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Effect of hydrodynamic and physicochemical changes on critical flux of milk protein suspensions

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Summary. The critical flux during ultrafiltration of whey protein concentrate and sodium caseinate suspensions was investigated. The weak form of critical flux was found for both suspensions. Critical flux of sodium caseinate was higher than that of whey protein concentrate. This could be due to the differences in particle size of the suspensions, resulting in a slower particle back transportation for small particles (whey proteins) compared to the larger casein micelles. Critical flux increased as crossflow velocity increased and decreased as concentration increased, suggesting that critical flux was determined by competition between rate of particle removal from the membrane surface and rate of particle movement towards the membrane surface. Influence of changing pH, addition of NaCl and $CaCl_2$ on the critical fluxes of both protein suspensions was also studied. Increasing pH led to an increase in critical flux for both protein suspensions, suggesting that electrostatic repulsive forces are involved in determining critical flux in both cases. Addition of NaCl gave rise to a decrease in electrostatic interactions due to an increase in ionic strength and ζ potential, and resulted in a decrease in critical flux for sodium caseinate, but had no significant effect for whey protein concentrate. Addition of $CaCl_2$ resulted in a decrease in the critical flux and had a more pronounced influence than NaCl. These results suggest that, in addition to electrostatic repulsive forces, other factors such as structure of protein may be involved in determining the critical flux.

Keywords: Ultrafiltration, milk protein, critical flux, membrane, fouling.

Several methods to avoid or reduce the severity of membrane fouling have been pursued in recent decades. In addition to cleaning, two major approaches to avoid fouling can be identified. These are hydrodynamic (e.g. changing the flow regime across the membrane surface, controlling the wall concentration) and surface modification (changing the surface/foulant affinity) (Muir & Banks, 1985; Reis *et al.* 1997; Cheryan, 1998). Avoiding membrane fouling by controlling hydrodynamic conditions, using the critical flux concept has been proposed by Field *et al.* (1995). Their study demonstrated the possibility of operating under non-fouling conditions. This is achieved by maintaining the permeate flux below a critical value. Flux under these conditions is constant with processing time. Increasing the flux above this

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critical value leads to a significant increase in fouling resistance. As a result flux cannot be maintained by increasing transmembrane pressure (TMP). The permeate flux corresponding to this critical value is then called 'critical flux'.

Two forms of critical flux were proposed by Wu *et al.* (1999). The 'strong' form of critical flux exists if the flux with a suspension is identical to the flux of clean water at the same TMP. The 'weak' form exists if the relationship between TMP and flux is linear, but the slope of the line differs from that of water. Critical flux is then determined as the point at which the linear relationship between flux and TMP breaks down. This linearity can be investigated either by stepwise increasing TMP and measuring the permeate flux, or stepwise increasing permeate flux and measuring the TMP (Wu *et al.* 1999; Mänttäri & Nyström, 2000). Critical flux can also be determined by setting the flux and directly observing particles on the membrane surface (Li *et al.* 1998). Critical flux is then defined as the point at which deposition commences. This method is complicated and is only applicable for transparent membranes and very dilute suspensions. However, these two methods have been shown to give similar results (Li *et al.* 2000).

Critical fluxes of various feed materials have been investigated. Different studies have used protein (BSA) and yeast suspensions (Field *et al.* 1995; Chen, 1998; Wu *et al.* 1999), but most have used non-food materials (e.g. latex, silica, $CaCO_3$), as they are more well-defined in terms of their physical and physicochemical properties (Chen *et al.* 1997; Harmant & Aimar, 1998; Huisman *et al.* 1999).

Some applications using the critical flux concept have already demonstrated benefits, in terms of fouling and rejection during microfiltration of skimmed milk (Gésan-Guiziou *et al.* 1999), ultrafiltration of skimmed milk (Grandison *et al.* 2000) and nanofiltration of cheese whey and waste effluents (Jeantet *et al.* 2000; Mänttäri & Nyström, 2000). Critical flux involves the onset of fouling due to particles in the feed (Chen, 1998). For filtration of skimmed milk and milk based products, whey protein and casein fractions play an important role in fouling (Lee & Merson, 1976; Merin & Cheryan, 1980; Tong *et al.* 1988). Critical flux mainly involves these two components, but no comparison of their relative influence has been reported. Information on the critical flux of whey protein and casein is important for understanding and controlling fouling by milk-based products during membrane filtration.

The aim of this study was to determine the critical flux during ultrafiltration of whey protein concentrate and sodium caseinate suspensions, and thus gain a better understanding of their role on the onset of fouling. Effects of crossflow velocity (in the turbulent flow regime), protein concentration, pH, NaCl and $CaCl_2$ on critical flux were investigated.

Materials and methods

Whey protein and sodium caseinate suspensions

Whey protein powder (800 g protein/kg, 60 g lactose/kg, 60 g fat/kg, 30 g ash/kg and 50 g moisture/kg) was supplied by MILEI GmbH (Stuttgart 70191, Germany), and sodium caseinate powder (880 g protein/kg, 60 g fat/kg, 60 g ash/kg and 60 g moisture/kg) was supplied by Dairy Gold (Mitchelstown, CO, Ireland).

Whey protein and sodium caseinate suspensions were prepared at the required protein concentration by adding powder to soft water at 40–50 °C with agitation. Suspensions were then heated and maintained at 50 °C before use in the membrane system.

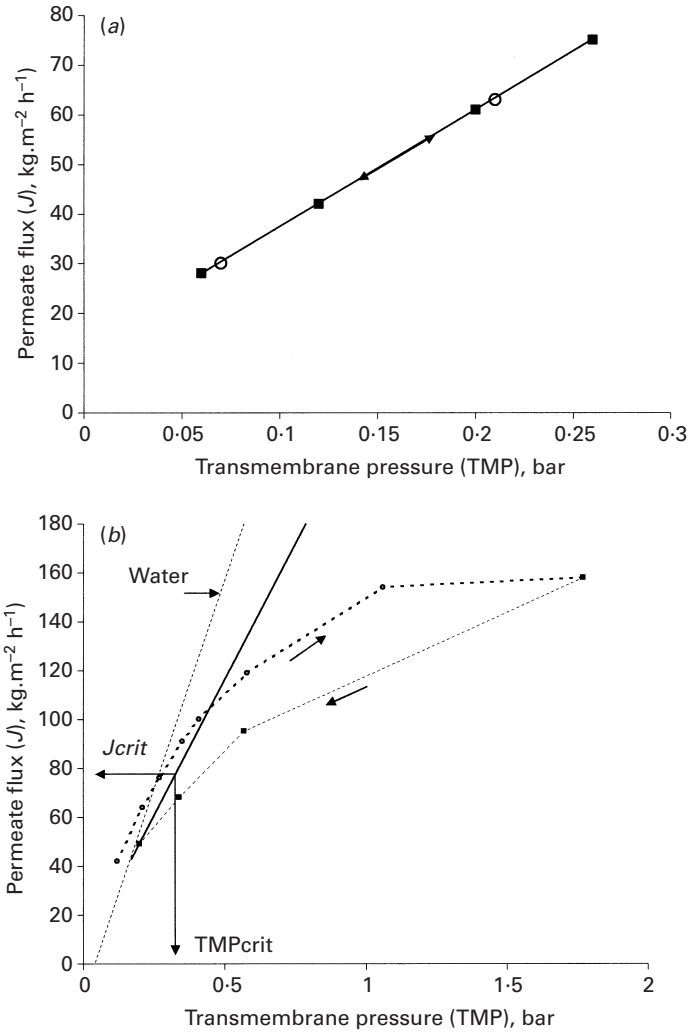

Fig. 1. The effect of stepwise increasing and decreasing transmembrane pressure (TMP) on permeate flux during ultrafiltration of whey protein suspensions (10 g/kg) at constant crossflow velocity 2·3 m s^{-1} and 50 °C: (*a*) below the critical flux; (*b*) above the critical flux (○, increasing TMP; ■, decreasing TMP).

Membrane rig and operating conditions

Tubular polyvinylidene fluoride (PVDF) membranes of high hydrophobicity were used (MWCO 200 kDa, internal diameter 12·5 mm, active membrane length 57·6 cm, membrane area 226 cm², Paterson Candy International, Whitchurch RG28 7NR, UK). PVDF membranes are negatively charged under normal operating pH (ζ potential reported to be −19·5 mV at pH 7, and −17·0 mV at pH 3; Bowen & Gan, 1990).

Pressure transducers were used to measure the pressure of the feed inlet, outlet and permeate (accuracy ±1 kPa). Permeate was collected and weighed (accuracy ±0·1 g) continuously to measure flow rate (accuracy within 5%). Temperature of the feed was controlled by a heat exchanger. All these parameters were measured every 1 min and monitored using a data logging system. Crossflow velocity (V) was controlled using a variable speed 4·4 kW centrifugal pump with

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motor speed controller. Crossflow velocities of 1·1, 1·7, 2·3, 2·8 and 3·4 m s^{-1} were achieved. [Note that wall shear stress is proportional to the square of crossflow velocity.] The system was pre-warmed to the experimental temperature (50 °C) using soft water. Feed (50 °C) was introduced to the system while the permeate outlet valve was completely shut-off. Feed flow rate and feed pressure were adjusted slowly to the initial starting values. TMP was controlled by opening the permeate valve to regulate the permeate pressure. Permeate was returned to the feed tank every 5 min after continuous measurement of flux.

Experimental procedure

Critical flux (J_{crit}) was determined by stepwise increasing TMP and examining the response of the permeate flux. Measurements were carried out over at least 15 min holding time at each TMP, to allow the system to stabilize. The relationship between TMP and permeate flux was then recorded. Critical flux was expressed as the point where the relationship starts to deviate from linearity, as proposed by Wu *et al.* (1999). All experiments were carried out in triplicate, and reported critical fluxes were averages of three runs.

Effects of varying the following hydrodynamic and physicochemical parameters on critical flux were determined with both sodium caseinate and whey protein concentrate solutions (10 g protein/kg unless stated otherwise):

- Crossflow velocities of 1·1, 1·7, 2·3, 2·8 and 3·4 m s^{-1} at pH 7·0.
- Protein concentrations (5, 10, 15, 20 and 30 g protein/kg) at pH 7·0 and constant crossflow velocity 2·3 m s^{-1}.
- pH (5·5, 6·2, 7·0 and 8·0), adjusted by adding acid (0·2 M-HCl) or alkali (0·2 M-NaOH), at constant crossflow velocity 2·3 m s^{-1}.
- Additions of NaCl (0·01, 0·02, 0·05 and 0·1 M) and $CaCl_2$ (0·001, 0·002 and 0·006 M) (VWR Int., Poole, BH15 1TD, UK) at constant crossflow velocity 2·3 m s^{-1}.

Fouling index was measured following processing runs during which fouling behaviour was studied, at conditions either below or above critical flux, for 2 h. The suspension was replaced with water at 50 °C for 2 min, followed by water at 20 °C for 5 min, circulated at crossflow velocity 2·3 m s^{-1} with the permeate valve closed. Permeate flux was then evaluated at TMP 0·5 bar, 20 °C, crossflow velocity 2·3 m s^{-1} for 5 min, to estimate the fouled membrane resistance (R_{mif}) using the following equation:

$$R_{mif} = \frac{\text{TMP}}{\mu_p J_{wf}} \tag{1}$$

where μ_p is water viscosity and J_{wf} is water flux of fouled membrane. Transmembrane pressure (accuracy within 5 %) was calculated by the following equation:

$$\text{TMP} = \frac{(P_i + P_o)}{2} - P_p \tag{2}$$

where P_i, P_o and P_p are the inlet, outlet and permeate pressure, respectively. The reported values take into account pressure losses in the pipe work external to the membrane.

For clean membrane, the resistance (R_m) was calculated by the following equation,

$$R_m = \frac{\text{TMP}}{\mu_p J_w} \tag{3}$$

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where J_w is water flux for the clean membrane.

Fouling index (FI) can be used to indicate the extent of fouling after the fouled membrane was flushed with water, and was calculated by the following equation:

$$FI = 1 - \frac{R_m}{R_{mif}} \tag{4}$$

Thus when $FI = 0$, no fouling was detected; and when $FI = 1$ it indicates that the membrane was fouled to the extent that there was no permeate flux, and fouling could not be removed by flushing with water.

Analyses

Scanning electron microscopy (SEM) was carried out on new PVDF membrane and fouled membrane samples to observe whether deposit remained on the membrane surface (Model 1450, Leo Electron Microscopy Ltd., Cambridge CB1 3HQ, UK). Fouled membranes were prepared under set conditions (below and above critical flux) and frozen to prevent microbial growth. Fouled membranes were cut into 4×4 mm^2 sections and observed directly without any coating material under the cooling stage using the variable pressure (VP) mode.

Zeta potential of whey protein and sodium caseinate suspensions, over the range of pH and following additions of NaCl and $CaCl_2$ described above, were investigated using a Zetasizer model 5000 (Malvern Instruments Ltd., Malvern WR14 1XZ, UK). This equipment allows measurement of particles in the size range 0·05–30 μm.

Size distribution of whey protein and sodium caseinate suspensions was measured by a Mastersizer 2000 (Malvern Instruments Ltd., Malvern WR14 1XZ, UK). The equipment allows measurement in the range 0·02–2000 μm.

Protein content of the feeds were measured by the macro-Kjeldahl method and protein contents of permeates were determined by the Bradford Assay (Sigma Aldrich Co. Ltd., Poole BH12 4QH, UK).

Protein transmission (estimated from protein content of permeates) was investigated at each level of TMP. No protein was detected in permeate for sodium caseinate either above or below the critical flux. For whey protein suspension, very small quantities (about 100 μg/l) were found, both below and above the critical flux indicating that protein transmission was too low to be meaningful, and hence results are not presented.

pH values of the suspension were measured using a digital pH meter.

Statistical analysis was carried out to determine the significance of differences between mean values for the critical fluxes by ANOVA (Windows package 10·1, SPSS UK Ltd., Woking GU21 1EB, UK).

RESULTS

Determination of critical flux

The relationship between critical flux and TMP for whey proteins is shown in Fig. 1. Figure 1*a* represents values below the critical flux in which permeate flux increased linearly as TMP was increased, and hysteresis was clearly negligible as TMP was decreased through the same sequence. This result suggests that very little irreversible fouling developed under these conditions. It should be noted however that J_{crit} values were considerably lower than J_w under the same conditions (e.g. J_{crit} at TMP = 0·26 bar, V = 2·3 m s^{-1}, 50 °C was 78 kg m^{-2} h^{-1}, while J_w was 170 kg m^{-2} h^{-1}). In contrast, obvious hysteresis was observed when permeate flux

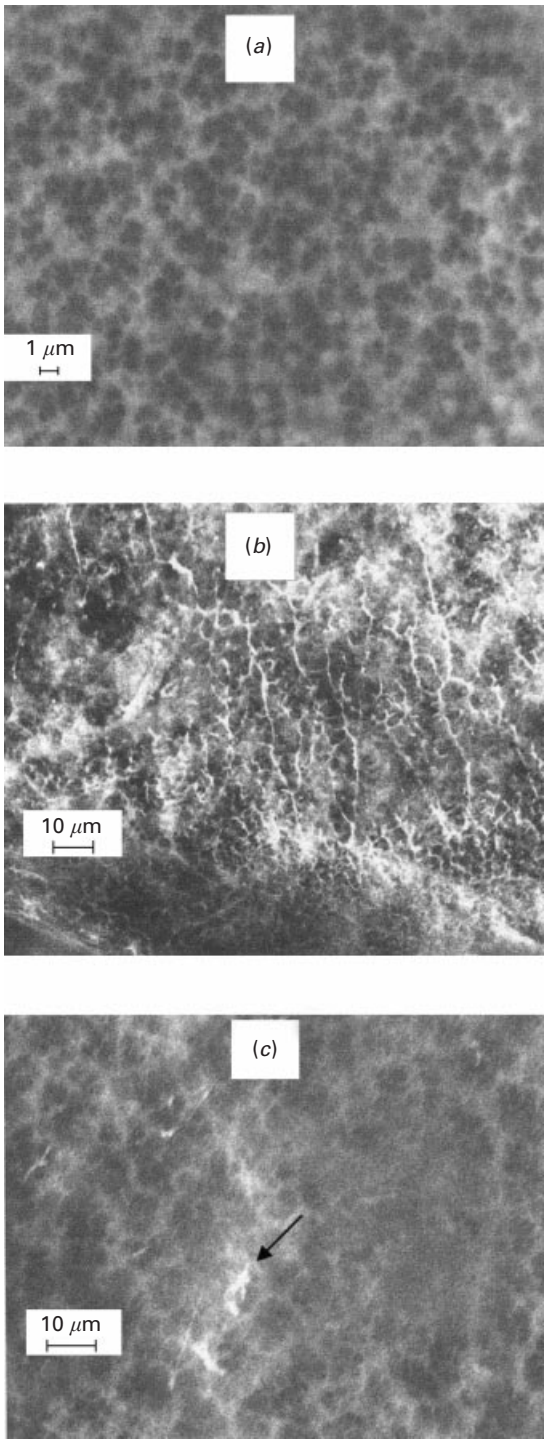

Fig. 2. For legend see facing page.

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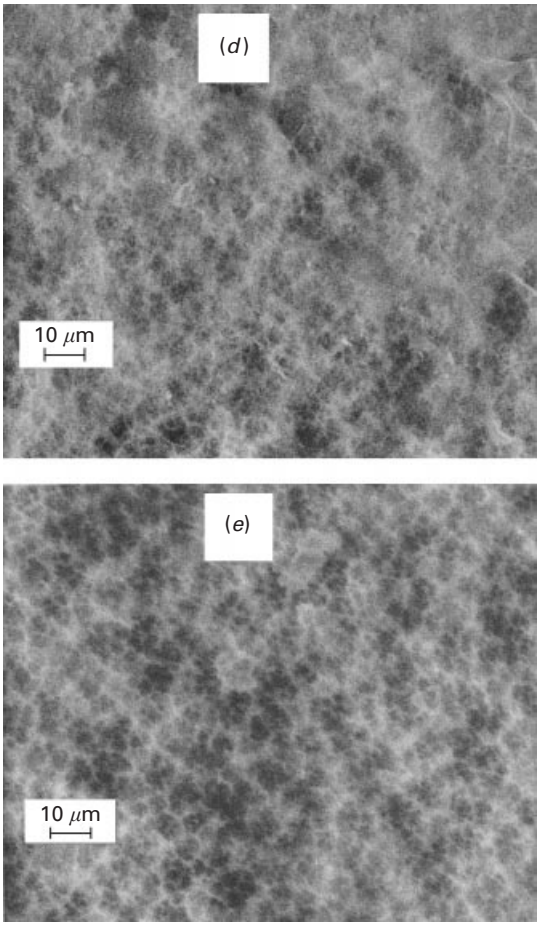

Fig. 2. Scanning electron micrographs of PVDF membrane surface: (*a*) clean membrane; (*b*) fouled by sodium caseinate suspension (10 g/kg), permeate flux (J) > critical flux (J_{crit}); (*c*) fouled by sodium caseinate suspension (10 g/kg), $J < J_{crit}$; (*d*) fouled by whey protein suspension (10 g/kg), $J < J_{crit}$; (*e*) fouled by whey protein suspension (10 g/kg), $J < J_{crit}$.

exceeded critical flux (Fig. 1*b*), indicating that fouling developed under these conditions resulting in a lower permeate flux at the same TMP. Critical flux of the suspension was determined where the relationship between TMP and permeate flux started to deviate from linear. Similar results were obtained for sodium caseinate suspension below and above the critical flux (data not shown). Critical flux values for whey protein concentrate and sodium caseinate were 78 kg m^{-2} h^{-1} and 122 kg m^{-2} h^{-1}, respectively. Since the slopes of the plots of TMP against permeate flux with both whey protein and sodium caseinate suspensions were lower than that for water, the critical fluxes obtained can be considered to be the weak form for both protein suspensions (Wu *et al.* 1999).

SEM examinations showed that the surfaces of membranes fouled below and above critical flux were completely different (Fig. 2). Below the critical flux, membrane surface was quite similar to that of a clean membrane. However, a small amount of material (presumably protein aggregate) was observed on membrane fouled below the critical flux for sodium caseinate suspensions (Fig. 2*c*). In contrast, membrane surfaces fouled above the critical flux (Fig. 2*b*, *d*) were different from

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Table 1. *Fouling index* (FI)† *determined under conditions below and above critical flux* (J_{crit}) *during ultrafiltration of milk protein suspensions. TMP – Transmembrane pressure*; *J – permeate flux*

(Values are mean ± SD for $n = 3$)

Sample	J†† (kg m^{-2} h^{-1})	TMP (bar)	*FI*
Sodium caseinate	80 ± 5	0·2 ± 0·01	0·09 ± 0·06
($J_{crit} = 122$)	202 ± 11	1·0 ± 0·02	0·45 ± 0·07
Whey protein	63 ± 4	0·2 ± 0·02	0·2 ± 0·02
($J_{crit} = 78$)	154 ± 14	1·0 ± 0·02	0·46 ± 0·03

† $FI = 1 -$ ratio of clean membrane resistance to fouled membrane resistance. *FI* determined at 20 °C; crossflow velocity 2·3 m s^{-1}; 10 g protein/kg.

†† Average value after 2-h experiment.

Table 2. *Zeta potential* (ζ) *of particles present in sodium caseinate and whey protein concentrate suspensions* (*10 g protein/kg*) *over a range of pH, added NaCl and added* $CaCl_2$

(Values are mean ± SD for $n = 3$)

	ζ (mV)	
	Caseinate	Whey
pH		
5·5	−25·9 ± 0·7	−17·4 ± 0·6
6·2	−28·1 ± 0·9	−22·3 ± 0·4
7·0	−28·7 ± 0·1	−23·6 ± 0·1
8·0	−30·1 ± 0·7	−24·4 ± 0·1
NaCl (M)		
0·00	−28·7 ± 0·1	−23·6 ± 0·1
0·01	−27·6 ± 0·1	−21·7 ± 0·9
0·02	−22·5 ± 0·8	−19·7 ± 0·8
0·05	−22·3 ± 0·7	−17·1 ± 0·7
0·10	−23·3 ± 0·5	−14·7 ± 0·5
$CaCl_2$ (M)		
0·000	−28·7 ± 0·1	−23·6 ± 0·1
0·001	−23·7 ± 0·3	−17·8 ± 0·3
0·002	−19·0 ± 0·4	−15·1 ± 0·4
0·006	−14·8 ± 0·5	−9·9 ± 0·5

clean membrane with a fouling layer covering the membrane, for both types of feed. This is more obvious for caseinate than whey protein.

The *FI* of the membrane fouled below the critical flux was low for both whey protein concentrate (0·02) and sodium caseinate (0·09) suspensions indicating that there was little irreversible fouling under these conditions (Table 1). Above the critical flux, however, *FI* values were much greater (0·45 for whey protein concentrate and 0·46 for sodium caseinate).

Zeta potential and size of particles in suspensions

The ζ potentials for both protein suspensions were negative, and increased in magnitude significantly as pH decreased (Table 2). The magnitude of ζ potential of whey protein concentrate particles decreased significantly as NaCl concentration increased. For sodium caseinate suspension, increasing NaCl concentration up to 0·02 M caused a decrease in ζ potential but further increasing NaCl concentration to 0·1 M led to little further change. It is possible that adding NaCl to sodium caseinate

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Table 3. *Critical flux* (J_{crit}) *of sodium caseinate and whey protein concentrate suspensions (both at a concentration of 10 g/kg) over a range of crossflow velocity* (V), *protein concentration* (C), *pH, added NaCl and added* $CaCl_2$

(Values are mean ± SD for $n = 3$)

	J_{crit} (kg m^{-2} h^{-1})	
Process conditions/treatment	Caseinate	Whey
V (m s^{-1}), at C = 10 g/kg		
1·1	66 ± 4	36 ± 1
1·7	93 ± 4	53 ± 2
2·3	122 ± 4	78 ± 2
2·8	162 ± 3	95 ± 4
3·3	188 ± 5	108 ± 4
C (g/kg) at V = 2·3 m s^{-1}		
5	145 ± 3	100 ± 5
10	122 ± 4	78 ± 2
15	90 ± 4	62 ± 2
20	74 ± 2	53 ± 3
30	52 ± 2	33 ± 2
pH, at V = 2·3 m s^{-1}		
5·5	47 ± 2	31 ± 6
6·2	114 ± 6	78 ± 2
7·0	122 ± 4	78 ± 2
8·0	122 ± 2	87 ± 4
NaCl (M), at V = 2·3 m s^{-1}		
nil	122 ± 4	78 ± 2
0·01	106 ± 3	77 ± 2
0·02	93 ± 2	75 ± 1
0·05	82 ± 4	75 ± 1
0·10	65 ± 3	71 ± 1
$CaCl_2$ (M), at V = 2·3 m s^{-1}		
nil	122 ± 4	78 ± 2
0·001	94 ± 5	59 ± 5
0·002	83 ± 1	45 ± 3
0·006	54 ± 3	33 ± 6

suspension not only increased the ionic strength, but also led to an exchange of sodium with colloidal calcium and thus produced changes in micelle structure (Farmelart *et al.* 1999), which may have affected ζ potential and particle size. The ζ potential for both suspensions greatly decreased with added $CaCl_2$. The decrease in ζ potential of both suspensions was much more pronounced for $CaCl_2$ than with NaCl. It was noted that adding 0·006 M-$CaCl_2$ to sodium caseinate suspension not only decreased ζ potential, but also caused an aggregation of protein, which could be observed with the naked eye.

The measured range of particle size for caseinate was 30–500 000 nm and for whey protein suspension was 30–1000 nm. Note that the particle size analyser used could not measure particles smaller than 20 nm, so the results probably do not cover the whole range of size distribution of these suspensions, especially whey proteins which are below this range.

The effect of hydrodynamic and physicochemical parameters on critical flux

Effects of varying crossflow velocity, protein concentration and pH, and the effects of adding NaCl and $CaCl_2$, on critical flux for both whey protein and sodium caseinate suspensions are shown in Table 3. Critical flux values were consistently about 50 % greater for sodium caseinate compared to whey protein suspensions, for any set of conditions.

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Critical flux for both whey protein concentrate and sodium caseinate suspensions increased markedly with increasing crossflow velocity. An approximately three-fold increase was observed as crossflow velocity was raised from 1·1 to 3·3 m s^{-1}.

Increasing the protein concentration produced a sharp decline in critical flux for both sodium caseinate and whey protein concentrate suspensions. In both cases critical flux fell to about one third as protein concentration was raised from 5 to 30 g/kg.

Critical fluxes of suspensions of both proteins were significantly affected by pH ($P < 0{\cdot}01$). In both cases critical flux increased sharply as pH increased from 5·5 to 6·2, with a more modest increase as pH rose from 6·2 to 8·0.

The critical flux of sodium caseinate suspensions was significantly reduced ($P < 0{\cdot}01$) by increasing NaCl concentration, but there was no significant effect for whey protein concentrate suspension.

Critical flux for both suspensions significantly decreased as concentrations of $CaCl_2$ were increased ($P < 0{\cdot}05$). Reductions in critical flux were greater compared with those observed when NaCl was added to the same ionic strength.

DISCUSSION

Critical fluxes of both sodium caseinate and whey protein suspensions were shown to be of the weak form according to the definition of Wu *et al.* (1999). Weak form of critical flux has been reported for several types of feed, especially those containing mixtures of solutes (Chen *et al.* 1997; Wu *et al.* 1999; Mänttäri & Nyström, 2000). Wu *et al.* (1999) found that deviation of flux from water flux, as observed with feeds displaying the weak form of critical flux, is caused by initial fouling of the membrane during the very initial stages of the experiment. Similarly, Madaeni *et al.* (1999) found that the flux immediately deviates from water flux before there is any evidence of a cake layer, suggesting that internal fouling takes place at the beginning of the experiment. This result is in agreement with Mänttäri & Nyström (2000), who found that the strong form of critical flux was only obtained if feed particle size was much greater than the molecular weight cut-off of the membrane, thus internal fouling is not expected. For both whey protein concentrate and sodium caseinate suspensions, it is possible that both irreversible fouling (as indicated by FI) and reversible fouling as well as concentration polarization were responsible for the flux deviation from water flux (Li *et al.* 1998). Irreversible fouling may be caused by protein and mineral salts (Merin & Cheryan, 1980). Fouling above critical flux could be mainly due to milk protein as shown in Fig. 2, in agreement with results from other authors (Taddéi & Daufin, 1989; Daufin *et al.* 1991). It is probable that increasing J above J_{crit}, leads to an increase in thickness of concentration polarization layer and particle deposit layer, and thus flux approaches limiting flux or pressure-independent region, where permeate flux is totally controlled by the rate of back transportation. Since the particle size of sodium caseinate is much larger than that of whey protein, the rate of back transport of sodium caseinate would also be expected to be higher. As a result, the limiting flux of sodium caseinate is expected to be higher than that of whey protein suspensions.

Critical flux is achieved when particle transport away from the membrane wall is balanced by particles moving towards the wall, hence no deposit is formed on its surface and irreversible fouling is negligible. Particle transport away from the membrane surface is therefore very important. Crossflow velocity is an important hydrodynamic factor involved with these mechanisms. As expected, increasing

crossflow velocity increased the critical flux while increasing protein concentration decreased the critical flux. Concentration of the feed is an important factor determining the transport of particles from the membrane surface. An increase in feed concentration results in a higher dynamic viscosity of bulk (data not presented) and hence a decreased transportation rate. It should be noted that changing feed concentrations in this case are associated with changes in ionic strength, which could also have contributed to changes in flux behaviour. The critical flux of whey protein concentrate was lower than for sodium caseinate, which may be due to differences in particle size and surface charge. Several mechanisms may be involved in solute transportation in membrane processes, depending on the physicochemical properties of the feed (Bacchin *et al.* 1995), including Brownian diffusion (for particle size < 100 nm), shear-induced diffusion (for particle size > 100 nm) (Davis & Leighton, 1987), and inertial migration (for particle size > 1000 nm) (Green & Belfort, 1980). Sodium caseinate suspensions (estimated size range 30–500 000 nm in this study) include casein micelles (50–200 nm) and protein aggregates (> 500 nm) (Povey *et al.* 1999). Whey protein concentrate suspensions (estimated size range 30–1000 nm in this study) are reported to contain protein aggregates (100–1000 nm), but a major component is individual whey proteins (4–10 nm) (Dejmek *et al.* 1996), which would not have been detected in this study. This suggests that the Brownian mechanism would dominate for whey protein concentrate suspensions (Jelen, 1977), while shear-induced diffusion would be more important for the sodium caseinate suspensions.

The higher critical flux of sodium caseinate compared to whey protein supports the suggestion that whey protein is a major component of fouling with milk (Tong *et al.* 1988; Vetier *et al.* 1988). An increase in crossflow velocity or wall shear stress is more important for removal of large particles. As a result only small particles (whey protein) remain and play a major role in fouling during membrane filtration of skimmed milk (Merin & Cheryan, 1980; Tong *et al.* 1988; Le Berre & Daufin, 1996; Grandison *et al.* 2000).

The decrease in critical flux as pH decreased suggests that electrostatic repulsive forces contribute to the critical flux. As casein micelles and most whey proteins are negatively charged at the normal pH of milk, decreasing pH would reduce this (as indicated by the change in potential, Table 2). Also the PVDF membrane normally has a negative charge. Since deposit or fouling at the critical flux should be negligible, interaction between particles, proteins and membrane may be important. Decreasing pH would result in a decrease in electrostatic repulsion between all these components, leading to increased deposition, and hence a decrease in critical flux (Bacchin *et al.* 1995). A similar result was found for ultrafiltration of BSA (Chen, 1998).

Addition of NaCl leads to an increase in both ionic strength and ζ potential, resulting in a decrease in electrostatic repulsive force (Bacchin *et al.* 1995), which could explain the observed decrease in critical flux of the caseinate suspension. This result is similar to data for microfiltration of polystyrene latex (Kwon & Vigneswaran, 1998). Interestingly, addition of NaCl had no significant effect on the critical flux of whey protein concentrate suspension which cannot easily be explained in terms of a decrease in electrostatic repulsion force, but it is possible that NaCl stabilized the whey proteins by enhancing hydration of the protein.

The critical fluxes of both sodium caseinate and whey protein suspensions were strongly affected by adding $CaCl_2$ (increasing the concentration of Ca^{2+}). The critical fluxes of caseinate suspensions were approximately 50 % greater than whey proteins at similar ionic strength (adjusted by adding NaCl and $CaCl_2$). This suggests that Ca^{2+} also caused a major change in protein structure. It is important to note that the

critical fluxes of both protein suspensions at the same ionic strength adjusted by $CaCl_2$ were lower than those adjusted by adding NaCl, suggesting that Ca^{2+} had a stronger effect on the critical flux compared with Na^+. It is possible that Ca^{2+} acts as a bridge between the carboxyl group of the protein and the membrane, which in turn reduces the critical flux (Bowen & Gan, 1990). Protein aggregation was also observed with 0·006 M-$CaCl_2$ for sodium caseinate, suggesting that there was an increase in particle size. This should lead to an increase in back transportation and thus an increase, rather than the observed decrease in critical flux. This suggests that the change in physicochemical properties and structure are important in determination of critical flux for sodium caseinate suspensions.

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