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On the origin of flux dependence in pH-modified skim milk filtration

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Abstract – The aim of this study was to contribute to identify the physico-chemical origin of flux variations, namely the limiting flux (maximum) and the critical flux (sustainable), in ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) of skim milks modified by addition of HCl or NaOH. Both the limiting and the critical fluxes varied in a nonpredictable way with pH but with close similar trends in UF, NF and RO, highlighting the leading role of the fluid behaviour. Physico-chemical characteristics of caseins, such as size and electrophoretic mobility, were measured in the pH range 1.9–11.5 and were correlated to fluxes in UF and to a less extent in NF and RO. Available data on the electrophoretic mobility of α -lactalbumin and β -lactoglobulin allowed to suggest that serum proteins would also participate in the flux variations with a possible specific impact of α -lactalbumin as an internal foulant in UF. The role of calcium and inorganic phosphate over the wide pH range was discussed by taking calculated salt equilibrium of milk as a function of acidic pH using a new software and new additional analyses in alkaline media. Results underlined the determining role of Ca^{2+} in the inorganic irreversible fouling of organic membranes allowing proposal of a simplified cleaning protocol over a wide pH range between 6.7 and 11.5.

ultrafiltration / nanofiltration / reverse osmosis / limiting flux / critical flux

摘要 – 不同 pH 的脱脂乳对膜过滤中通量的影响。本文研究了酸化和碱化的脱脂乳(添加盐酸或者氢氧化钠)进行超滤、纳滤及反渗透操作过程中通量变化的影响因素, 研究结果表明极限通量及临界通量都随着脱脂乳 pH 值呈现不规则变化, 但是变化趋势相近, 其中流体的特性起着决定性的作用。在 pH 1.9~11.5 时, 酪蛋白的粒径及电泳迁移率与超滤的通量相关, 但是对纳滤及反渗透的影响不大。 α -乳白蛋白和 β -乳球蛋白电泳迁移率的分析结果表明乳清白蛋白对通量的变化也有影响, 主要是 α -乳白蛋白是超滤过程膜的主要堵塞物。了计算出钙及无机磷酸盐的浓度与 pH 值之间的函数关系。在 pH 6.7~11.5 范围内简单的清洗步骤即可以有效去除钙对有机膜造成的不可逆污染。

超滤 / 纳滤 / 反渗透 / 极限通量 / 临界通量

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Résumé – Sur l'origine de la dépendance des flux en filtration de lait écrémé à pH modifié. L'objectif de cette étude était de contribuer à identifier les origines physico-chimiques des variations des flux critiques (maximum) et limites (durables) en ultrafiltration (UF), nanofiltration (NF) et osmose inverse (OI) de laits écrémés modifiés par ajout de HCl ou NaOH. Les flux limites et critiques variaient de façon imprévisible en fonction du pH mais avec des tendances similaires en UF, NF et OI, soulignant le rôle déterminant du fluide. Les caractéristiques physico-chimiques des caséines (taille, mobilité électrophorétique) ont été mesurées pour des pH entre 1,9 et 11,5 et corrélées aux variations de flux en UF et dans une moindre mesure en NF et OI. Les données disponibles sur la mobilité électrophorétique de l' α -lactalbumine et la β -lactoglobuline permettent de supposer que les protéines sériques participent également aux variations de flux avec un impact spécifique de l' α -lactalbumine comme colmatant interne en UF. Le rôle des minéraux (calcium et phosphate inorganique) a été appréhendé en utilisant un logiciel de calcul des équilibres salins en milieu acide, et analyses complémentaires en milieu alcalin. Les résultats soulignent le rôle déterminant de Ca^{2+} dans le colmatage irréversible des membranes organiques, permettant finalement de proposer un protocole simplifié de nettoyage pour une large gamme de pH entre 6,7 et 11,5.

ultrafiltration / nanofiltration / osmose inverse / flux limite / flux critique

1. INTRODUCTION

Membrane processes, namely ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), are widely used in the dairy industry, for the concentration of whole milk or target components, depending on the use of the obtained fractions [7]. Production at industrial scale as well as effluent treatment is performed by membrane processes well identified as clean, sober and safe in accordance with requirements of sustainable production. The main development limitation of such processes at industrial scale is due to the scientific and technological bottleneck of fouling governing fluxes and thus, productivity and cleaning aiming at restoring membrane performances and ensuring the safety of produced fluids and production equipments [5]. For a long time, the unique objective was to reach the maximum flux (i.e. the limiting flux), involving a high transmembrane pressure (TMP). This criterion has many disadvantages among which is the buildup of a thick fouling layer, closely packed and thus cohesive and hard to remove during the cleaning step. Moreover, in industrial production filtering process units, working at constant permeate

flux, fouling increase is balanced by an increase in TMP to attain the target flux level, entering in a vicious cycle leading to shortened production times and important cleaning difficulties. To avoid such problems, an original theoretical concept was proposed in the 1990s: filtration in critical or sub-critical conditions [12]. The aim was to propose nonempirical rules in order to understand how to manage membrane processes for a long-term use, and thus how to ensure a sustainable production using such processes. For this purpose, a boundary value of flux, the so-called critical flux, is proposed. Below this value, reversible deposit can be built up on the membrane surface and above this value an irreversible deposit appears that can only be removed by chemical cleaning. Consequently, a range of stable conditions for filtration could be suggested to the user for checking the production. This concept was earlier proposed on a hydrodynamics background and mainly described in microfiltration and UF of model solutions (latex, silicates, etc.) designed for the purpose [2, 16, 32], and has also been shown successful for the filtration of milk products [13, 14, 17, 18, 33–35]. Globally, these works

mainly concerned parametric studies of hydrodynamics conditions of filtration, highlighting flux variations and sometimes those of retentions [13, 14, 17, 33–35]. Whatever the fluids, the impact of the physico-chemical environment was rarely taken into account and mainly through small variations of pH and ionic strength [4, 11, 13, 14, 17, 26, 33–35].

With the aim of a better mastering of standard milk filtration and new dairy products and/or effluent treatments (acid, transient and alkaline), this paper contributes to study wide pH variations from 2.7 to 11.5 on the limiting and critical fluxes measured with spiral membranes either in UF, NF or RO. The behaviour of the whole fouling is only considered through the destabilisation of the fouling layer due to pH variations. From a scientific point of view, the main question arising during this study concerns the identification of the origin of flux dependence vs. the pH of modified milks. Several parameters are a priori considered for a better understanding of the interdependency of physico-chemical characteristics of filtered fluids and membrane processes. Our approach considers the role of the physico-chemical characteristics of caseins (size and charge through the electrophoretic mobility measurements) either in micelle or in aggregate forms, as they are known to be responsible for flux limitation at natural milk pH. The possible impact of serum proteins is taken into account in the discussion, using previous characterisations of their charges [23, 24], knowing that most of them are no more soluble and can be associated to caseins after the ultra high temperature (UHT) treatment.

The role of different forms of calcium salts is also considered as they can enter in the composition and cohesion of the fouling layer through interactions with various proteins. As speciation of salts is not directly possible in such complex media, we have used theoretical calculations from a new software dedicated to salts' equilib-

rium in skim milk and developed in INRA (Rennes, France) [20] but only available for acidic conditions up to now. Thus, precipitate, free and soluble-linked species of calcium and phosphate salts are calculated. Because the speciation in alkaline media is not well known and no software is available, we take experimental data from [1]. The latter are less detailed and only distinction of soluble and insoluble forms can be taken into account.

2. MATERIALS AND METHODS

2.1. Fluids

The skim milk (UHT, Lait de Montagne, Carrefour, Levallois, France) contained, on average, $31.5 \text{ g}\cdot\text{L}^{-1}$ proteins (out of which $27 \text{ g}\cdot\text{L}^{-1}$ caseins) and $48 \text{ g}\cdot\text{L}^{-1}$ carbohydrates (mainly lactose, $\text{MW} = 342 \text{ g}\cdot\text{mol}^{-1}$) (according to the provider) and various salts (on average $8 \text{ g}\cdot\text{L}^{-1}$) according to [7]. The natural pH of skim milk was close to $\text{pH} = 6.6\text{--}6.7$, as expected. Adjustments of pH in the range 1.9–11.5 were carried out by the slow addition of HCl or NaOH, under magnetic stirring and the pH remained stable during the whole filtration time of nearly 6 h. HCl (concentrated, for analysis, Acros, Geel, Belgium) as well as NaOH (pellets, Prolabo, Fontenay-sous-Bois, France, rechap 97%) were used for preparing the stock solutions (1 or $2 \text{ mol}\cdot\text{L}^{-1}$) used. Deionised water used for solutions and membrane rinsing was filtered ($1 \mu\text{m}$).

2.2. Filtration experimental set-up and membranes

Three different spiral wounded membranes as well as two different filtration experimental set-ups were used in this study. Common procedures concerned:

- The use of a unique membrane of each type that was cleaned according

to the appropriate procedure (see below) until recovery of the hydraulic resistance (R_m , calculated from the well-known Darcy's relationship) after each experiment. The accuracy on measured fluxes was $\pm 5\%$.

- The choice of a constant flow rate during the cross-flow filtration leading to a constant cross-flow velocity (v) depending on the membrane process (see below).
- The temperature was kept constant at 25 ± 2 °C during filtration.
- All experiments were performed in batch mode with a volume reduction ratio (VRR) of 1 corresponding to a total recycling of both retentate and permeate in the feed tank.
- The increase in flux was gradually achieved by increasing the TMP in the appropriate range for each filtration type (see below).

2.2.1. Spiral UF

The spiral UF membrane used in this study was made of polyethersulphone (PES, HFK-131 from Koch, Lyon, France, 6.5 m^2 , molecular weight cut off (MWCO) = $5\text{--}10 \text{ kg}\cdot\text{mol}^{-1}$). The hydraulic resistance of the virgin membrane was $R_m = 2.1 \pm 0.3 \times 10^{13} \text{ m}^{-1}$.

The UF was performed on a pilot designed by TIA (Bollène, France) with 25 L of fluid being processed at each filtration. All the experiments were conducted at a constant flow rate of $10 \text{ m}^3\cdot\text{h}^{-1}$ corresponding to an average cross-flow velocity (v) close to $v = 0.3 \text{ m}\cdot\text{s}^{-1}$. TMP increased from 1.2 to 5.2 bar with an accuracy of ± 0.1 bar.

2.2.2. Spiral NF

The spiral NF membrane used in this study was made of polyamide (PA, Desal 5 DL from Osmonics, Delft, The Netherlands, 2.5 m^2 , MWCO = $150\text{--}300 \text{ g}\cdot\text{mol}^{-1}$, $R_m =$

$6.5 \pm 0.3 \times 10^{13} \text{ m}^{-1}$). The NF was performed on a second pilot designed by TIA (Bollène, France) with 10 L of fluid processed at each filtration. All the experiments were conducted at a constant flow rate of $750 \text{ L}\cdot\text{h}^{-1}$ corresponding to v close to $0.1 \text{ m}\cdot\text{s}^{-1}$. TMP increased from 5.0 to 25.0 bar with an accuracy of ± 0.5 bar.

2.2.3. Spiral RO

The spiral RO membrane was a composite organic one (TFC HR from Koch, Lyon, France, 2.5 m^2 , NaCl retention of 99.5%, $R_m = 27 \pm 2 \times 10^{13} \text{ m}^{-1}$). The RO was performed on the same pilot as NF at $790 \text{ L}\cdot\text{h}^{-1}$ (v close to $0.1 \text{ m}\cdot\text{s}^{-1}$). TMP increased from 7.5 to 30.0 bar with an accuracy of ± 0.5 bar.

2.2.4. Irreversible fouling and cleaning

Part of the overall fouling is generated by a sub-layer strongly bounded to the membrane corresponding to the so-called irreversible fouling. Hydraulic resistance due to irreversible fouling established at limiting flux ($R_{\text{irrev. limiting}}$) was determined from water flux after the rinsing step following the "milk" filtration. $R_{\text{irrev. limiting}}$ corresponds to the target value to remove during the cleaning step. Efficient cleaning steps depend on both membranes and modified skim milks. For membranes used in UF, NF and RO, similar cleanings were performed (50 °C, 1 h, VRR = 1) according to two different procedures depending on the pH of the modified milk. HNO_3 (pH 1.6) and an alkaline formulated detergent (P3-Ultrasil 10 at 0.4 wt.% pH 12.0, containing chelant(s) and surfactant(s) provided by Ecolab, Issy-les-Moulineaux, France) were used as single step or in cascade.

The procedures were first established for UF membrane and then applied to NF and RO membranes with similar efficiency. The reversible part of fouling of spiral membranes

in UF, NF and RO were first removed by water rinsing whatever the pH, before the chemical cleaning steps began.

- For $\text{pH} > 5.0$, UF, NF and RO spiral membranes were cleaned ($50\text{ }^{\circ}\text{C}$, 1 h) with the alkaline formulated detergent. This procedure is efficient as more than 90% of initial flux is recovered whatever the membrane. This procedure was first established for UF membrane and proved to be efficient for more than 25 filtration cycles that alternated skim milk UF at natural pH and cleaning.
- For acidic pH between 3.0 and 4.7, the previous procedure was not efficient enough. So a cascade of acid and alkaline detergents was tested. Due to salts' presence in the irreversible fouling layer, the use of the acid step for solubilisation of minerals is needed. In order to avoid the precipitation of hydroxide in/on the membrane, we started with the acid step (HNO_3 , $\text{pH} = 1.6$, $50\text{ }^{\circ}\text{C}$, 1 h) prior to the alkaline, one described before.
- For pH close to 2.8, UF membranes were dramatically fouled. One acidic and five alkaline cleaning steps were needed to restore the membrane initial flux.

Thus, too acidic pH do not reveal to be compatible with sustainable requirements. Then, the following experiments were limited to $\text{pH} \geq 3.7$. Finally, taking into account the cleaning problematic leads to a limitation in the pH range of modified skim milk that can be acceptable for UF, NF and RO with organic membranes. A sustainable process only corresponds to the filtration of slightly acidic to neutral and alkaline pH, whatever the obtained retentions.

2.2.5. Limiting and critical flux determination

To determine both fluxes, UF, NF or RO of a given fluid was performed by

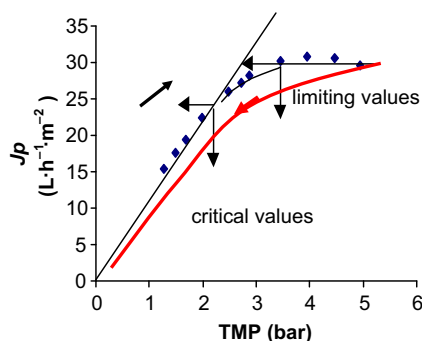


Figure 1. Experimental determination of critical and limiting fluxes in UF: a linear relationship was observed below the critical point (J_{critical} and $\text{TMP}_{\text{critical}}$). Beyond the limiting pressure ($\text{TMP}_{\text{limiting}}$) the constant flux corresponds to the limiting flux (J_{limiting}) with TMP, transmembrane pressure and J , flux.

increasing step by step the TMP, with values depending on the membrane. Each increase of TMP was realised after reaching the plateau value of flux (J) for the previous TMP. Filtration for a given TMP was performed for about 30–100 min depending on the TMP. Typical plot of J at plateau value vs. TMP is shown in Figure 1. A linear relationship is observed below the critical point (J_{critical} and $\text{TMP}_{\text{critical}}$) corresponding to critical conditions of filtration. Beyond the limiting pressure ($\text{TMP}_{\text{limiting}}$) the flux does not change anymore and a constant maximal value corresponding to the limiting flux (J_{limiting}) is reached. This procedure can be used only if the occurrence of an irreversible deposit at limiting flux had been previously checked. This can be done by a stepwise decrease in TMP from the limiting flux to a value lower than the critical flux. Occurrence of the critical flux is checked if a hysteresis is evidenced on the J vs. TMP graph due to an evolution of the irreversible fouling upon which the reversible fouling is built. According to Wu et al., classification [32] all experimental curves led to define

“critical flux of weak form”, meaning that the permeability (slope) in sub-critical conditions is always lower than the permeability to pure water, whatever the membrane process and pH. Limiting fluxes were determined with a precision close to 5% but critical fluxes were obtained by extrapolation of the J vs. TMP curve with a poorer precision close to 10%.

2.3. Physico-chemical characterisation of casein and aggregates

2.3.1. Size distribution of casein micelles and aggregates

The size distribution of particles and aggregates was first determined by laser light scattering (LLS), using a Mastersizer 2000 granulometer (Malvern Instruments, Worcestershire, UK) at two different wavelengths (He/Ne laser: 633 nm and electroluminescent diode: 466 nm) at room temperature. Five hundred microlitres of unfiltered modified skim milks were injected in the cell containing about 100 mL of Milli-Q water at 1500 rpm stirring at 25 °C. Refractive indexes were set at 1.34 and 1.59 for solution and particles, respectively.

2.3.2. Size and electrophoretic mobility of casein micelles and aggregates

Hydrodynamic particle diameters were measured by dynamic light scattering (DLS) on a Zetasizer 3000 HS (Malvern Instruments, Worcestershire, UK). Measurements were carried out at 90° scattering angle, 633 nm wavelength and 25 °C temperature. The refractive index solution was set at 1.341 and the viscosity of dispersive solution at 1.02×10^{-3} Pa·s. Diluted milks were 1.2 µm filtered prior to analysis, allowing characterisation of the smaller particles. An average size (Z_{average}) from electropho-

retic measurement (electrophoretic dynamic light scattering (EDLS), simultaneously measured as size from DLS) was also determined with an accuracy of ± 5 nm.

Electrophoretic mobility (μ , velocity to electric field ratio of casein micelles or aggregates) was also measured with a Zetasizer 3000 HS (Malvern Instruments, Worcestershire, UK) after 1.2 µm filtration. To discuss the change in casein charge with the pH, the zeta potential is commonly used [6, 21]. It is inferred from the measurement of μ that is a proportional value. However, recent theoretical developments ([30] and related papers) pointed out that a single zeta potential value is not so clearly defined for a porous particle, even if the charge exists. As casein micelles can be considered as porous particles, we select the experimental μ value rather than a questionable inferred zeta potential. μ was measured with an accuracy of $0.4 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ close to the isoelectric point and with a better accuracy of $0.2 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for higher values.

For both size and μ measurements, dilution of modified and unmodified skim milks was achieved with the respective aqueous phase (ultrafiltrate at the same pH) to avoid equilibrium displacement according to previously validated protocol ([26] and related papers).

2.4. Chemical oxygen demand analysis

The chemical oxygen demand (COD) was measured with a 160 DCO kit (Macherey Nagel, Molsheim, France) with an accuracy better than 5% after appropriate dilution by water if necessary. Finally, accuracy on retentions, defined according to

$$\text{Retention of COD} = 1 - \frac{\text{permeate COD}}{\text{retentate COD}} \quad (1)$$

was lower than 10%.

2.5. Calculation for salt speciation with the pH variations

Only modelling is possible to deal with the various forms of salts that cannot be measured. As a first attempt of correlation between fluxes and milk composition, we base our discussion on the available information on salt speciation over the wide pH range of this study, using skim milk composition. Several complementary (very heavy) analyses might be performed in order to evidence the exact composition of UHT milk salt fractions that could be slightly different from that of the un-treated skim milk.

2.5.1. Theoretical calculations in the acidic pH range

Theoretical calculations were made using a new software based on dissociation constants proposed by Mekmene et al. [20] allowing the calculation of mineral distribution, in unmodified and modified skim milks, in various forms in the aqueous phase as minerals or linked to casein. Concentrations of ionic species, namely free, complexed (corresponding to soluble forms of calcium associated to phosphate, citrate and chloride) or precipitated forms (corresponding to nanoclusters of calcium phosphate included in casein micelles and not to free calcium phosphate precipitate in suspension in the aqueous phase), can be calculated according to the pH adjusted by HCl addition. In this study we mainly focus on calcium and phosphate soluble salts in the aqueous phase of milk. For calculation, selected concentrations are chosen as those of the average composition of skim milk: Ca, Mg, Na, K, inorganic phosphate and Cl as 30, 5, 22, 38, 21 and 27, respectively (in mmol·L⁻¹). Caseins are taken at 25 g·L⁻¹ and their binding with Ca is based on phosphoserine and carboxylate sites of proteins. Figure 2 shows the predicted concentration for calcium in the pH range 2.0–6.7.

The inorganic phosphate is fully soluble at a pH lower than 5.5 and then precipitates with calcium in the nanoclusters contributing to the casein micelles' or aggregates' cohesion. Three zones can be distinguished for calcium forms that are not linked to caseins:

- (i) $2.0 < \text{pH} < 3.0$
Two main forms exist, free (Ca^{2+}) and complex ones, in a roughly constant amount with a free to complex forms ratio close to 2.
- (ii) $3.5 < \text{pH} < 5.5$
 Ca^{2+} amount decreases slightly with the pH and conversely complex forms increase until a free to complex forms ratio is close to 1.
- (iii) $5.5 < \text{pH} < 6.7$
 Ca^{2+} amount decreases strongly with the pH and complex forms decreased slightly as calcium phosphate precipitate increases in the nanoclusters linked to caseins.

2.5.2. In the alkaline pH range

At alkaline pH the release of calcium from caseins was observed during the destructure of micelles connected to the progressive milk transparency increase. In the absence of proteins Ca^{2+} would immediately enter in various possible combinations with phosphate, citrate and hydroxyl ions, possibly leading either to soluble or precipitated components. Among the latter are calcium phosphate and calcium hydroxide precipitates, calcium citrate and di-citrate complexes.

The presence of proteins in the aqueous phase strongly modifies this equilibrium, and no precipitate can be evidenced as proved by the milk transparency observation. A model of the complex evolution of salts and association with caseins was recently proposed [1]. To summarise, one can consider in a first attempt that no more Ca^{2+} exists in the modified milks at alkaline pH and that

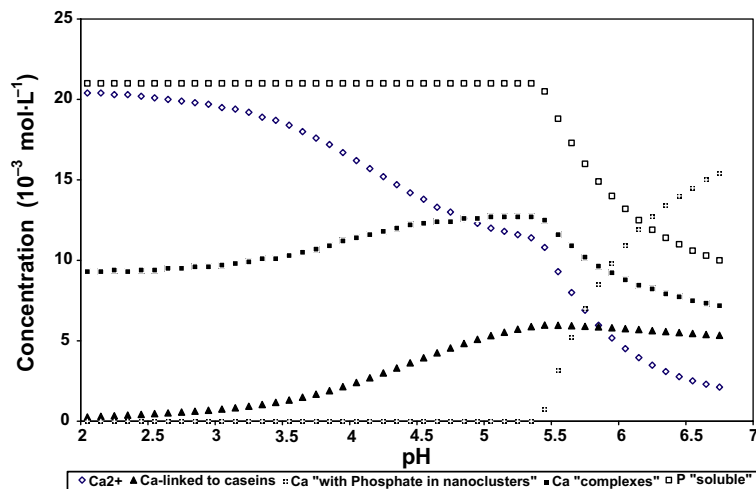


Figure 2. Theoretical calculations on Ca and P of milk according to the software in the pH range 2.0–6.7.

whole calcium is engaged in combinations either in complex soluble forms or with casein aggregates. The pH close to 9 appeared as a key point in this system, corresponding more or less to the end of the calcium leakage in the aqueous phase. Adapting experimental results of [1] for soluble and non-soluble forms of calcium, empirical correlations were established (Fig. 3) for further calculation of soluble forms (without description of various complexed forms) and associated with caseins for calcium and phosphate. At this time, it was not possible to enter in a more detailed speciation of soluble forms corresponding mainly to citrate and phosphate complexes.

3. RESULTS

3.1. Physico-chemical characterisation of caseins and casein aggregates

Figure 4 shows the size distribution of caseins and casein aggregates measured by

LLS on modified milk without prior filtration of the sample. At natural pH of milk, particles of about 2.2 μm size probably correspond to residual fat particles in the UHT skim milk.

Size is then determined from DLS on 1.2 μm filtered milks. At natural pH of milk, casein micelles exhibit a size distribution between 20 and 700 nm (data not shown), in good agreement with the literature data, whatever the calculation mode or the technique itself [4, 8, 15, 19, 29]. Z_{average} (from EDLS) is found close to 210 nm, in good agreement with part of the literature data [4, 15, 19] even if sometimes a value close to 100 nm has been reported ([8] and related papers) in good agreement with our own results from the mean size calculated on the particle number (calculation mode highlighting small particles); this is not contradictory with having an average size of different value. Decreasing the pH from 6.7 to 5.1, slight changes are evidenced in the size distribution but Z_{average} remains close to 210 nm. Increasing the pH from 6.7 to 11.0 induces the disappearance of

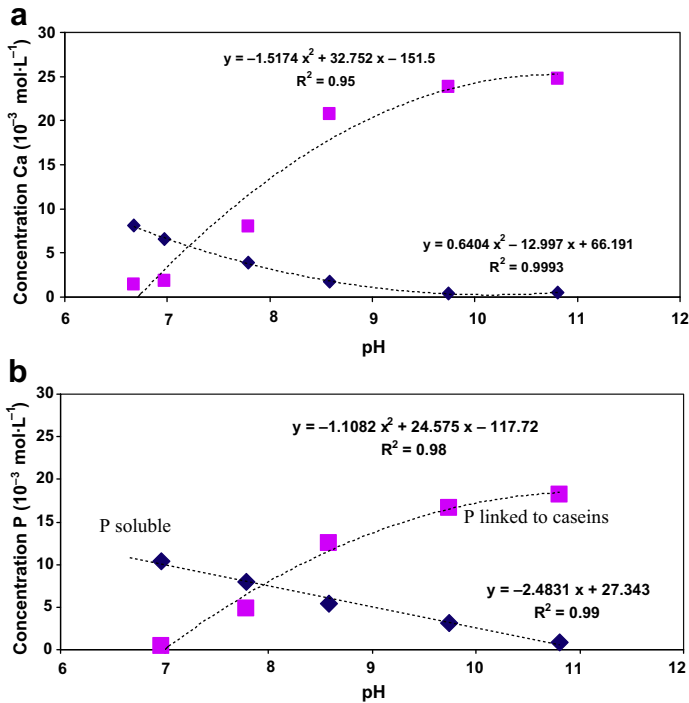


Figure 3. Calcium (a) and inorganic phosphate (b) forms at alkaline pH adapted from [1] – (♦) soluble form and (■) linked to caseins.

native casein micelles and the appearance of aggregates, mainly of micrometre magnitude. Z_{average} of aggregates lower than $0.8 \mu\text{m}$ s decreased first up to pH close to 9 and then increased (Fig. 5).

Figure 6 shows the variation in the electrophoretic mobility of particles made of caseins (and lower than $1.2 \mu\text{m}$) vs. pH. As expected, μ tends towards zero at pH 4.6, which corresponds to the casein isoelectric pH. μ of smaller particles is not modified by pH increase up to 11.5, even if casein micelles are denatured and replaced by “casein aggregates”.

As a conclusion for physico-chemical characterisations, it can be drawn that size and electrophoretic mobility are two independent and complementary characteristics

of particles made from caseins. As casein aggregates may vary quite strongly with pH, further discussion can be divided into three parts:

- (i) High acidic pH range ($3.7 < \text{pH} < 4.7$)
The electrophoretic mobility is close to zero as caseins are at their isoelectric pH. They formed micrometric aggregates that precipitate. Such uncharged caseins are able to build up a deposit at the membrane wall during further UF, NF or RO.
- (ii) Low acidic pH range ($5.1 < \text{pH} < 6.7$)
The electrophoretic mobility increases linearly with pH. The average diameter of caseins, whatever their forms, remains close to $Z_{\text{average}} = 210 \text{ nm}$.

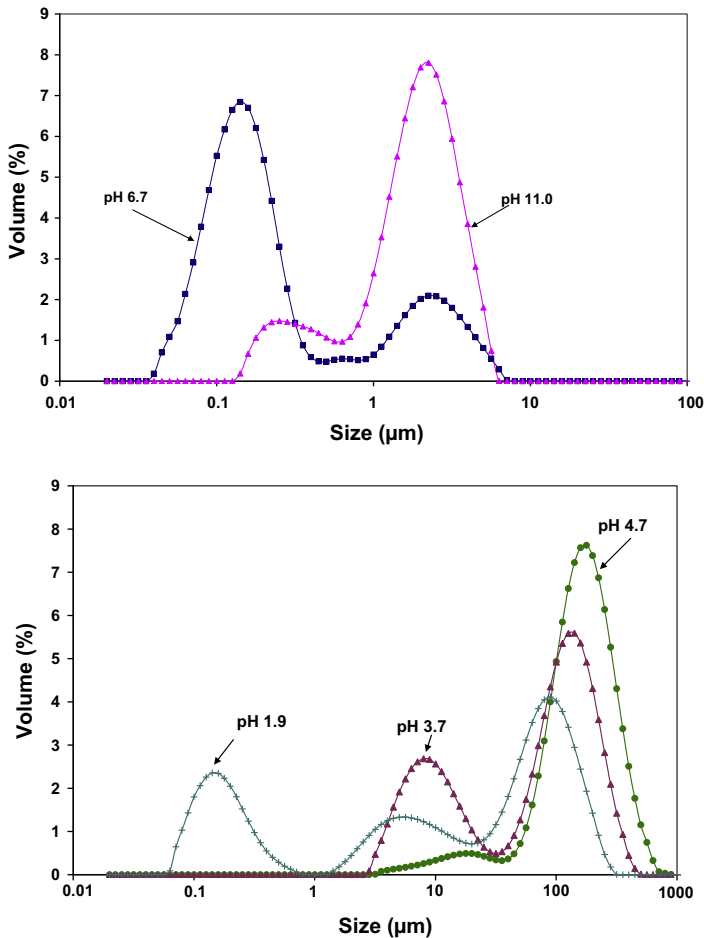


Figure 4. Size distribution by LLS of particles of natural and modified skim milks in alkaline and in acidic pH range (for both, no filtration before measurements).

Accordingly, repulsive electrostatic interactions involving casein aggregates and charged membrane may occur. All the flux and retention variations observed during filtrations are then correlated with variations of the μ as the average size is roughly constant.

(iii) Neutral to alkaline pH range ($6.7 < \text{pH} < 11.0$)

The electrophoretic mobility is constant and equal to $-1.9 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$.

A bimodal size distribution is evidenced, one centred around 2.4 μm and the other one around 80–250 nm. By increasing the pH, the smaller particles tend to disappear and a plateau minimum value is observed at pH close to 9. The smallest particles, native casein micelles ($Z_{\text{average}} = 210 \text{ nm}$ at natural milk pH), are progressively replaced by smaller aggregates up to $Z_{\text{average}} = 90 \text{ nm}$ at pH 9. Then, the average size again increases

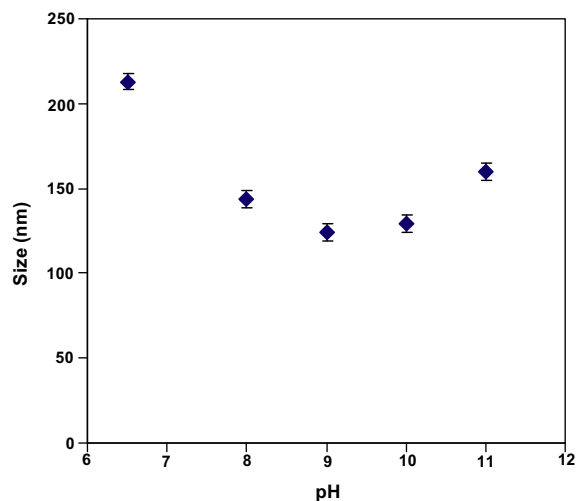


Figure 5. Size of casein aggregates (Z_{average}) vs. pH of modified skim milk (sample after 1.2 μm filtration).

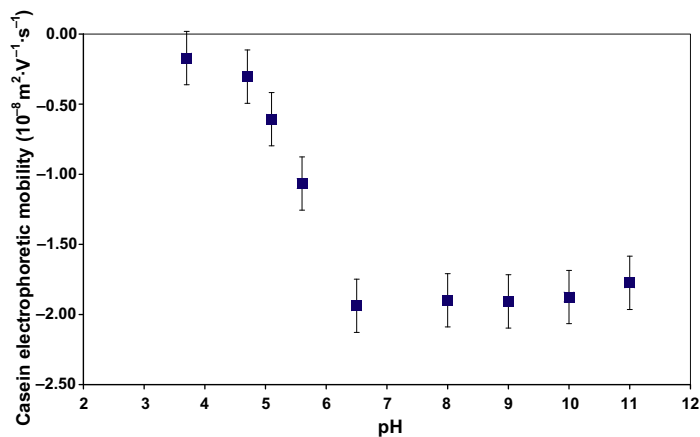


Figure 6. Electrophoretic mobility (μ) of caseins whatever their forms vs. pH ($\mu \pm 0.2 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).

up to $Z_{\text{average}} = 150 \text{ nm}$ with increasing pH, with a concomitant calcium leakage from caseins up to pH 9. Secondly aggregation of smaller aggregates occurs, which may be due to the formation of new calcium phosphate bonds with

caseins. As the electrophoretic mobility is constant and highly negative, electrostatic interactions involving caseins are expected during filtration and may play a significant role in both flux and retention of charged solutes, whatever

the pH. So, all the flux and retention variations observed during UF, NF or RO at alkaline pH are then correlated to the casein sizes' variations.

3.2. Filtration of skim milks in the 3.7–11.5 pH range

3.2.1. Limiting and critical flux variations with pH

Figure 7 shows both critical and limiting fluxes vs. pH in UF, NF and RO. The limiting and critical fluxes behave similarly, whatever the considered membrane process, meaning that the behaviour is mainly monitored by the filtered fluid in comparison with the membrane type.

3.2.2. Fouling

As it is the case for the fluxes, complex variations of the resistance due to the whole fouling at limiting flux (R_f) are observed with pH (data not shown). Whatever the pH, R_f is always lower than $20 \times 10^{13} \text{ m}^{-1}$ in UF, whereas it ranges from 60×10^{13} to $200 \times 10^{13} \text{ m}^{-1}$ in both NF and RO.

Resistance due to the irreversible part ($R_{\text{irrev. limiting}}$ only at limiting flux) is always lower than $6 \times 10^{13} \text{ m}^{-1}$ in UF and lower than $13 \times 10^{13} \text{ m}^{-1}$ in both NF and RO. Generally, the irreversible fouling in NF is intermediate between those of UF and RO (Fig. 8). $R_{\text{irrev. limiting}}$ varies with pH in a non-predictable linear way for both UF and RO. Further investigations are needed to understand the origin of this linear correlation. The increase in $R_{\text{irrev. limiting}}$ for pH lower than 5 may be related to the occurrence of mineral irreversible fouling at very low pH (see below).

3.2.3. Cleaning needs

Another approach to describe the fouling is to consider the needs for cleaning. For all

pH and membranes, an alkaline cleaning step is needed, meaning that an organic irreversible fouling exists in UF, NF and RO.

The membrane resistance is recovered after the first alkaline cleaning step for all filtrations performed with milk whose pH > 5, meaning that mainly organic components are in the irreversible fouling in/on the membrane.

Our previous experiments on UF membrane cleaning fouled by skim milk at natural pH showed that no acid step is needed for a long-term use (more than 30 consecutive cycles of skim milk UF followed by an alkaline cleaning and already partial validation at industrial scale) [9] that is fully coherent with the analysis of the irreversible fouling, evidencing only proteins on the membrane in this particular case [3, 22, 27]. Further analysis of irreversible fouling of UF membranes fouled by pH modified skim milk in the range 5.0–6.7 would be done to confirm whether some small amount of inorganic components enter in the irreversible fouling or not. Whatever the conclusion, it is already shown that the alkaline cleaning step is efficient enough and that inorganic compounds could be present only in small quantities.

For UF, NF and RO filtrations performed with acid-modified milks, with pH lower than 5.0, the alkaline step is not sufficient and an acid one is needed to restore the membrane flux. This need clearly shows that minerals are in the irreversible fouling for such pH (the role of origin of minerals will be discussed in the following section).

3.2.4. Retention of COD

Retention of COD is measured at both limiting and critical fluxes for UF, NF and RO experiments. Table I shows that retention is roughly independent of the flux. For effluents' treatment purpose, typical COD retentions are in good agreement with retentions observed for dairy effluents at natural pH [31]. Consequently, for effluent

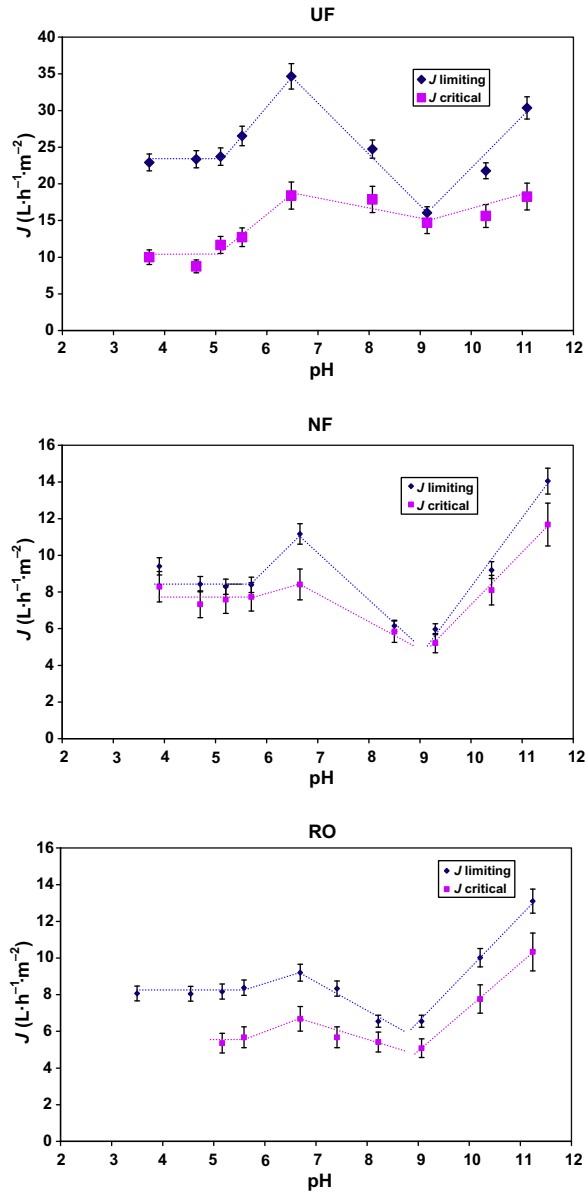


Figure 7. Behaviour of critical and limiting fluxes with pH in UF, NF and RO of modified skim milk.

treatment, whatever the membrane process, it can be drawn that the productivity is mainly due to the flux mastering as the retentions are constant.

Considering that pH variation of milk induces ionic strength variation that might be greater than $73 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ (according to the software calculations the ionic strength

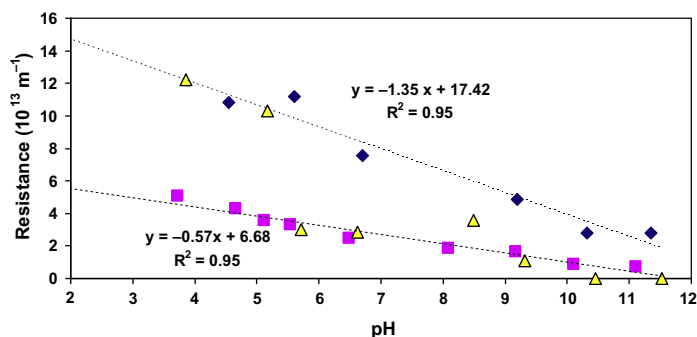


Figure 8. Irreversible hydraulic resistance at limiting flux in UF (■), NF (▲) and RO (◆) vs. the pH of modified skim milk.

Table I. COD retentions at limiting and critical fluxes during UF, NF and RO.

Retention (%)	pH range	At limiting flux	At critical flux
UF	3.7–6.0	56 ± 6	50 ± 4
UF	6.5–11.5	54 ± 4	40 ± 5
NF	3.7–11.5	99.2 ± 0.8	99.2 ± 0.7
RO	3.7–11.5	> 99.9	> 99.9

will be in the $151\text{--}73 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ range for pH from 2.0 to 6.7, respectively), the question arises “why the ionic strength modification does not affect the membrane performances?”. A partial answer can be given looking at the components responsible for the COD, namely mainly proteins and lactose. Proteins are charged solutes for which an increase in the ionic strength might provoke a decrease in retention due to an increasing screening of charges. Experimentally, the observed retention is 100% in NF and RO as expected and greater than 90% in UF, whatever the pH. Due to the low cut-off of the UF membrane one can consider that retention mechanism is thus mainly due to size exclusion and that only a minor part of the retention can be modulated by the ionic strength.

The main part of COD in permeate is due to lactose, an uncharged solute, the retention of which is thus independent of the ionic strength. This is confirmed by quantitative analyses not shown here.

4. DISCUSSION

Here is a first attempt to propose possible physico-chemical origins of flux variations; their is a global approach common to UF, NF and RO in a wide pH range, since as already mentioned above, the filtered fluid characteristics are most reliable parameters to be taken into account.

4.1. Possible components of the whole fouling and their possible location

As a general approach, one can consider four types of components that could a priori be involved in the membrane fouling: caseins, serum proteins, lactose and minerals. According to the ability of components to cross the membrane towards the permeate, one can distinguish the ability to foul the membrane inside the pore or at the milk/membrane interface or in the accumulated layer outside of the membrane.

4.1.1. Small components as lactose and minerals

Lactose as well as minerals are able to cross the membranes, whatever their type, consequently, they would be able to participate in the internal as well as in the external fouling. As lactose is not a pH-dependent component, its role is not discussed here. As it is easy to solubilise in water, it was already proved that lactose does not enter in the composition of the irreversible fouling at natural pH of milk in UF [6, 22, 27]. For the mineral fraction of milk, the pH-dependent components mostly correspond to calcium and phosphate salts, the role of which will be discussed in the following section.

4.1.2. Caseins

Whatever the membrane process, caseins, either in micelles or in aggregated forms, cannot cross the membranes. Consequently, they can only contribute to the external fouling, meaning that they can be present in the accumulated layer or at the interface. Accordingly, their behaviour will be discussed according to a common approach for UF, NF and RO.

4.1.3. Serum proteins

In NF and RO, proteins cannot cross the membrane and the corresponding fouling can only be on the membrane surface at the interface with milk or in the accumulated layer. UF is a different case, since at natural milk pH, only α -lactalbumin can permeate, as evidenced by reverse-phase HPLC (RP-HPLC) (data not shown). The irreversible fouling was previously studied by streaming potential measurements, both along the membrane surface and through the pores [25]. It was evidenced that the membrane isoelectric point (iep) of the surface moved towards the iep of β -lactoglobulin, whereas the membrane iep

inside the pore is shifted towards that of the α -lactalbumin. Thus, one may think that internal fouling due to proteins corresponds to α -lactalbumin, whereas external fouling at the membrane interface is mainly made of β -lactoglobulin during UF of skim milk at natural pH.

Protein retention during UF is roughly constant and > 98% when decreasing the pH of milk from 6.7 to 3.7, as evidenced by whole protein quantification performed by FTIR-ATR (data not shown). Therefore, only part of α -lactalbumin probably cross the membrane, whatever the pH and may constitute the internal fouling.

At alkaline pH in the range 8.0–11.0, protein retention during UF is roughly constant and close to 90%. The increase of proteins in the permeate is incompatible with only full α -lactalbumin transmission, meaning that other small denatured and soluble proteins are able to cross the membrane. Identification of these proteins has not been performed yet and numerous and delicate quantitative analyses would be necessary [28] to be affirmative on this particular point. Consequently, the internal fouling can be modified, regardless of the natural pH of milk.

Finally, whatever the pH, serum protein fouling can form a priori on the UF membrane surface, at the interface as well as in the pores but the composition would be modified according to the pH range: an acidic to neutral one and an alkaline one.

4.2. Possible impact of proteins on fluxes

As explained before, variations of caseins properties can only modify the accumulated layer.

4.2.1. Role of charge in the 5.1–6.7 pH range

In the 5.1–6.7 pH range, casein average size (Z_{average}) is constant, whereas the

charge significantly varies as evidenced by μ variations. Limiting and critical fluxes are plotted against those of casein aggregates in this pH range (Fig. 9).

In UF, both fluxes vary linearly with casein electrophoretic mobility. The fluxes are high when the absolute value of μ is high, meaning that repulsive electrostatic interactions, involving caseins (whatever their forms), may be involved in the flux variations. Of course, the free casein aggregates, in suspension in the aqueous phase, do not correspond directly to the fouling at the membrane wall, but they can govern the cohesion of a more or less compact layer that regulates fluxes. For comparison, limiting fluxes of a UF zirconia membrane (with a MWCO of $10 \text{ kg}\cdot\text{mol}^{-1}$, M5 Carbosep, Orelis, Miribel, France) adapted from [26] are reported in Figure 9. Looking at the J_{limiting} vs. μ graph for both UF organic and inorganic membranes, it appears that the slope is independent of the membrane material with similar cut-off or pore size.

Looking at the plot of both limiting and critical fluxes vs. casein electrophoretic mobility for NF and RO, it appears that the slope is roughly zero, highlighting that the fluxes' dependency on electrostatic interactions is much more important for a membrane with larger pores (UF) than for a membrane with smaller pores and dense membrane (NF and RO).

A question that arises is then "even if the accumulated layer provokes a flux limitation, is the difference in flux variation with pH really due to the accumulated layer or to the internal fouling occurring in UF and not in NF and RO?"

The linear decrease of flux can be explained taking into account the internal fouling of the membrane by salts: one can assume that when the pH increases from 5.0 to 6.7, the free calcium decreases in milk, leading to a decrease in the internal fouling due to calcium. This is in good agreement with the occurrence of a more or less important mineral irreversible

fouling due to calcium with pH (see below). Such a phenomenon can occur in UF, NF and RO since small ions are able to enter the three membrane types. According to an important difference in the slopes of J vs. pH, it is not possible to attest that salts present in the internal fouling solely contribute to flux variations.

An important difference between the three membranes can be related to α -lactalbumin internal fouling (perhaps not native here, see below), which can enter in the UF membrane but cannot do so in NF and RO membranes.

Thus, caseins, whatever their form, can be only partly responsible for flux variations.

4.2.2. Role of casein size in the 6.7–11.0 pH range

For $\text{pH} > 6.7$, the charge of casein aggregates is high and constant, meaning that electrostatic interactions can be involved in the fouling layer cohesion. Roughly the size of the particles increases progressively in this pH range up to $2.2 \mu\text{m}$, but the average behaviour of the smaller particles is quite complicated (Fig. 5). Looking at the size evolution of the smaller particles in the filtration media (Fig. 5) and the flux behaviour in this pH range (Fig. 7), it is clear that flux increase is related to size increase in the smaller particles, even if they are the minor part and whatever the filtration process. So, the cohesion of the fouling layer is partly controlled by the size of particles entering in its composition: bigger particles favour higher and less cohesive fouling deposit, and thus higher fluxes contrary to smaller particles. Once again, slopes of J vs. pH in this range are low in NF and RO compared to UF, meaning that only part of the accumulated layer can be responsible for flux variation and that other components of milk play a role.

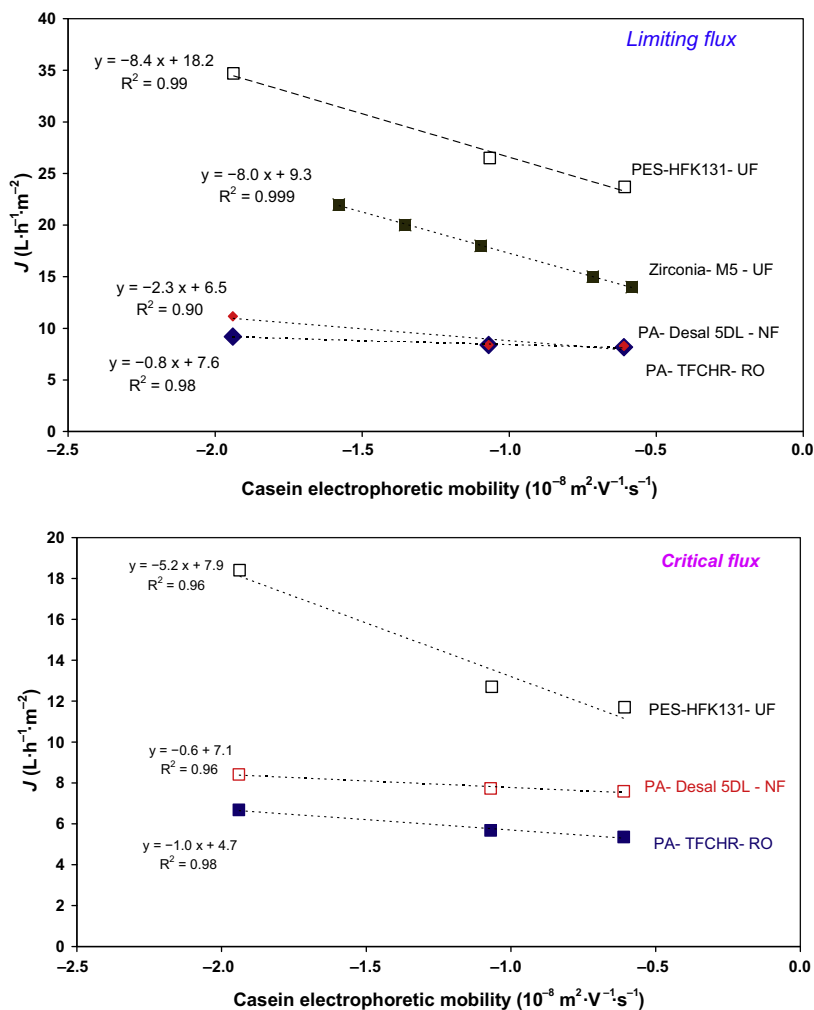


Figure 9. Correlation between limiting flux and critical flux and casein electrophoretic mobility for different membrane types in the pH range 5.1–6.7. The results for zirconia UF membrane are adapted from [26].

4.2.3. Possible impact of serum proteins on fluxes in the 4.6–6.7 pH range

Electrophoretic mobility of native α -lactalbumin and β -lactoglobulin was theoretically determined from their primary

sequence and then measured at pH 7 by capillary electrophoresis in previous studies [23, 24]. These studies concluded that theoretical values are not correct in the case of serum protein behaviour at pH 7 in borate as well as in phosphate buffer, including ionic strength effects in the $10\text{--}200 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ range.

Nevertheless, experimental mobility of $-1.1 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for α -lactalbumin and $-1.6 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and $-1.5 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ was measured for the A and B variants of β -lactoglobulin, respectively. Knowing the isoelectric point of each protein, 4.2–4.5 and 5.1 for α -lactalbumin and β -lactoglobulin, respectively, it can be concluded that the electrophoretic mobility should be zero at such pH. Thus when decreasing the pH from 6.7 to 4.6, the electrophoretic mobility of α -lactalbumin would increase from about $-1.1 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to 0. Similarly, μ would increase from about $-1.5 \times 10^{-8} \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ to 0 for β -lactoglobulin in the same pH range. These μ variations as well as the order of magnitude of the electrophoretic mobility of serum proteins are close to those determined here for caseins. Thus, when filtering un-treated skim milk it will be difficult to infer whether flux differences with pH are due to caseins and casein aggregates and/or serum proteins. Moreover, as serum proteins are partly denatured in UHT skim milk, discussion about their respective impact on fluxes is of course limited. Nevertheless, it can be assumed that effect of charges of serum protein on flux behaviour might be superimposed to that of caseins, if any. Thus, the role of α -lactalbumin as an internal foulant of the UF membrane proposed in the previous section would be in good agreement with such considerations.

4.3. Possible impact of minerals on fluxes

Minerals can a priori participate in the whole fouling, whatever its location for UF, NF and RO membranes. Empirical correlations between the limiting flux observed in UF and different forms of both calcium and phosphate are suggested and shown in the following section. As flux variations are significantly different mainly for

pH > 9, only conclusions at very alkaline pH can be extrapolated as well in NF and RO.

4.3.1. Neutral to acidic pH

For pH lower than 7.0, empirical linear correlations can be found between limiting flux in UF and soluble calcium concentration (Fig. 10). The higher the soluble calcium, the lower the limiting flux. Similar trends are evidenced with phosphate (Fig. 10). Precipitates of calcium phosphate in the form of nanoclusters embedded in casein aggregates do not increase the overall fouling contrary to soluble calcium that favours in-situ fouling of membrane. Thus, it can be drawn that soluble calcium acts as a promoter of inorganic fouling in/on the membrane during filtration. In order to clarify the role of various forms of the soluble calcium fraction on the membrane fouling, empirical linear correlations are found mainly with Ca^{2+} (Fig. 11) and to a less extent for complexed forms.

4.3.2. Alkaline pH

Roughly linear correlations between UF limiting flux and calcium forms either soluble or associated to caseins, are obtained in different regions of the alkaline pH range (Fig. 12). This suggests a role of soluble calcium ions in the overall fouling, then according to the pH, a role of casein aggregates containing calcium and phosphate in association. For pH lower than 8.2, where soluble calcium (only complexed forms) is predominant, the higher the soluble calcium, the lower the limiting flux, highlighting that soluble complexes do not limit fluxes. For pH > 8.2, where calcium and phosphate, associated to casein aggregates, are predominant, the higher fluxes are related to the higher content of associated ions, with probably a similar role as the nanoclusters in casein aggregates at acidic pH. A more detailed explanation based on

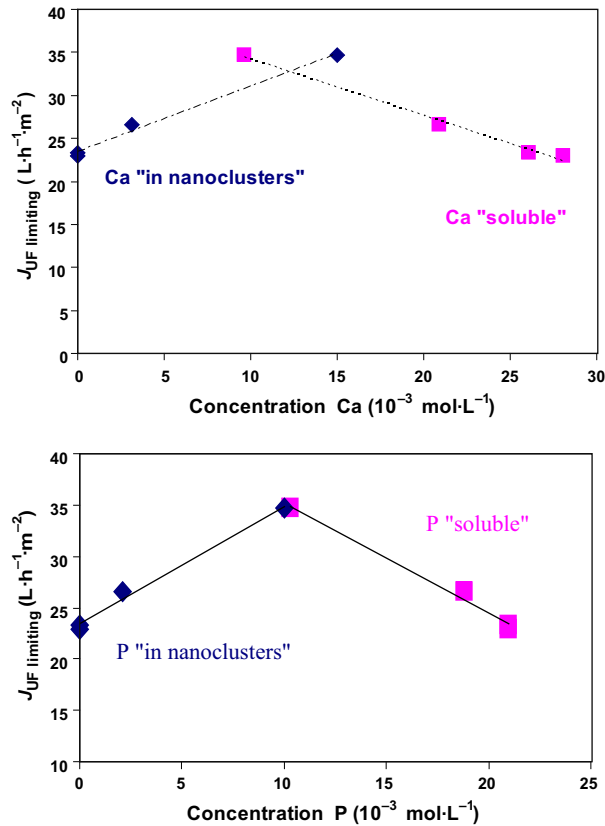


Figure 10. Empirical correlation between theoretical Ca (a) and P (b) concentrations in various forms and limiting flux in UF for pH lower than 7.0.

calcium complex forms cannot be proposed as the respective amounts of these complexes are not available at that time.

4.3.3. Conclusion on whole fouling and minerals

As a conclusion, all these empirical correlations suggest that calcium salts play a role in the overall fouling, both in soluble forms and those associated to casein aggregates, in addition to the impact of the casein aggregates themselves and to that of α -lactalbumin in UF. Similar conclusions can be drawn for NF and RO, except for

α -lactalbumin. Further investigations are needed for a better understanding of the whole phenomenon and the origin of variation of cohesion of casein aggregates must be studied looking at the role of associated calcium and phosphate either in nanoclusters at acidic pH or in associated forms that have to be quantified at alkaline pH.

4.3.4. Irreversible fouling at limiting flux and consequence on cleaning

For pH lower than 5.0 (Figs. 2 and 7), when considering the requirement of an

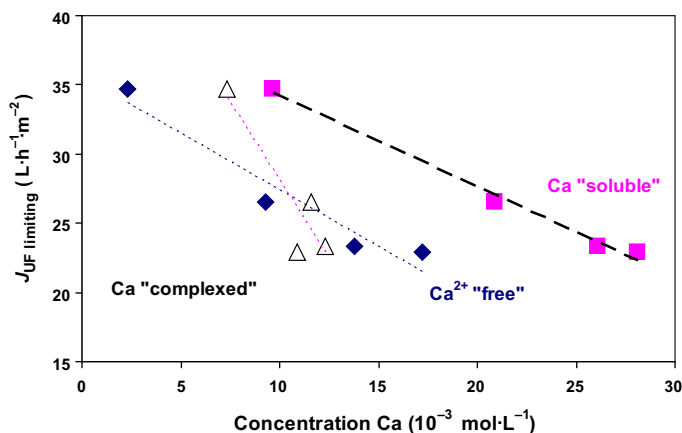


Figure 11. Empirical correlations between limiting flux in UF and theoretical calcium concentration in various soluble forms for pH lower than 7.0.

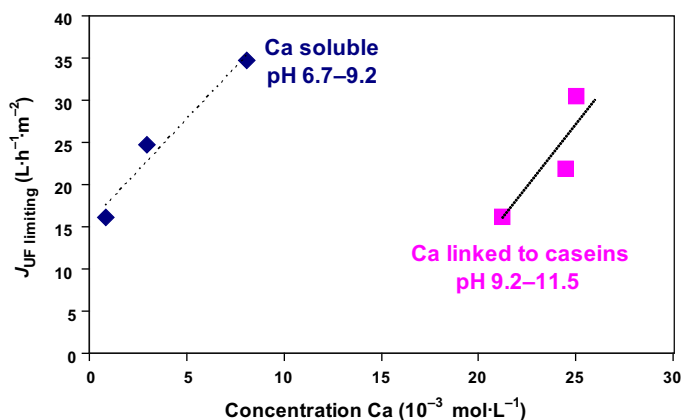


Figure 12. Empirical correlation between soluble calcium and calcium associate phosphate in casein aggregates with the limiting flux in UF in the pH range 6.7–11.5.

acid step during membrane cleaning, it indirectly highlights the presence of an irreversible fouling due to inorganic components. When pH increases from 3.7 to 5.0, the Ca^{2+} amount in modified milk strongly decreases and the acid cleaning step is always needed. So, it can be deduced that Ca^{2+} amount is related to

severe inorganic irreversible fouling in/on organic membrane, whatever the technique (UF, NF and RO) and the organic active layer of either PES (UF) or various PA (NF and RO).

Considering the cleaning needs for filtration of unmodified and alkaline modified milks, we have observed that no acid

cleaning step is needed. For neutral to alkaline pH, Ca^{2+} is always lower than $2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ and soluble calcium is mainly engaged in soluble complexes with phosphate and citrate. Then, Ca^{2+} appears as the main promoter of the inorganic irreversible fouling in/on the organic membranes, whereas calcium phosphate engaged with casein in micelles or aggregates or in soluble complexes has no severe consequence on the cleaning step as calcium is not disposable.

This phenomenon suggests that if the solubility limit of calcium salts is not reached in the bulk solution, meaning that Ca^{2+} exists in solution, it is not the same case at the membrane surface and probably in the pores. It can be suggested that concentration polarisation occurs in close vicinity of the membrane wall, playing the role of a destabilising surface provoking the mineral nucleation, and thus their precipitation, regardless of the salt accumulation. An unanswered question concerns also the behaviour of proteins (and probably mainly β -lactoglobulin) at the milk/membrane interface as the salting out effect can also occur, favouring gel formation. Nevertheless, we thought that this second eventuality would lead to a reversible fouling as gel formed before the membrane pore entrance during UF of skim milk has already been shown to be easily removed by water rinsing [10]. Further studies are needed to definitely conclude on this particular point.

Complementary in-depth study of the PES-UF membrane cleaning when fouled by unmodified skim milk has confirmed that minerals are not discernable in the irreversible part of the fouling layer, and thus we have suggested that acid cleaning step is not needed for such filtrations [10, 22]. Then, a single step of alkaline cleaning can be sufficient for filtrations performed with modified milks in the 6.7–11.5 pH (an additional disinfection step must be added for the safety of equipment of food industry). This proposal (without the disin-

fection step) is successfully tested, and thus validated during this study in UF, NF and RO. Moreover, partial validation at industrial scale is already done in PES-UF for natural pH and a systematic validation is in progress at industrial scale.

5. CONCLUSION

The aim of this study was to identify the possible physico-chemical origins of flux variations, namely the limiting flux (maximum) and the critical flux (sustainable), in UF, NF and RO of skim milks modified by the addition of HCl or NaOH. Both the limiting and the critical fluxes are pH dependent in a nonpredictable way with close similar trends in UF, NF and RO, highlighting the leading role of the fluid behaviour. From physico-chemical characteristics of caseins (size and electrophoretic mobility), we have shown that variations of electrostatic interactions and aggregates' size partly control fluxes. Charges of the two main serum proteins, α -lactalbumin and β -lactoglobulin, vary similarly as casein charge in the 4.6–6.7 pH range. Then, impact of serum proteins, if any, would be superimposed to that of caseins in a nondistinguishable way. Some differences observed between UF, NF and RO may be due to internal fouling by α -lactalbumin that only exists in UF. The role of minerals (calcium and inorganic phosphate) is taken into account through empirical linear correlations between fluxes and soluble element forms, using a software dedicated to the mineral speciation in acid media together with additional analyses in alkaline media. Results suggest that soluble minerals are involved in the whole fouling, regardless of the pH. A careful analysis of cleaning protocols of membranes vs. pH indirectly shows this particular role of minerals in the irreversible fouling. Results evidence the determining role of free calcium (Ca^{2+}) in the inorganic fouling of organic membranes.

Although already associated calcium would not be involved in the irreversible fouling of membranes, free calcium is prone to precipitate in/on the membrane during filtration, probably due to a higher concentration at the membrane interface owing to concentration polarisation and a destabilising role played by the membrane surface. Finally, on the basis of this mineral role, we have shown that a simplified cleaning protocol with only one single alkaline step is efficient enough for UF, NF and RO fouled by skim milks in the 6.7–11.5 pH range.

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