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Impact of colloidal interactions on the flux in cross-flow microfiltration of milk at different pH values: A surface energy approach

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ABSTRACT

The effect of colloidal interactions between casein micelles on the flux of a tubular ceramic membrane at cross-flow microfiltration (MF) of skim milk was studied. Filtration experiments were performed at a pH range of 6.8–5.9. Compared to filtration of milk at its native pH (6.8), the flux was reduced and membrane fouling proceeded faster when acidified milk was filtered. To explain the observed flux behavior, a new interaction model for casein micelles was developed, which incorporates on the basis of the extended DLVO (xDLVO) theory hydrophilic and hydrophobic interactions in the form of Lewis acid–base forces, which were derived from protein surface energies. It could be shown that deposit layer build-up is strongly influenced by the charge-dependent protein surface hydrophilicity, whereas electrostatic interactions between proteins can be neglected in high ionic strength fluids like milk.

1. Introduction

Fouling reduces the efficiency of membrane-based operations in food, beverage, water treatment and biological processes. Different models explaining the development of a deposit layer as a function of cross-flow filtration conditions exist [1–8]. While those models adequately predict foulant deposition on the membrane surface, little is known about the structure of the formed deposit layer during the filtration of complex colloidal solutions, which results from a complex interplay between particle–particle interactions and hydrodynamic forces. For the filtration of fluids containing model colloids, models were developed which can describe structural properties, like thickness and porosity, of the deposit layer. These models correlate the drag force of filtrate flow towards the membrane, which compresses the particle layer, with a particle interaction force. The latter can either be attractive or repulsive depending on the physico-chemical nature of the interacting particles, particle separation distance and environmental conditions [9–14]. Often, repulsive electrostatic interactions are identified as the major force preventing particle aggregation of already deposited particles and also hindering further particle deposition on the layer. The decisive properties therefore are the net surface charge of the interacting particles and the ionic strength of the solution. Tang et al. [15,16] showed that the limiting flux during reverse osmosis (RO) of humic acid at a low ionic strength was proportional to the square of the surface charge density. They concluded that the limiting flux was reached when the drag force of filtrate flow was equal to the repulsive force between an approaching foulant and the deposit layer. This barrier force prevents further foulant deposition and was reported to be dominated by electrostatic repulsion. A similar explanation was put forward by Faibish et al. [17] and Palecek and Zydney [18] regarding the pH dependency of flux of a silica suspension and model proteins, respectively.

In the MF of milk, casein micelles are retained by the membrane and are known to be the main deposit layer constituent, while the much smaller whey proteins permeate to a large extent [19]. Caseins are the major protein component (~28 g/l) of milk and are organized in a complex micellar structure with an average micelle diameter of about 180 nm and an isoelectric point of ~4.6. The exact structure of the micelle is still under debate, but a consensus has been reached that most of the surface of a micelle is covered by the highly charged and hydrophilic part of κ-casein, lending colloidal stability to the micelle at native pH of milk of 6.8 [20–23]. The most detailed model for casein micelle interactions known to us was developed by Tuinier and de Kruif [24]. According to their model, the surface charge of the casein micelles is strongly shielded by the high ionic strength of milk serum (~80 mM), which is the background electrolyte for milk proteins. Therefore, electrostatic repulsion between casein micelles is very small. Due to the high ionic strength, the κ-casein surface layer can be considered

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as a salted brush, which has a charge-dependent and thus pH-dependent height. This model describes the interaction between micelles as the sum of Van-der-Waals attraction and steric repulsion between the κ-casein brushes. Below pH 5.9, the brush height is reduced significantly. Therefore, steric repulsion decreases. It can be expected that these pH-dependent alterations of colloidal interactions strongly affect the flux during milk MF.

Studies on the impact of milk acidification on MF flux are rare. Rabiller-Baudry et al. [25] and Bouzid et al. [26] recently analyzed changes in the critical and limiting fluxes during the ultrafiltration (UF) of skim milk over a broad pH range. They found that in the pH range of 6.7–4.7, the mean micelle diameter was constant and that critical and limiting flux decreased linearly with the absolute value of the casein zeta potential. The authors stated that the decreased flux was due to the reduced electrostatic repulsion between casein micelles in the deposit layer, resulting in a denser structure. This conclusion, however, is contradictory to the interaction theory for casein micelles presented by Tuinier and de Kruif [24] (see also [27–29]), where the electrostatic contribution to the overall interaction between micelles is assumed to be negligibly small at a pH of 6.8. Consequently, a further reduction of electrostatic repulsion should not significantly affect the flux. This contradiction has so far not been addressed in membrane literature. Since the change in κ-casein brush height is very small at pH 6.8–5.9 [24], a reduction of steric repulsion can be excluded. The reduction of flux between pH 6.8 and 5.9 can be explained neither by reduced electrostatic repulsion nor by decreased steric repulsion according to the current casein interaction theories. Thus, both models fail to explain the colloidal behavior of casein micelles during filtration. Other interactions like hydrophilic repulsion and hydrophobic attraction are probably also of importance. Therefore, it appears to be attractive to refine those models by including previously neglected interactions.

Van Oss [30] extended the classical DLVO theory, which is based on Van-der-Waals and electrostatic interactions, by including hydrophilic repulsion and hydrophobic attraction – the so-called xDLVO theory – using a surface energy approach. The theoretical background of this approach will be presented in Chapter 2. The interaction between mineral particles like clay and glass could be adequately described using the xDLVO theory, while the DLVO approach failed [31]. Kim et al. [14] could correctly predict the MF and UF flux of silica suspension using a filtration model based on surface energies. Furthermore, a good agreement between the prediction of the xDLVO theory and AFM measurement was found for colloid–membrane interactions [32,33]. It will be interesting to adopt the xDLVO theory to complex colloidal structures like casein micelles.

Hence, the purpose of this study was to explain the pH dependency of flux during MF of skim milk in the pH range of 6.8–5.9 by including non-DLVO forces in a new interaction model for casein micelles using a surface energy approach. Focus was put on interactions between casein micelles forming deposit layers, while interactions between casein micelles and the membrane were found to affect the filtration results to a much smaller extent in comparison. This pH range was chosen because here other colloidal properties such as size and surface shape are not affected, in contrast to pH values further below pH 5.9.

2. xDLVO theory

2.1. DLVO and xDLVO interaction

The particle interaction theory outlined below is extensively discussed by van Oss [34] and citations therein.

The total interaction energy ΔU_{cwc} as a function of particle separation distance, x, of two identical particles (e.g. between casein micelles, c) interacting in aqueous media, w, can be expressed according to Eq. (1) as:

$$\Delta U_{\mathrm{cwc}}(x) = \Delta U_{\mathrm{cwc}}^{\mathrm{LW}}(x) + \Delta U_{\mathrm{cwc}}^{\mathrm{EL}}(x) + \Delta U_{\mathrm{cwc}}^{\mathrm{AB}}(x) \tag{1}$$

where the indices LW, EL and AB stand for Lifshitz–Van-der-Waals, electrostatic and Lewis acid–base interactions, respectively. The first two terms of the right-hand side represent the classical DLVO model, while the third term accounts for the polar electron donor/electron acceptor interactions, which can either be repulsive (hydrophilic repulsion) or attractive (hydrophobic attraction). LW and AB interaction energies can be obtained by surface thermodynamics [34].

2.2. Surface tension and free energy of adhesion

The surface-energetic properties of condensed media and liquids can be described by their surface tension (γ) components:

$$\gamma^{\mathrm{tot}} = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}} \quad \text{with} \quad \gamma^{\mathrm{AB}} = 2\sqrt{\gamma^{+}\gamma^{-}} \tag{2}$$

where γ^{+} represents the electron acceptor parameter and γ^{-} the electron donor parameter.

The free interaction energy of adhesion $\Delta G_{\mathrm{cwc}}^{\mathrm{LW}}$ caused by Lifshitz–Van-der-Waals interactions of two particles, c, immersed in water, w, is given by Eq. (3):

$$\Delta G_{\mathrm{cwc}}^{\mathrm{LW}} = -2\left(\sqrt{\gamma_c^{\mathrm{LW}}} - \sqrt{\gamma_w^{\mathrm{LW}}}\right)^2 \tag{3}$$

and the free energy of adhesion caused by acid–base interactions can be calculated with Eq. (4):

$$\Delta G_{\mathrm{cwc}}^{\mathrm{AB}} = -4\left(\sqrt{\gamma_c^{+}\gamma_c^{-}} + \sqrt{\gamma_w^{+}\gamma_w^{-}} - \sqrt{\gamma_c^{+}\gamma_w^{-}} - \sqrt{\gamma_c^{-}\gamma_w^{+}}\right) \tag{4}$$

The free energy of adhesion per unit area represents the interaction energy per unit area of two planar surfaces brought into contact with each other.

2.3. Interaction energies between two spherical colloids

Converting the interaction energies for planar surfaces to those of spherical colloids by the Derjaguin approximation [36,37] and introducing the specific decay functions for each interaction results in interaction energies $U_{\mathrm{cwc}}(x)$ of two spheres as a function of particle separation distance x.

Non-retarded Van-der-Waals interactions can be described by Eq. (5):

$$\Delta U_{\mathrm{cwc}}^{\mathrm{LW}}(x) = \frac{-H_{\mathrm{A}} \cdot R_1 R_2}{6x \cdot (R_1 + R_2)} \tag{5}$$

where R_1 and R_2 denote the radii of the interacting particles. H_{A} is the Hamaker constant, which can be calculated from the LW component of the free energy of adhesion (Eq. (3)).

$$H_{\mathrm{A}} = -12\pi \cdot l_0^2 \cdot \Delta G_{\mathrm{cwc}}^{\mathrm{LW}} \tag{6}$$

where l_0 is the equilibrium distance and is usually set to 0.158 nm [35].

The AB interaction energy decays exponentially with the separation distance and can be written for interacting spheres as:

$$\Delta U_{\mathrm{cwc}}^{\mathrm{AB}}(x) = \frac{2\pi R_1 R_2}{R_1 + R_2} \cdot \lambda \cdot \Delta G_{\mathrm{cwc}}^{\mathrm{AB}} \cdot e^{\frac{l_0 - x}{\lambda}} \tag{7}$$

where λ is the decay length of AB interactions in aqueous media. Usually $\lambda = 1$ nm is chosen as a characteristic value [34,38].

For constant surface potential, the relationship in Eq. (8) can be derived for electrostatic interactions:

$$\Delta U_{\mathrm{cwc}}^{\mathrm{EL}}(x) = \pi\varepsilon\varepsilon_0 \frac{R_1 R_2}{R_1 + R_2} \cdot \zeta_1 \zeta_2 \cdot \ln[1 + e^{-\kappa x}] \tag{8}$$

where ε_0 is the dielectric permitivity of the vacuum and ε is the dielectric constant of the suspending fluid (for water $\varepsilon = 80$),