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RELATIONSHIP BETWEEN β-LACTOGLOBULIN DENATURATION AND FOULING MASS DISTRIBUTION IN A PLATE HEAT EXCHANGER

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ABSTRACT

Few investigations have attempted to connect the mechanism of dairy fouling to the chemical reaction of denaturation (unfolding and aggregation) occurring in the bulk.

The objective of this study is to contribute to this aspect in order to propose innovative controls to limit fouling deposit formation.

Experimental investigations have been carried out to observe the relationship between the deposit mass distribution generated in a plate heat exchanger (PHE) by a whey protein isolate (WPI) mainly composed of β-lactoglobulin (β-Lg) and the ratio between the unfolding and aggregation rate constants.

Data analysis showed that: i) β-Lg denaturation is highly dependent on the calcium content, ii) for each fouling solution, irrespective of the imposed temperature profile, the deposit mass in each channel vs the ratio of the unfolding and aggregation rate constants are well correlated.

This study demonstrates that both the knowledge of the thermal profile and the β-Lg denaturation rate constants are required in order to predict accurately the deposit distribution along the PHE.

INTRODUCTION

In the dairy industry, heat treatments are carried out in order to ensure food security and to impart several functionalities to milk and its derivatives, like thermal stability, viscosity, or gelation (Mulvihill and Donovan, 1987; Sava et al., 2005, Schmitt et al., 2007).

Fouling deposit formation on heat exchanger surfaces is a major industrial problem of milk processing plants, which involves frequent cleaning of the installations and hence resulting in excessive rinsing water and harsh chemicals use. A number of studies have reported the drastic economic costs of fouling. Fouling and the resulting cleaning of the process equipment account for about 80% of the total production costs (Bansal and Chen, 2006). According to Tay and Yang (2006), the total heat exchanger fouling costs for highly industrialized countries are about 0.25% of the Gross National Product. In the USA, total fouling costs have been estimated as US $ 7 billion (Müller-Steinhagen et al., 2000).

Milk fouling deposit is complex in nature. Deposit is formed by a mixture of inorganic salts (mainly calcium) and proteins (largely whey proteins). The key role played by β-Lg has been recognized in most milk fouling studies (Lalande et al., 1985; De Jong et al., 1993; Changani et al., 1997).

The mechanism of thermal denaturation of β-Lg is the subject of a considerable number of interesting studies (Iametti et al., 1996; Qi et al., 1997; Tolkach and Kulozik, 2007; Petit et al., 2011) that resulted in a number of hypothetical models describing the thermal behavior of β-Lg in heated solutions. The widely accepted model is a succession of two steps: an unfolding step and an aggregation step (De Jong et al., 1992). The native β-Lg first unfolds and exposes the core containing reactive sulfhydryl groups. The unfolded β-Lg then reacts with the similar or other protein molecules and forms aggregates (Bansal and Chen, 2006).

Many studies have been carried out in an attempt to identify fouling mechanisms. The mechanisms are complicated and involve chemical reactions and heat and mass transfer processes (Changani et al., 1997). Burton (1988) lists the following possible processes involved in the formation of fouling deposits:

1. Reactions in the product, which convert one or more of its constituents into a form capable of being deposited on the surface;
2. Transportation of the product constituents (foulant or foulant precursor) to the surface;
3. Adsorption of a layer of some fouling material to the surface to form an initial layer;
4. Deposition of further fouling material on the initial layer, compensated by the mechanical removal of material through the shear forces caused by the flow of products across the deposited-liquid interface.

Lalande and René (1988) suggested that fouling occurs due to the aggregation of proteins already attached to the wall with protein in the fluid at the solid-liquid interface. Fouling in a heat exchanger depends on bulk and surface processes. The deposition is a result of a number of stages (Belmar-Beiny et al., 1993):

1. Denaturation and aggregation of proteins in the bulk;
2. Transport of the aggregated proteins to the surface;
3. Surface reactions resulting in incorporation of protein into the deposit layer;
4. Possible re-entrainment or removal of deposit.

Belmar-Beiny et al. (1993) and Schreier and Fryer (1995) proposed that fouling was dependent on the bulk and surface reactions and not on the mass transfer. The work of Fryer and Slater (1984) of deposition, under defined conditions in a simple tubular apparatus, have been interpreted to suggest that bulk processes may be involved in milk fouling.

Belmar-Beiny et al. (1993) also used a tubular heat exchanger fouled with whey protein concentrate to study the role of bulk and surface reactions in fouling phenomena. A simple model was proposed in which fouling was correlated with the volume of fluid hot enough to produce unfolded and aggregated proteins. This result highlighted the importance of denaturation reactions in bulk. On the other hand, van Asselt et al. (2005) showed that β-Lg aggregates are not involved in the fouling reactions. However, since Belmar-Beiny et al. (1993) and van Asselt et al. (2005) works, the exact role of the unfolded and aggregated proteins as foulant precursor is still not wholly understood. There is still a lack of knowledge between the chemical reactions occurring in the bulk (unfolding and aggregation of β-Lg), there consequences on foulant precursor concentrations and the extent of fouling.

In this study, we propose to partially fill this gap by investigating the chemical reactions of β-Lg denaturation occurring in the bulk, for two WPI model fouling solutions, and their link with the fouling phenomena.

The main objective of this work is to investigate whether a relationship can be established between the distribution of the dry fouling deposit mass in each PHE channel and the β-Lg rate constants (computed at the mean channel temperature) of the model fouling solutions, for various operating conditions (processing parameters inducing various thermal profiles).

MATERIALS AND METHODS

Fouling model fluids

The model fluids used in this study were reconstituted from WPI Promilk 852FB1 supplied by Ingredia (France). The composition of the powder is shown in Table 1.

For each experiment, 1% (w/w) β-Lg solutions with various calcium concentrations were prepared by mixing 10 g of WPI powder in 1 L reverse osmosis water at room temperature. Then, different quantities of a molar calcium chloride (anhydrous, 96%, Acros Organics, Thermo Fisher Scientific, Waltham, MA, USA) solution were added to the β-Lg solution to obtain the two model fouling solutions containing respectively: i) 1% (w/w) β-Lg and 100 ppm of total calcium, ii) 1% (w/w) β-Lg and 120 ppm of total calcium.

Table 1. Composition of WPI powder

Component	Promilk 852FB1 (% w/w)
Total proteins	80.1
β-Lg	66.0
α-lactalbumin	13.3
Minerals	2.9

Only a small range of calcium content was studied because it is admitted that a very slight chemical variation results in a large variation in the fouling formation (Petit et al., 2011, Khaldi et al., 2015). The calcium concentration of the two model solutions was determined by atomic absorption spectrometry with a Spectro AA 55B apparatus (Varian, Palo Alto, CA, USA).

Thermal denaturation experiments

All thermal denaturation experiments were conducted on twelve samples of 2 mL that were put in stainless steel tubes (350 mm length, 10 mm core diameter, 1 mm wall thickness), to be closer to the actual conditions on the PHE (Fig. 1). The samples were then preheated at 60°C (for the range of temperatures below 80°C) or 65°C (for the range of temperatures over 80°C) in a first water bath. Once the temperature of 60 or 65°C is reached, the samples were placed in a second water bath (from 90°C for the lowest temperatures to 100°C for the highest temperatures) to attain the desired holding temperature. The second water bath was used in order to reduce the heat increase time and the denaturation level before sampling. The first sample was taken when the sample temperature was equal to the desired holding value. The eleven other samples were maintained during a time sufficient in a last water bath, taken off at different times and cooled down immediately in a beaker with melting ice to stop further β-Lg denaturation.

Fig. 1. Picture of the tube-sample used for β-Lg thermal denaturation experiments

The temperature profile in samples placed in the three water baths was determined using a sensor connected to a temperature measurement acquisition system, placed in a stainless steel tube filled with water (Fig. 2).

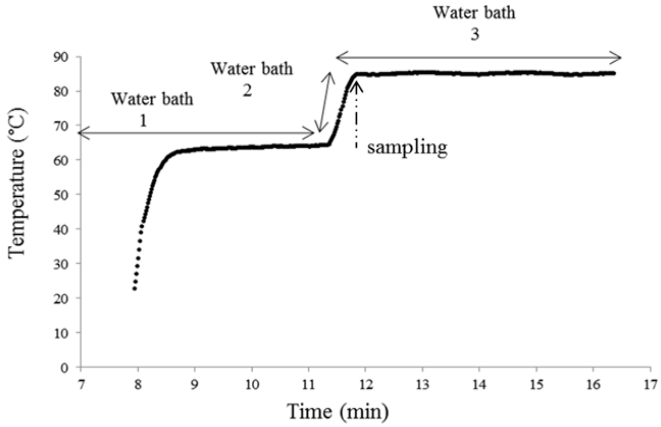

Fig. 2. Temperature profile in samples placed in the three water baths

HPLC analysis

The soluble (native and unfolded) β-Lg concentration in the samples was evaluated by HPLC after precipitation of the aggregated protein at pH 4.6 and their removal by centrifugation (9000 rpm for 30 min at 4°C). The chromatographic system (Waters, Milford, Massachusetts, USA) included a 717 Plus autosampler, a 616 quadratic pump system, a Jones Model 7971 column oven, a CLHP ACE 300 Å C4 separation column and the associated guard column (Advanced Chromatography Technologies, Aberdeen, United-Kingdom), a 486 UV-visible spectrophotometer and an acquisition software (Millenium 3.2, Waters).

The mobile phases used in HPLC were 0.1 % (v/v) trifluoroacetic acid (99 %, Acros Organics, Thermo Fisher Scientific, Waltham, Massachusetts, USA) in Milli-Q water, and 0.1 % trifluoroacetic acid in a mixture of 80% acetonitrile (HPLC grade, Thermo Fisher Scientific, Waltham, Massachusetts, USA) and 20% Milli-Q water.

The HPLC analyses were carried out at the following conditions: flow rate 1 $mL.min^{-1}$, injection volume 20 µL, temperature 40°C, elution of the proteins using a gradient of acetonitrile and detection of the eluted proteins at wavelength 214 nm. Analyses were repeated three times for each standard or sample. Calibration standards in the range from 0.5 to 4 $g.L^{-1}$ were prepared by dissolving β-Lg powder in Milli-Q water. For each experiment, the sample concentrations were calculated by averaging the three measured chromatographic areas and converting this area value into a β-Lg concentration using the HPLC calibration curve.

Determination of the β-Lg rate constants

The reaction model used in this study is derived from the work of Tolkach and Kulozik (2007). The denaturation reaction concerns the transformation of soluble species (noted S) into aggregates (noted A) which is described by the chemical equation $S \rightarrow A$ and defined in equation 1.

$$-\frac{dC_S}{dt} = k_n {C_S}^n \quad (1)$$

where C_s is the soluble β-Lg concentration and k_n the denaturation rate constant for a reaction order equal to n.

For each temperature, the corresponding denaturation rate constant was determined from the Arrhenius plot. The relation between the denaturation kinetic rate and the heat treatment temperature is given by equation 2.

$$\ln(k_n) = \ln(k_n°) - \frac{E_A}{RT} \quad (2)$$

where k_n^0 is the denaturation frequency factor, E_A the denaturation activation energy, R the universal gas constant and T the temperature.

The value of n was varied from 1 to 2 to determine the reaction order that gives the best fit of the experimental data plotted versus time. The value of n = 1.5 reaction order was suitable for the whole β-Lg denaturation reaction in the investigated temperature range (from 65 to 92°C).

Determination of the deposit mass distribution

Fouling experiments were carried out on a pilot plant, Fig. 3. The fouling rig was composed of two distinct zones: i) a pre-heating zone composed of a heat exchanger with V7 types plates (Vicarb, Alfa-Laval, France), 9 passes (one channel-per-pass), necessary to preheat the model fluid; ii) a heating zone composed of a PHE (Vicarb, model V7, Alfa-Laval, France).

The PHE set-up consisted of 10 plates, i.e. 5 passes (one channel-per-pass) of about 0.074 m^2 exchange surface (0.495 m length, 0.15 m width), were installed in a counter-current configuration to optimize the heat transfer, as represented in Fig. 4. The defined design permitted to be closer to industrial heat treatment conditions.

The temperature profile inside the heat exchanger was simulated with Sphere software (previously developed at our laboratory): temperatures in all passes of hot and cold fluids were calculated from the knowledge of fluids inlet temperature and flow rate, plate properties and exchanger design. The temperature profile is controlled by the heat exchanger inlet parameters: product and hot fluid inlet

temperatures (T_{ip} and T_{ih}) and product and hot water flow rates (respectively Q_p and Q_h). This was achieved with the operating conditions indicated in Table 2, displaying the average values of temperatures and flow rates recorded during each heat treatment experiment.

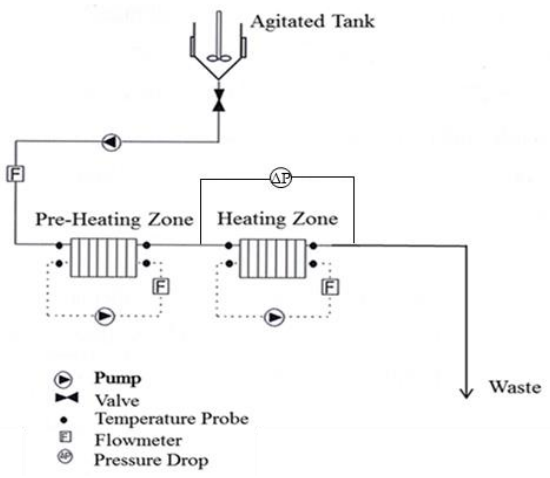

Fig. 3. Schematic diagram of the experimental set-up carried out for fouling experiments with the 1% (w/w) WPI model solutions

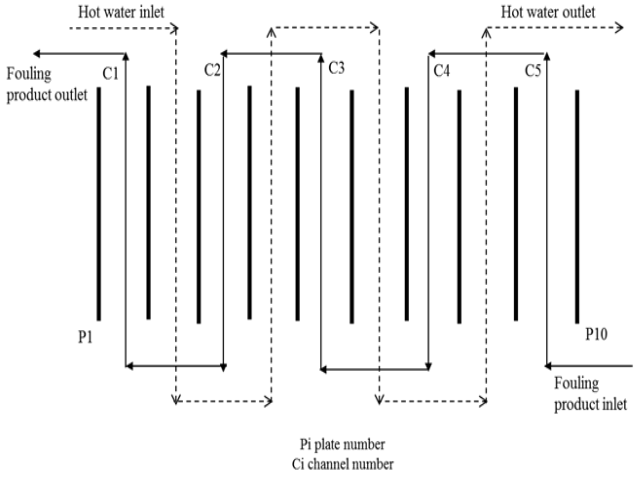

Fig. 4. Plate heat exchanger flow arrangement

The temperature profiles displayed in Fig. 5 were obtained by Sphere simulations by employing the operating conditions summarized in Table 2. Eight fouling runs were conducted with WPI solutions containing two calcium concentrations (100 and 120 ppm).

Heat exchanger plates were weighted before each heat-treatment experiment. After being dried in an air oven at 50°C, fouled plates were weighted at ambient temperature and the dry deposit mass on each plate was deduced by subtraction.

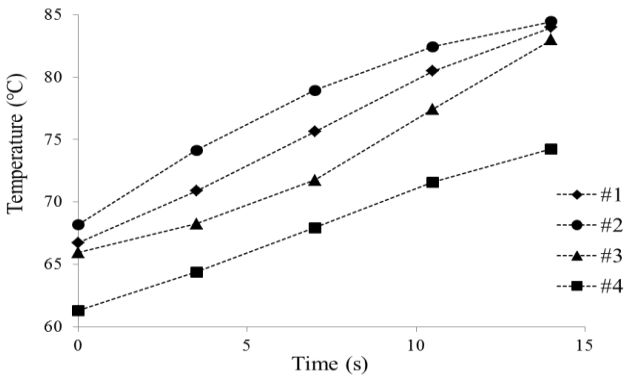

Fig. 5. The imposed thermal profiles in the PHE

Table 2. Operating conditions investigated with the pilot-scale experimental set: mean inlet and outlet temperatures and flow rates of β-Lg concentrate and hot water

Thermal profile number	Total calcium content (ppm)	T_{ip} (°C)	T_{op} (°C)	Q_p ($L.h^{-1}$)	Q_h ($L.h^{-1}$)
#1	100	65	85	300	300
#2	100	65	85	300	900
#3	100	65	85	300	150
#4	100	60	75	300	300
#1	120	65	85	300	300
#2	120	65	85	300	900
#3	120	65	85	300	150
#4	120	60	75	300	300

The amount of fouling was also monitored by calculating the fouling resistance. A linear relationship was visible between the average fouling resistance R_f, defined by equation 3, and the fouling thickness, assuming that the deposit layers are covered uniformly.

$$\frac{1}{U_{g(t)}} = \frac{1}{U_{g(0)}} + R_f \qquad (3)$$

Where $U_{g(0)}$ and $U_{g(t)}$ are the overall heat transfer coefficients at the beginning of fouling runs (i.e. the overall heat transfer coefficient before the occurrence of fouling) and at time t (i.e. the overall heat transfer coefficient including the additional contribution of fouling).

RESULTS AND DISCUSSION

Arrhenius plots for the β-Lg denaturation of the model solutions

The Arrhenius plots for the denaturation reaction at two calcium concentrations (100 and 120 ppm) were presented in Fig. 6. This figure shows the temperature influence on the β-Lg denaturation kinetic rate in the range from 65 to 92°C.

Two mechanisms appear in Fig. 6, separated by an Arrhenius critical temperature of about 80°C. This slope

change suggests two temperature ranges: below the critical temperature, the β-Lg denaturation reaction is unfolding limited which means that the unfolding reaction is slower than aggregation, and over 80°C, β-Lg denaturation is limited by the aggregation reaction and in that case, aggregation is the slower reaction.

These results are in agreement with Petit et al. (2011). Even in the case of quasi-pure β-Lg model solution, the critical temperature that splits the Arrhenius plot in two linear parts was estimated at 80°C, each temperature range being related to the predominance of the unfolding or aggregation mechanisms, indicating that denaturation kinetic rates varied with temperature. However, this slope break is less clear in the case of our model fouling solution, probably due to its more complex composition (mixture of β-Lg and α-lactalbumin).

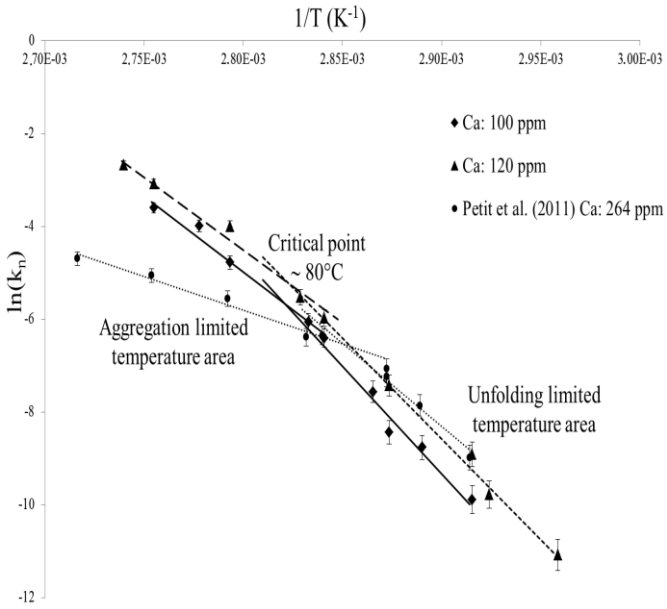

Fig. 6. Arrhenius plot for the β-Lg denaturation at various calcium concentrations

Fig. 6 also shows that β-Lg denaturation kinetics increased with calcium concentration. Even if the exact contribution of calcium on the denaturation of β-Lg is still unclear, it is speculated that calcium induces protein charge shielding or conformational changes in β-Lg structure (Simons et al., 2002; O'Kennedy and Mounsey, 2009) favouring both unfolding and aggregation reactions. This result illustrates that it is essential to know the exact content of calcium in the fouling solutions to have a clear view of the denaturation reaction. This information not commonly evaluated nowadays in literature is essential to the development of accurate model of fouling based on engineering denaturation reaction.

The frequency factor logarithms (ln k^0) and activation energies (E_A), obtained by fitting Arrhenius plots regressions for the unfolding denaturation mechanism (noted unf) and aggregation denaturation mechanism (noted agg) are shown in Table 3.

Table 3. Denaturation parameters at the two calcium concentrations

Denaturation parameter	100 ppm total calcium	120 ppm total calcium
Unfolding		
$\ln(k^0_{unf})$	124.8	117.2
$E_{A\ unf}$ (kJ.mol^{-1})	384.5	271.2
Aggregation		
$\ln(k^0_{agg})$	86.3	83.1
$E_{A\ agg}$ (kJ.mol^{-1})	360.7	260.4

For the two WPI model fouling solutions (100 and 120 ppm of calcium), the knowledge of the kinetic parameters (frequency factors and activation energies) allowed the determination of the unfolding rate constant (noted k_{unf}) and the aggregation rate constant (noted k_{agg}):

$$\ln(k_{unf}) = \ln(k^0_{unf}) - \frac{E_{A\,unf}}{R\,T} \quad (4)$$

$$\ln(k_{agg}) = \ln(k^0_{agg}) - \frac{E_{A\,agg}}{R\,T} \quad (5)$$

Fouling mass distribution in the PHE

Fig. 7 represents the deposit layer formed in the first and last channels of the PHE, at respectively 65°C (inlet temperature) and 85°C (outlet temperature), after fouling run conducted with 1% (w/w) WPI solution containing 100 ppm of total calcium. At the highest temperature, the fouling layer is white, very thick and homogeneous. It clearly appears that very low fouling is obtained in the first channel of the PHE, where the bulk temperature is lower than 70°C. Fouling is not expected to occur under 65-72°C (Lalande et al., 1989; Visser and Jeurnink, 1997). These observations are in agreement with Foster et al. (1989) work, which showed that deposit increases with temperature, making fouling rougher and more adherent to hot surfaces.

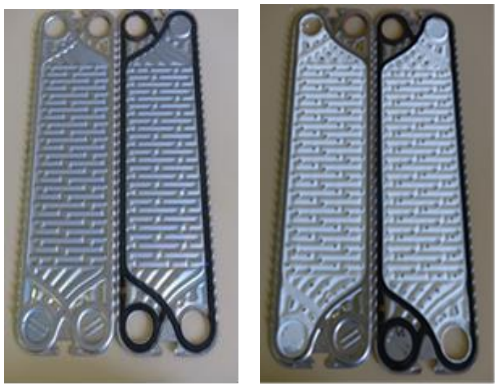

Fig. 7. Deposit collected on heat exchanger surface in the first and last channels of the PHE

Fig. 8 represents the fouling results obtained with 1% (w/w) WPI model solution containing 100 and 120 ppm of total calcium at different temperature profiles. This figure shows that the dry deposit is not uniform and is distributed differently depending on the thermal profile and the calcium concentration. Indeed, for the first solution at 100 ppm calcium, the deposit mass increases monotonically to reach a maximum in the 5th channel, whatever the imposed thermal profile. However, at 120 ppm calcium, the deposit mass reached a stationary value of about 40 g over 74°C (2nd channel temperature), for the first three temperature profiles, which consisted in a fouling maximum limit. This increasing deposit mass at low temperatures resulted from the strong increase of β-Lg denaturation level between 65°C (1st channel temperature) and 74°C (2nd channel temperature), temperature range for which the β-Lg denaturation reaction becomes significant (Havea et al. 2001; Linmark-Mansson et al., 2005). The thermal profile #4 increases monotonically, reaching a maximum of 12.5 g in the 5th channel.

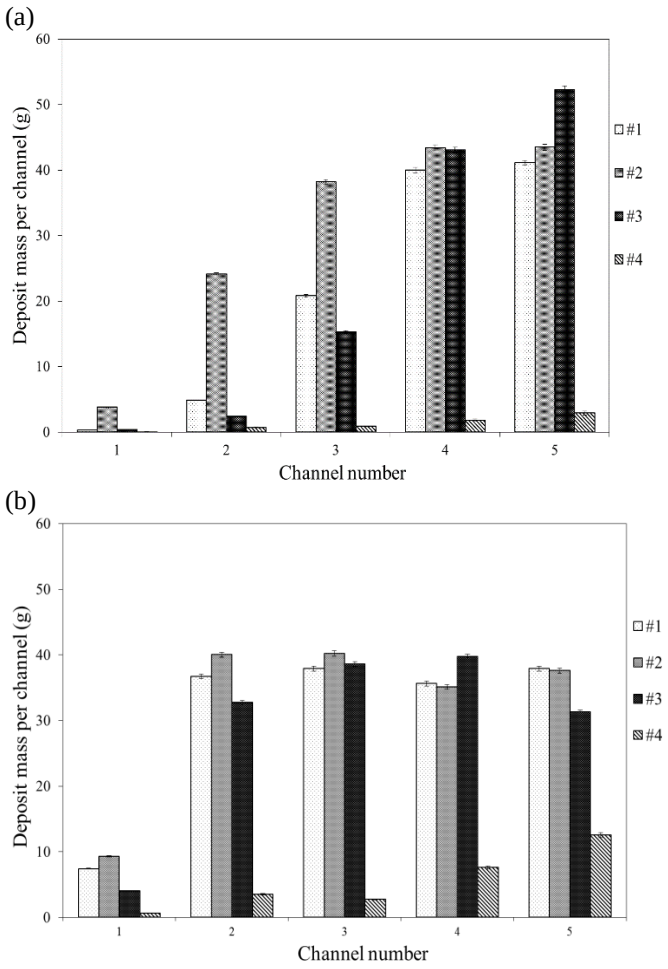

Fig. 8. Effect of the temperature profile on fouling mass distribution for the two fouling solutions:
1% (w/w) WPI solution containing (a) 100 ppm calcium, (b) 120 ppm calcium
(#i corresponds to the thermal profile number from 1 to 4)

The deposit mass is negligible, for the thermal profile #4 at 100 and 120 ppm calcium, owing to the lack of denatured β-Lg in the bulk at such low temperatures. It is suggested that β-Lg fouled hot surfaces only when the bulk temperature was high enough to allow β-Lg denaturation.

Fig. 9 represents the effect of the temperature profile on the total amount of deposit mass in the PHE for the two fouling solutions. It can be observed that, for the same inlet and outlet product temperature, the total deposit mass varied with the calcium concentration. This is the case of the thermal profile #1, for which the total deposit mass goes from 104 g at 100 ppm calcium to 154 g at 120 ppm calcium. This was also observed for the temperature profiles #3 and #4. However, for the thermal profile #2, the total amount of deposit was very close at 100 and 120 ppm calcium.

This difference of fouling distributions obtained at various calcium concentrations demonstrates the major role of the temperature profile on β-Lg fouling and its distribution in the PHE.

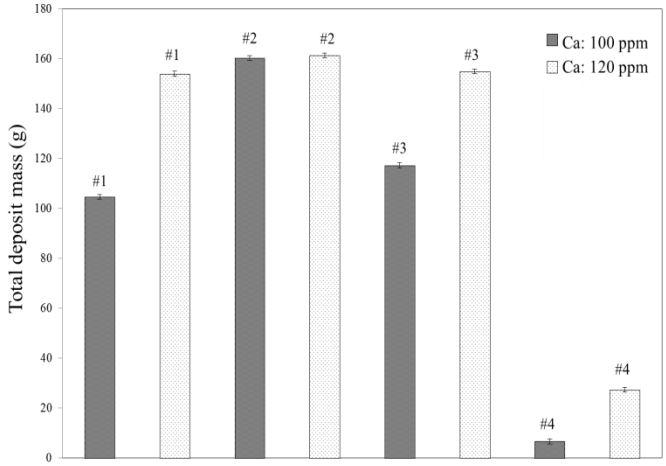

Fig. 9. Total amount of deposit mass in PHE with varying calcium concentration for the eight fouling runs
(#i corresponds to the thermal profile number from 1 to 4)

Effect of thermal profiles and calcium concentration on fouling rate

Fig. 10 shows the fouling rate behaviour during heating of the WPI solution at 100 and 120 ppm calcium in the PHE, for each thermal profile. An increase in the fouling rate with time is evident. A difference between the fouling rates can be observed for the four temperature profiles, at 100 ppm and 120 ppm calcium.

The results also show that the fouling potential of WPI in the PHE increases with the increasing temperature. Indeed, for temperature range of 65-85°C, fouling rate is altered and favoured by higher amount of calcium in the model fluid. It can be noted that for the thermal profile #4 (60-75°C), fouling resistance curves for calcium content of 100 and 120 ppm calcium were superposed. This confirms the assumption of Daufin et al. (1987), Xiong (1992) and Simons et al. (2002), who asserted that calcium can interact

with the aspartic and glutamic acid carboxyl group of the β-Lg, and so, favour the growth of the deposit by stabilizing protein aggregates.

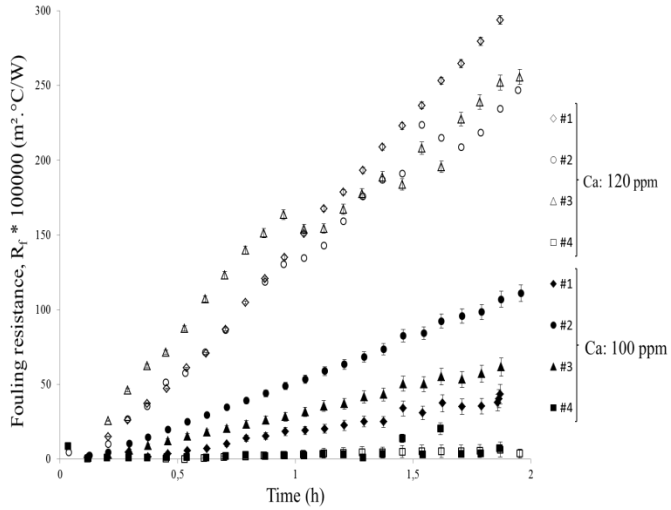

Fig. 10. Fouling resistance evolution with time during heating along the PHE with varying thermal profiles and calcium contents
(#i corresponds to the thermal profile number from 1 to 4)

Relationship between β-Lg heat denaturation rate constants and the distribution of the deposit mass along the PHE

To study the relationship between the chemical reaction of the β-Lg denaturation and the deposit formation rate within the PHE, the deposit mass distribution in the different channel of the PHE was plotted against $r = k_{unf}/k_{agg}$ (Fig. 11).

The ratio r was calculated for each temperature profile and calcium content, knowing the bulk temperature profile along the PHE (simulated by Sphere software).

For each fouling solution, it could be observed that the deposit mass per channel could be gathered on a unique curve (master curve), whatever the imposed thermal profile. The two master curves, representing the deposit mass per channel vs the ratio r, were characterized by two different zones.

Indeed, the curve of the dry deposit mass at 100 ppm calcium showed a sharp increase at values of r close to 0.28 (relative to the fouling beginning), then reaching a plateau at r = 0.99. For the second solution (WPI solution containing 120 ppm of calcium), the increase of r values starts later at 0.38 and the maximum of the deposit mass derived from the fitting curve takes place at r = 0.77, before reaching a plateau.

For the two fouling model solutions and the operating conditions investigated in this study, it can be shown that the range of r, where the increase of deposit mass occurs, is located between 0.28 and 0.99 corresponding to bulk temperatures ranging from 69.8 and 80°C. The fact that the deposit mass increases sharply, when r is below 1, shows that the unfolding zone control the growth of the deposit mass. It appears clearly that the deposit mass per channel increase till the aggregation reaction consumes unfolded species under aggregates forms. This result is in agreement with the previous observation of van Asselt et al. (2005) and consistent with Blanpain-Avet et al. (2012) work. Indeed, these authors conclude from fouled deposit analysis by Raman spectroscopy that protein aggregates are not present in the deposit. This result is also supported by the recent publication of Bouvier et al. (2014) which shows that a correlation can be established between the unfolded β-Lg content within the PHE and the dry deposit mass distribution.

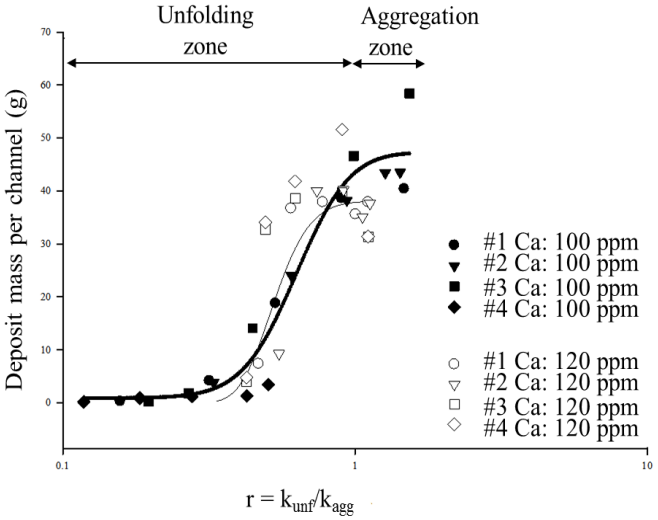

Fig. 11. Correlation between the ratio of unfolding and aggregation rate constants and the dry deposit masses
(#i corresponds to the thermal profile number from 1 to 4)

The representation adopted (dry mass deposit per channel vs r) gives an unprecedented view of the β-Lg competitive reactions (unfolding and aggregation) governing the growth of fouling for a WPI solution.

Thus, the determination of the ratio r that could be easily derived from the identification of the heat-induced denaturation kinetic by means of laboratory experiments, made it possible to obtain guidelines on the extent of fouling deposit mass and its distribution. Such approach is important in order to choose the adequate processing parameters and minimize fouling phenomena.

CONCLUSIONS

Fouling experiments were performed with WPI solutions at two different calcium concentrations, in order to investigate the effect of the operating conditions associated to the chemical denaturation reactivity of heat treatment in a PHE on the deposit formation. The extent of fouling deposit was monitored by weighing the mass of the dry fouling deposit on the plates.
It was shown that:

- β-Lg denaturation is a complex process, catalyzed by high calcium concentration, with a two-step mechanism highly dependent on the calcium content;
- An increase of the calcium content in the fouling solution induced a strong increase in the β-Lg denaturation level and consequently in the fouling mass within the PHE at high temperatures;
- The fouling mass depends on the ratio $r = k_{unf}/k_{agg}$. This indicator demonstrates the competition between the unfolding and the aggregation reactions;
- The dry deposit mass on each pass of the PHE is well correlated with r showing that this parameter is important to understand β-Lg denaturation phenomena at molecular scale and could be used to predict the mass distribution of fouling deposit.

NOMENCLATURE

Ca	calcium concentration, ppm
C_s	concentration of the total soluble β-Lg, kg m^{-3}
E_A	activation energy, J. mol^{-1}
k_n	denaturation rate constant, $g^{1-n} L^{n-1} s^{-1}$
k_n^0	denaturation frequency factor, $g^{1-n} L^{n-1} s^{-1}$
k_{unf}	unfolding rate constant, $g^{1-n} L^{n-1} s^{-1}$
k_{agg}	aggregation rate constant, $g^{1-n} L^{n-1} s^{-1}$
n	heat-induced denaturation reaction order
Q	flow rate, $m^3 s^{-1}$
r	ratio between the unfolding and aggregation rate constants
R	the universal gas constant equal to 8.314, J $mol^{-1} K^{-1}$
R_f	fouling resistance, m^2 °C W^{-1}
T	temperature, K
U_g	overall heat transfer coefficient, W $m^{-2} K^{-1}$

Subscript

agg	aggregation
C_i	channel number
h	hot water
p	product
P_i	plate number
unf	unfolding
#i	thermal profile number

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