
Δt_{osc} :	Oscillation phase duration (s)
Δt_{crit} :	Critical step duration (s)

Reference List

[1] F. Gaucheron, The minerals of milk, Reprod. Nutr. Develop. 45 (2005) 473-483.

[2] G. Brans, C. G. P. H. Schroen, R. G. M. van der Sman, R. M. Boom, Membrane fractionation of milk: state of the art and challenges, J. Membr. Sci. 243 (2004) 263-272.

[3] J. L. Maubois, New applications of membrane technology in the dairy-industry, Aust. J. Dairy Technol. 46 (1991) 91-95.

[4] G. Gésan-Guiziou, E. Boyaval, G. Daufin, Critical stability conditions in crossflow microfiltration of skimmed milk: transition to irreversible deposition, J. Membr. Sci. 158 (1999) 211-222.

[5] A. J. E. Jimenez-Lopez, N. Leconte, O. Dehainault, C. Geneste, L. Fromont, G. Gésan-Guiziou, Role of milk constituents on critical conditions and deposit structure in skimmilk microfiltration (0.1µm), Sep. Pur. Technol. 61 (2008) 33-43.

[6] O. Le Berre and G. Daufin, Skimmilk crossflow microfiltration performance versus permeation flux to wall shear stress ratio, J. Membr. Sci. 117 (1996) 261-270.

[7] P. Bacchin, M. Meireles, P. Aimar, Modelling of filtration: from the polarised layer to deposit formation and compaction, Desalination 145 (2002) 139-146.

[8] P. Bacchin, D. Si-Hassen, V. Starov, M. J. Clifton, P. Aimar, A unifying model for concentration polarization, gel-layer formation and particle deposition in cross-flow membrane filtration of colloidal suspensions, Chem. Eng. Sci. 57 (2002) 77-91.

[9] F. Pignon, G. Belina, T. Narayanan, X. Paubel, A. Magnin, G. Gésan-Guiziou, Structure and rheological behavior of casein micelle suspensions during ultrafiltration process, J. Chem. Phys. 121 (2004) 8138-8146.

[10] V. Chen, A. G. Fane, S. Madaeni, I. G. Wenten, Particle deposition during membrane filtration of colloids: Transition between concentration polarization and cake formation, J. Membr. Sci. 125 (1997) 109-122.

[11] S. Metsamuuronen, J. Howell, M. Nystrom, Critical flux in ultrafiltration of myoglobin and baker's yeast, J. Membr. Sci. 196 (2002) 13-25.

[12] G. Gésan-Guiziou, G. Daufin, E. Boyaval, O. Le Berre, Wall shear stress: effective parameter for the characterisation of the cross-flow transport in turbulent regime during skimmed milk microfiltration, Lait 79 (1999) 347-354.

[13] W. Kühnl, A. Piry, V. Kaufmann, T. Grein, S. Ripperger, U. Kulozik, Impact of colloidal interactions on the flux in cross-flow microfiltration of milk at different pH values: A surface energy approach, J. Membr. Sci. 352 (2010) 107-115.

[14] O. Le Berre and G. Daufin, Microfiltration (0,1 µm) of milk: effect of protein size and charge, J. Dairy Res. 65 (1998) 443-455.

[15] M. Rabiller-Baudry, G. Gésan-Guiziou, D. Roldan-Calbo, S. Beaulieu, F. Michel, Limiting flux in skimmed milk ultrafiltration: impact of electrostatic repulsion due to casein micelles, Desalination 175 (2005) 49-59.

[16] W. Youravong, A. S. Grandison, M. J. Lewis, The effects of physico-chemical changes on critical flux of skimmed microfiltration, Songklanarakin J. Sci. Technol. 24 (2002) 929-939.

[17] A. Bouchoux, B. Debbou, G. Gésan-Guiziou, M. H. Famelart, J. L. Doublier, B. Cabane, Rheology and phase behavior of dense casein micelle dispersions, J. Chem. Phys. 131 (2009) 165106-165111.

[18] A. Bouchoux, P. E. Cayemitte, J. Jardin, G. Gésan-Guiziou, B. Cabane, Casein Micelle Dispersions under Osmotic Stress, Biophys. J. 96 (2009) 693-706.

[19] A. J. E. Jimenez-Lopez, Structuration du dépôt de matière à la membrane lors de la microfiltration tangentielle (0,1 μm) de lait écrémé, PhD Thesis (2007), INRA UMR STLO Agrocampus Rennes, France.

[20] R.M. Sandblöm (Alfa-Laval), Filtering process, Sweden Patent No. 7416 257 (1974).

[21] P. Resmini, L. Pellegrino, R. Andreini, F. Prati, Determinazione delle sieroproteine solubili del latte per HPLC (cromatographia liquida ad alta prestazione) in fase inversa, Sci. E. Technica Latterio-casearia 40 (1989) 7-23.

[22] D. G. Dalgleish, Measurement of Electrophoretic Mobilities and Zeta-Potentials of Particles from Milk Using Laser Doppler Electrophoresis, J. Dairy Res. 51 (1984) 425-438.

[23] T. Huppertz and P. F. Fox, Effect of NaCl on some physico-chemical properties of concentrated bovine milk, Int. Dairy J. 16 (2006) 1142-1148.

[24] Y. Le Graët and G. Brulé, Effects of pH and ionic-strength on distribution of mineral salts in milk, Lait 73 (1993) 51-60.

[25] O. Mekmene, Y. Le Graët, F. Gaucheron, A model for predicting salt equilibria in milk and mineral-enriched milks, Food Chem. 116 (2009) 233-239.

[26] R. M. Mcdonogh, T. Gruber, N. Stroh, H. Bauser, E. Walitza, H. Chmiel, H. Strathmann, Criteria for Fouling Layer Disengagement During Filtration of Feeds Containing A Wide-Range of Solutes, J. Membr. Sci. 73 (1992) 181-189.

[27] D. M. Krstics, M. N. Tekic, M. D. Caric, S. D. Milanovic, Static turbulence promoter in cross-flow microfiltration of skim milk, Desalination 163 (2004) 297-309.

[28] R. Tuinier and C. G. De Kruif, Stability of casein micelles in milk, J. Chem. Phys. 117 (2002) 1290-1295.

[29] P. T. Tessier, V. J. Verruto, S. I. Sandler, A. M. Lenhoff, Correlation of diafiltration sieving behavior of lysozyme-BSA mixtures with osmotic second virial cross-coefficients, Biotechnol. Bioeng. 87 (2004) 303-310.

[30] C. Bonnet-Gonnet, L. Belloni, B. Cabane, Osmotic pressure of latex dispersion, Langmuir 10 (1994) 4012-4021.

[31] P. Müller-Buschbaum, R. Gebhardt, S. V. Roth, E. Metwalli, W. Doster, Effect of calcium concentration on the structure of casein micelles in thin films, Biophys. J. 93 (2007) 960-968.

[32] M. Mellema, F. A. M. Leermakers, C. G. de Kruif, Molecular mechanism of the renneting process of casein micelles in skim milk, examined by viscosity and light-scattering experiments and simulated by model SCF calculations, Langmuir 15 (1999) 6304-6313.

Table 1: Physico-chemical characteristics of the casein micelles and concentration of total (Ca_{total}) and soluble calcium (Ca_s) at 48 °C in thermized skimmed milk presenting various ionic strengths (I)

Thermized skimmed milks	Casein micelles characteristics		Calcium content		
	Average diameter nm	Electrophoretic mobility μ (10^{-7} m^2 $s^{-1}V^{-1}$)	*Ca_{total} g L^{-1}	Ca_s g L^{-1}	Ca_s/Ca_{total}
reference I = 0.072 M	174±13	31.1±1.2	1.19±0.01	0.23±0.01	0.19±0.02
I = 0.157 M	187±14	27.3±1.2	1.18±0.01	0.24±0.01	0.20±0.02
I = 0.247 M	181±1	22.9±1.2	1.18±0.02	0.25±0.01	0.21±0.02
I = 0.372 M	184±11	15.5±1.2	1.21±0.01	0.28±0.01	0.23±0.02

I: Ionic strength
*Ca_{total} concentration slightly changed because of differences in milks (season, cow species, food of cows…) during the duration of the experimental period.

Table 2: Critical wall shear stress (τ_{wcrit}), average of the transmembrane pressure (TMP), hydraulic resistances (total fouling (R_f), polarized layer (R_p), deposit (R_d), irreversible (R_{id}) and reversible (R_{rd}) part of the deposit) and total soluble protein transmission (Tr) during microfiltration of skimmed milk at various ionic strengths. The initial membrane resistance is $R_m = 0.51 \pm 0.02 \times 10^{12}$ m^{-1}.

I (M)	τ_{wcrit} (Pa)	TMP_i 10^5 (Pa)	TMP_f 10^5 (Pa)	R_f 10^{12} (m^{-1})	R_p 10^{12} (m^{-1})	R_d 10^{12} (m^{-1})	R_{id} 10^{12} (m^{-1})	R_{rd} 10^{12} (m^{-1})	Tr_i (%)	Tr_f (%)
0.072	55	0.12±0.01	0.20±0.01	1.84±0.15	0.86±0.01	0.98±0.02	0.60±0.01	0.38±0.03	66±1	53±1
0.157	60	0.11±0.01	0.60±0.01	6.48±0.01	0.77±0.01	5.71±0.02	0.67±0.01	5.04±0.03	75±1	46±1
0.247	66	0.16±0.01	0.94±0.01	10.43±0.01	1.16±0.29	9.27±0.30	0.87±0.01	8.40±0.30	63±2	41±1
0.372	72-80	0.12±0.01	1.82±0.05	20.43±0.02	1.05±0.01	19.38±0.05	2.96±0.05	16.42±0.10	77±1	17±3

TMP_i = average TMP for τ_w = 120 Pa before CHC
TMP_f = average TMP for τ_w = 120 Pa after CHC
Tr_i = average Tr for τ_w = 120 Pa before CHC
Tr_f = average Tr for τ_w = 120 Pa after CHC

Table 3: Characterization of TMP oscillations at the critical step (τ_{wcrit}) during microfiltration of skimmed milk at various ionic strengths

I (M)	N_{osc} (-)	Fr (s^{-1})	Amp_{osc} (10^5Pa)	$\Delta t_{osc}/\Delta t_{crit}$ (-)	Sl_{TMP} (Pa s^{-1})
0.072	56	0.036	$1.6\ 10^{-8}$	1.00	4.25
0.157	33	0.023	$4.9\ 10^{-6}$	0.76	5.39
0.247	15	0.018	$4.9\ 10^{-5}$	0.55	12.09
0.372	0	0.000	-	0.00	22.17

I: Ionic strength
N_{osc}: number of oscillations during TMP oscillation phase
Fr: frequency of the TMP oscillations
Amp_{osc}: amplitude of the TMP oscillations
$\Delta t_{osc}/\ \Delta t_{crit}$: ratio between the duration of the oscillation phase and the duration of the critical step
$Sl_{TMP:}$ slope of the linear fit of the increase in TMP during the TMP oscillation phase

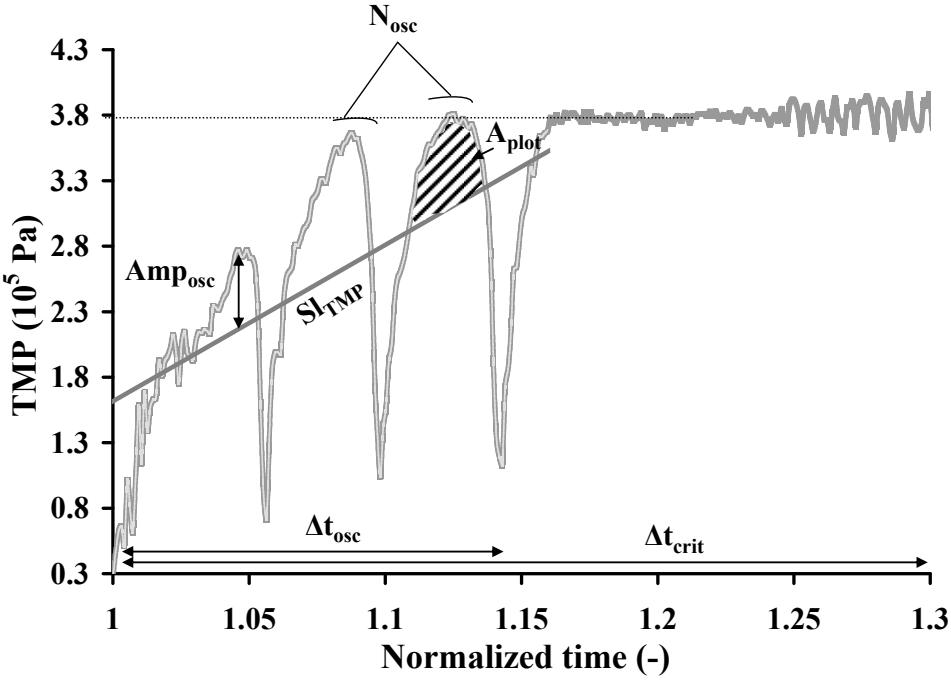

Figure 1: Main parameters for the characterization of TMP oscillations at the critical hydrodynamics conditions (CHC).

Sl_{TMP} (Pa s^{-1}): slope of the TMP signal versus time after linearization corresponding to the overall increase in TMP during the oscillation phase

Δt_{osc} (-): normalized duration of the TMP oscillation phase

Δt_{crit} (-): normalized total duration of the critical step

N_{osc} (-): number of oscillations

Fr (s^{-1}): TMP oscillations frequency as

$$Fr = \frac{N_{osc}}{\Delta t_{osc}}$$

Amp_{osc} (Pa): amplitude of the TMP oscillations as

$$Amp_{osc} = \frac{A_{plot}}{\Delta t_{osc}}$$

A_{plot} (Pa): the filled area between the two plots and calculated through

$$A_{plot} = \int_{\Delta tosc} TMP(t)dt - \int_{\Delta tosc} (Sl_{TMP} \times t + a)dt$$

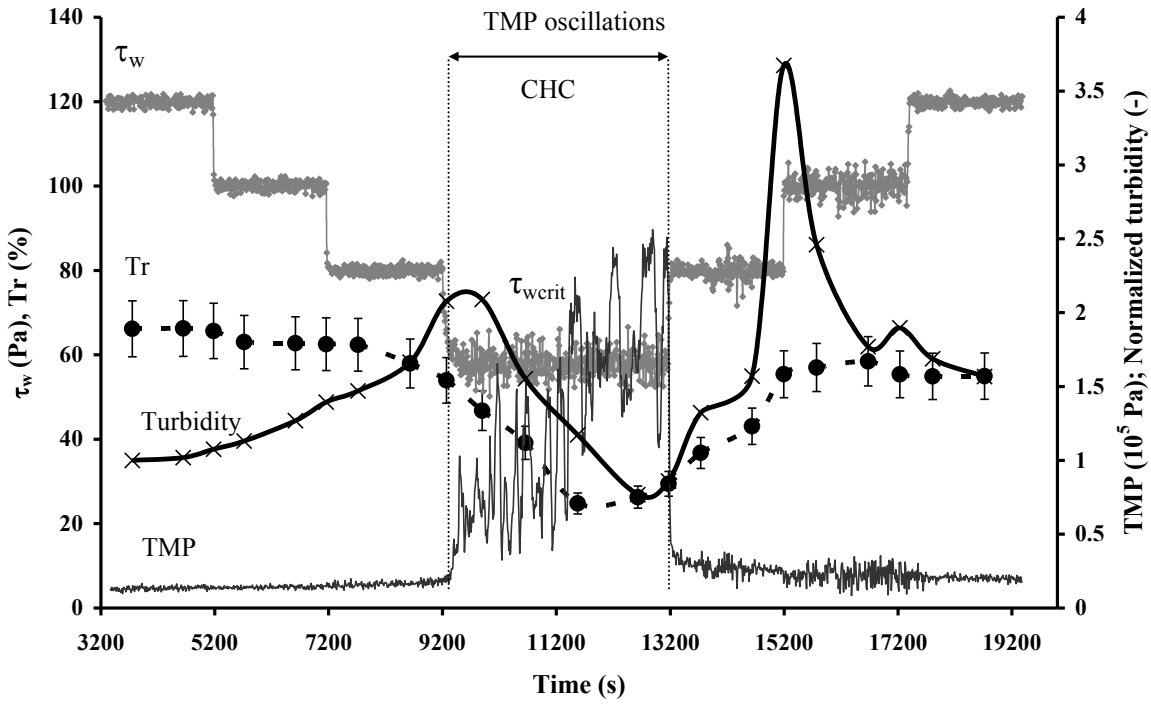

Fig 2: Evolution of the transmembrane pressure (TMP), wall shear stress (τ_w), total soluble proteins transmission (Tr) and casein micelles transmission (Normalized turbidity) during reference thermized skimmed milk (I = 0.072 M) microfiltration before, during and after the Critical Hydrodynamic Conditions (CHC).
Operating conditions: T = 48°C, J = 50 L h^{-1} m^{-2}, pH = 6.55

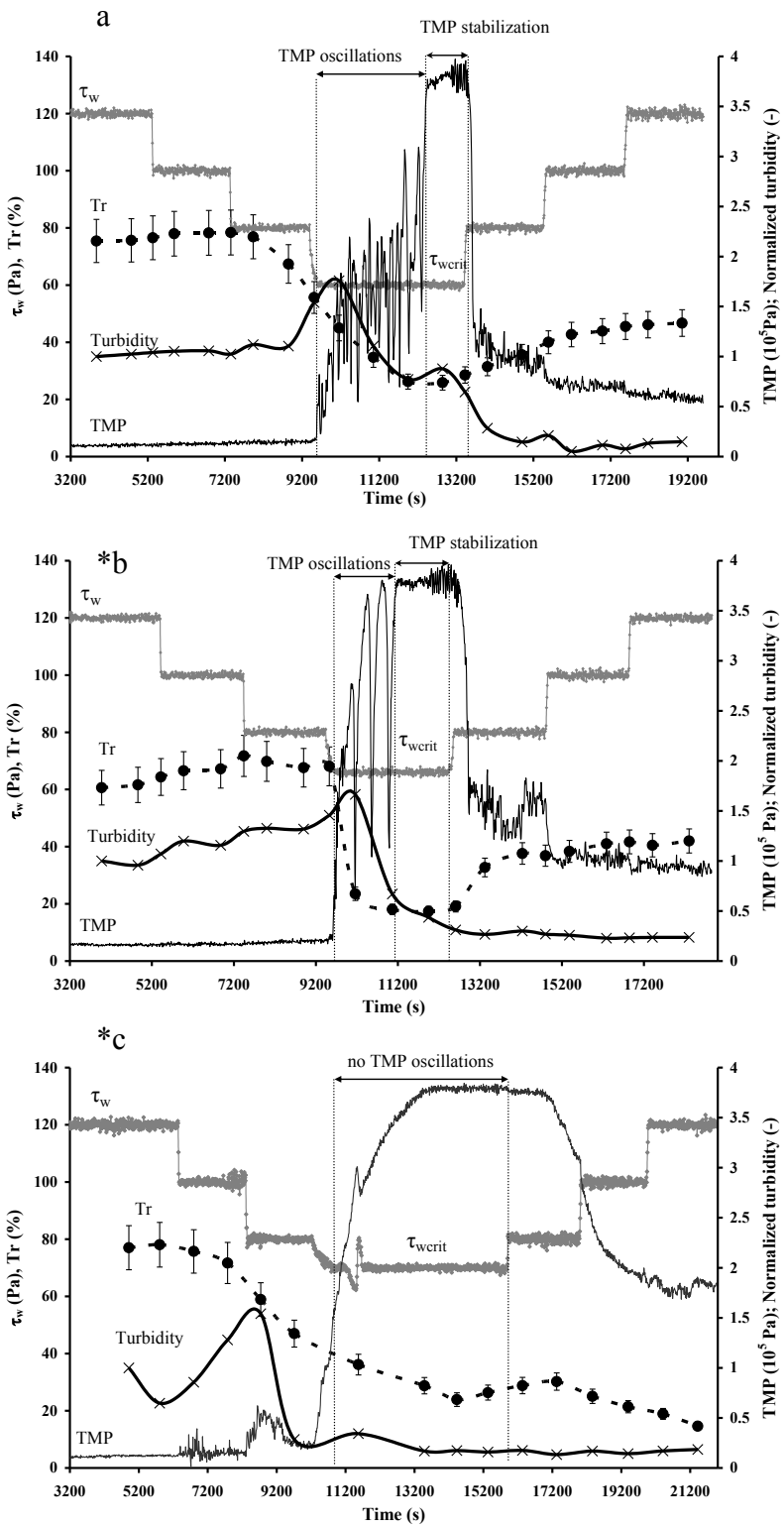

Figure 3 : Evolution of the transmembrane pressure (TMP), wall shear stress (τ_w), total soluble proteins transmission (Tr) and casein micelles transmission (Turbidity) during microfiltration of skimmed milk at different ionic strengths (a) I = 0.157 M, (b) I = 0.247 M and (c) I = 0.372 M, before, during and after the Critical Hydrodynamic Conditions (CHC, τ_{wcrit}). Operating conditions: T = 48°C, J = 50 L h^{-1} m^{-2}, pH = 6.55

*b: The duration of the critical step was reduced to 48 minutes as the permeate compartment was dangerously empting because of the high fouling

*c: The duration of the critical step was 1 h 20 because during the first 20 minutes no oscillation was observed. τ_w was decreased and increased again in order to check than the critical step was really reached.

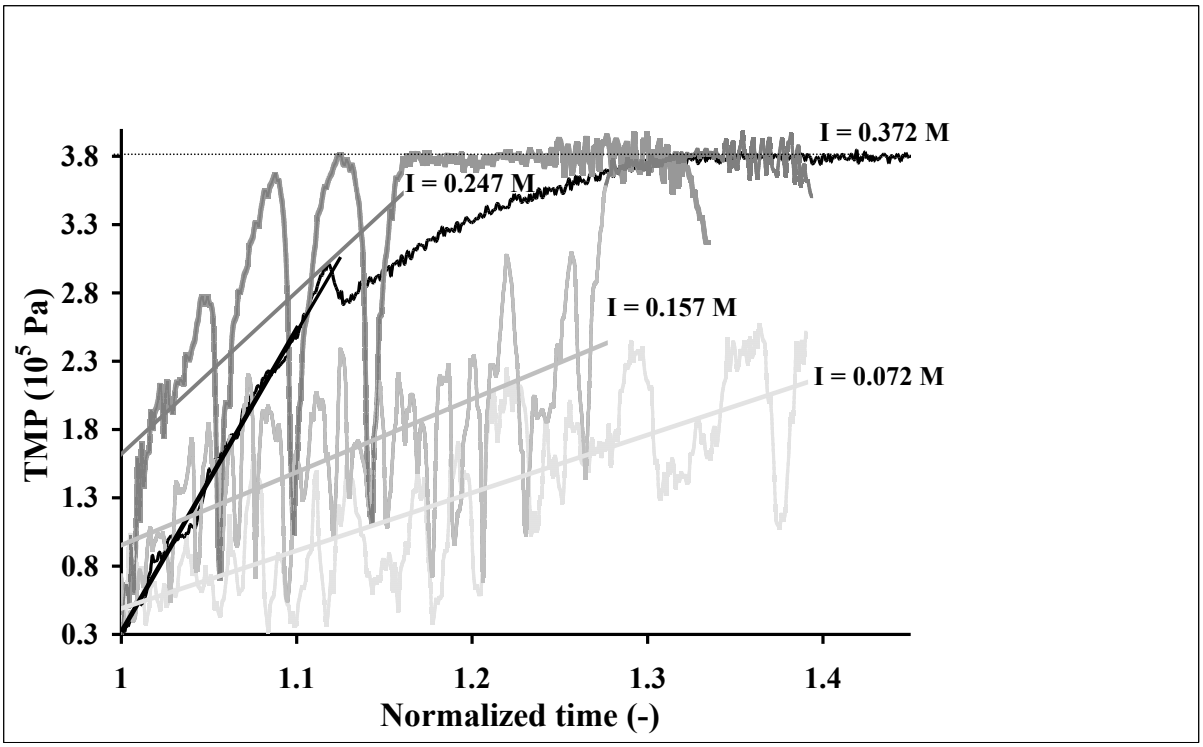

Figure 4: Evolution of the transmembrane pressure (TMP) at the critical step (τ_{wcrit}) versus time (see calculation 3.3) during microfiltration of skimmed milk at different ionic strengths (I = 0.072-0.372 M).
Operating conditions: T = 48°C, J = 50 L h^{-1} m^{-2}, pH = 6.55
Time scale corresponded to the normalized time with reference (t= 1) to the beginning of the oscillation phase.

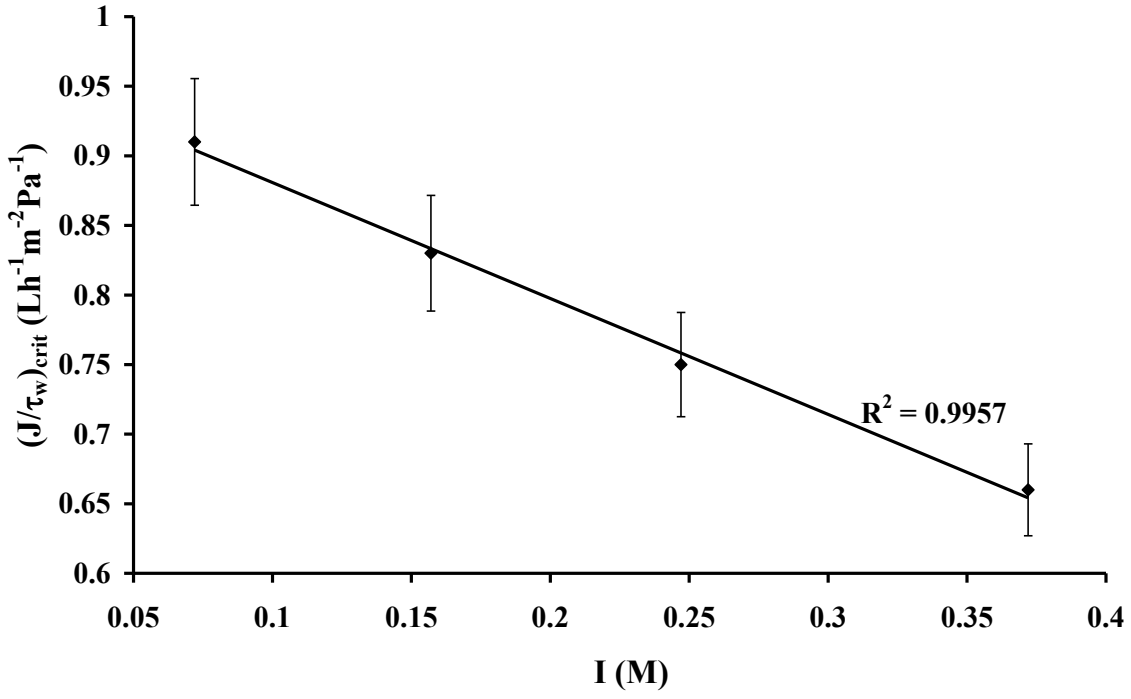

Figure 5: Impact of the ionic strength on the critical ratio $(J/\tau_w)_{crit}$ during microfiltration of skimmed milk.
Operating conditions: T = 48°C, J = 50 L h^{-1} m^{-2}, pH = 6.55