

Unsteady-state flux behaviour in relation to the presence of a gel layer

Citation for published version (APA):

Oers, van, C. W., Vorstman, M. A. G., Muijselaar, W. G. H. M., & Kerkhof, P. J. A. M. (1992). Unsteady-state flux behaviour in relation to the presence of a gel layer. *Journal of Membrane Science*, 73(2-3), 231-246.
[https://doi.org/10.1016/0376-7388\(92\)80132-4](https://doi.org/10.1016/0376-7388(92)80132-4)

DOI:

[10.1016/0376-7388\(92\)80132-4](https://doi.org/10.1016/0376-7388(92)80132-4)

Document status and date:

Published: 01/01/1992

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Unsteady-state flux behaviour in relation to the presence of a gel layer*

C.W. van Oers, M A G. Vorstman, W.G.H.M. Mujselaar and P J A M Kerkhof

Department of Chemical Process Technology, Eindhoven University of Technology (The Netherlands)

(Received July 31, 1991, accepted in revised form April 23, 1992)

Abstract

The unsteady-state flux behaviour has been studied for silica and dextran in a stirred ultrafiltration cell. Under the experimental conditions dextran and silica show a clearly different flux behaviour. During the filtration of dextran only a polarization layer is built up. For silica also a gel layer formation occurs. As a result the time to reach steady-state flux is less than a minute for dextran, whereas the formation of the silica gel layer takes more than one hour. The osmotic pressure model provides a good description of the flux for the experiments with dextran. If mass transfer coefficients are used which are higher than those electrochemically measured the transient flux for silica can be rather well predicted by the gel-polarization model. The use of flux measurements under unsteady-state conditions as an indication for the presence of a gel layer is discussed.

Keywords concentration polarization, ultrafiltration, gel layer, unsteady-state flux

Introduction

Several models are available to describe the flux behaviour during ultrafiltration. The osmotic pressure model [1,2] and the boundary layer resistance model [3] are based on the formation of a polarization layer. According to the gel-polarization model [4] also a gel layer is formed at the membrane surface.

The question which of the models is 'correct' has caused years of discussion [5,6]. Nowadays most researchers seem to recognize that the gel-

layer model and the osmotic pressure model describe two different physical phenomena.

For our study of the interactions of solutes near the membrane surface it is important to know whether a gel layer is present or only a polarization layer. A gel layer can be several times thicker than a polarization layer. It is expected that solutes experience more hindrance if a gel layer of a rejected component has to be permeated than when a polarization layer of a rejected component has to be passed. Information on the amount of solute present near the membrane surface may be obtained by studying the flux behaviour of solutions in which only the rejected component is present.

As shown by Wijmans et al. the three models mentioned above predict almost equivalent permeate fluxes under steady-state conditions,

Correspondence to C.W. van Oers, Dep. Chem. Proc. Techn., Eindhoven University of Technology, P.O. Box 513, FT-hal 1-30, 5600 MB Eindhoven, The Netherlands.

*Paper presented at the Int. Symp. on "Progress in Membrane Science and Technology", Enschede, Netherlands, June 25–28, 1991.

especially at higher concentrations [3,7]. For this reason it is very difficult to conclude from experimental steady flux data which mechanism is valid. Trettin and Doshi [8] showed that flux measurements in an unstirred cell at various pressures can be used to determine whether the pressure independent ultrafiltration is gel-limited or osmotic pressure limited. The membrane concentration is pressure independent in the gel-limited case, whereas in the osmotic pressure limited case the membrane concentration is a function of pressure. However, especially when the osmotic pressure is a strong function of the concentration the pressure range must be carefully chosen in order to find a discernable change in the membrane concentration.

Since the polarization layer and the gel layer can differ considerably in layer thickness we expect a difference in flux behaviour in a stirred cell under unsteady-state conditions as a result of the time needed to build up the layers. The amount of solute transported to the membrane surface for the formation of a gel layer can be several times larger. Therefore the formation of the gel layer will take longer than the build-up of the polarization layer. This leads to a different flux behaviour during the period that the layers are building up and steady-state flux is not yet reached.

In this paper we will describe the unsteady-state behaviour of two model components: dextran and silica. Silica is known to form a gel layer under certain conditions [9,10]. Dextran solutions cause considerable osmotic pressures and their filtration is likely to be osmotic pressure limited [3,5]. Experimental fluxes under unsteady-state conditions will be compared with fluxes predicted by the gel-polarization and the osmotic pressure model. Since according to Wijmans et al. [3] the boundary-layer resistance model is equivalent to the osmotic pressure model, it is not considered separately. An attempt will be made to discriminate between

gel-limited and osmotic pressure limited filtration based on the unsteady-state flux measurements.

Theory

Concentration polarization

Both the osmotic pressure model and the gel-polarization model incorporate the phenomenon of concentration polarization (Fig 1) [11]. Based upon the film theory the formation of a polarization layer can be described with the following equation

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

Initial and boundary conditions:

$$t=0 \quad 0 \leq x \leq \delta_{pol} \quad C = C_b$$

$$t>0 \quad x=0 \quad C = C_b$$

$$x = \delta_{pol} \quad vC_m = D \left(\frac{\partial C}{\partial x} \right)_{x=\delta_{pol}} + vC_p$$

The diffusion coefficient D is considered to be constant.

Osmotic pressure model

To describe the permeate flux the osmotic

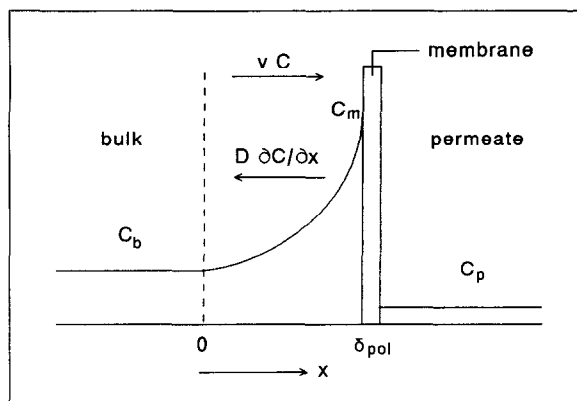


Fig 1 Concentration polarization

pressure caused by the enhanced concentration at the membrane surface is taken into account [2]. The permeate flux is given by

$$v = \frac{\Delta P - \Delta \pi}{\mu_p R_m} \quad (2)$$

$\Delta \pi$ is the osmotic pressure at the high-pressure side of the membrane minus the osmotic pressure at the permeate side of the membrane. If the solutes used are nearly completely rejected the osmotic pressure at the permeate side can be neglected. $\Delta \pi$ can be expressed as a function of the concentration at the membrane surface C_m [12]:

$$\Delta \pi = A_1 C_m + A_2 C_m^2 + A_3 C_m^3 \quad (3)$$

A_1 , A_2 and A_3 are the virial coefficients

Solving eqns. (1)–(3) the ultrafiltration flux can be calculated as a function of time. After the polarization layer has been built up the equation for steady flux is used instead of eqn. (1):

$$v = k_m \ln \frac{C_m - C_p}{C_b - C_p} \quad (4)$$

where $k_m = D/\delta_{pol}$ is the mass transfer coefficient in absence of a net flux. The change in the bulk concentration due to the batch filtration is taken into account.

Gel-polarization model

In the gel-polarization model the flux decline with increasing bulk concentration during ultrafiltration is explained by the formation of a gel layer [4]. The gel-polarization model is based on the assumption that the concentration at the membrane surface can not exceed a certain value, the gel concentration C_g . Starting a filtration first the formation of a polarization layer takes place. After the gel concentration has been reached the net solute flux does not lead to a further increase of the concentra-

tion at the membrane surface but to an increasing thickness of the gel layer, δ_g :

$$\rho_g \frac{\partial \delta_g}{\partial t} = vC - D \frac{\partial C}{\partial x} - vC_p \quad (5)$$

Although the membrane concentration does not change during the build-up of the gel layer the concentration profile in the polarization layer still changes due to a decrease in flux. We assume that the amount of solute necessary for accumulation of the concentration in the polarization layer is negligible compared with the material needed to build up the gel layer. The influence of the change of the concentration profile on back-diffusion due to the decrease in flux is taken into account in the model calculations. Integration of eqn. (5) with respect to x at given t with the boundary conditions $x=0$, $C=C_b$ and $x=\delta$, $C=C_g$ provides a relationship for the net solute flux at each permeate flux v .

$$\rho_g \frac{\partial \delta_g}{\partial t} = v \frac{e^\alpha C_b - C_g}{e^\alpha - 1} - vC_p \quad (6)$$

where $\alpha = v\delta/D$ and $\delta = D/k_m$

Taking the resistance of the gel layer into account the flux is expressed by the following equation:

$$v = \frac{\Delta P - \Delta \pi}{\mu_p (R_m - R_g)} \quad (7)$$

If the gel layer is considered as a packed bed of solute particles or molecules the resistance R_g can be calculated by [13]:

$$R_g = \frac{170 (1 - \epsilon)^2}{\epsilon^3 d_{par}^2} \delta_g \quad (8)$$

Equations (1) and (2) are used to calculate the time needed to reach C_g . The flux during the formation of the gel layer is found by solving eqns. (6)–(8). Besides the increase in the bulk concentration due to the permeation of solvent also changes in bulk concentration through the formation of the gel layer are taken into account. Part of the solute is located in the

gel layer and does not participate in the bulk concentration. For the calculation of the bulk concentration only the amount of solute actually present in the bulk solution is used

Experimental

Materials

Dextrans of different molecular weight were used for the ultrafiltration experiments: dextran T250 (MW=266,000 Da, ICN chemicals), dextran T70 (MW=73,500 Da, Sigma Chemical) and dextran T40 (MW=39,000 Da, Sigma Chemical). Silica particles (Aerosil 200, primary particle diameter=12 nm) were obtained from Degussa

The dead-end ultrafiltration experiments were performed with asymmetric YM5 and YM10 membranes having a MW cut-off of 5000 Da and 10000 Da, respectively (regenerated cellulose, Amicon). The rejection of the solutes/particles was > 99%.

Apparatus and procedure

Flux measurements with dextran were carried out in a stirred batch cell (Amicon, type 2000A) The diameter of the cell was 14×10^{-2} m. The bar-like stirrer had a diameter of 12×10^{-2} m. The effective area of the circular membrane was 144×10^{-4} m².

The experiments with silica were performed in a similar cell with the possibility to collect the permeate in two separate streams (Fig 2) The membrane area connected with the inner permeate section was 67×10^{-4} m², the area connected with the outer section was 75×10^{-4} m²

Both cells were pressurized with nitrogen gas and the temperature was controlled with a thermostat. The amount of permeate was determined gravimetrically. The bulk volume at the start of each experiment was 2×10^{-3} m³.

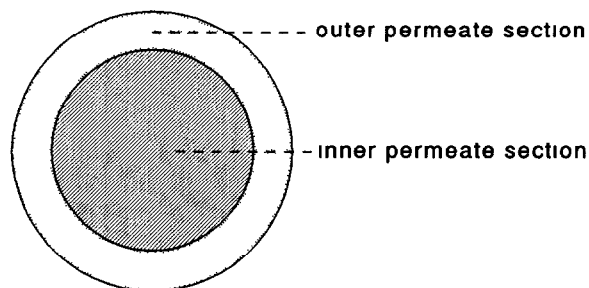


Fig 2 Permeate collection in two streams

Before and after each ultrafiltration experiment the pure water flux (PWF) was measured in order to determine the membrane resistance. Both dextran and silica were found not to effect the PWF of the membranes used. Therefore it can be assumed that the flux measurements were not affected by adsorption. Prior to filtration silica suspended in water was placed in an ultrasonic bath for two hours in order to break up silica agglomerates (except for experiment Sil6, which was treated only one hour) The bulk concentration at the start of all experiments was 7 kg/m³, except for Sil1 where a concentration of 2.5 kg/m³ was used

Model parameters

In this section the values for the parameters used for the model calculations are given; first for dextran, next for silica

Dextran

Osmotic pressure

Several authors present osmotic pressure data for dextran of different molecular weights [3,14,15] Figure 3 shows the osmotic pressure versus the solute concentration Comparing the various osmotic pressure data it can be seen that there is not much influence of the molecular

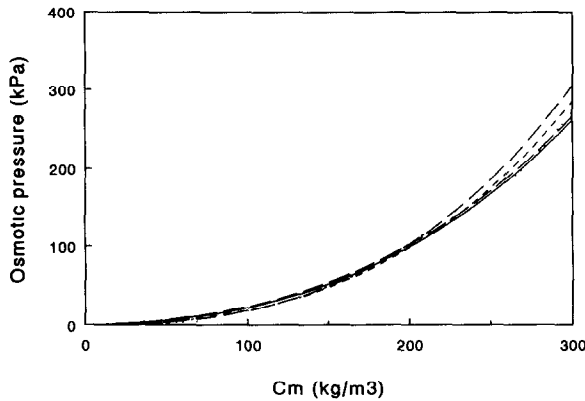


Fig 3 Osmotic pressure data for dextrans of different molecular weight (—) T525 [13], (---) T70 [5], (- - -) T70 [12], (- - -) T500 [13], (···) T500 [5]

weight. For the model calculations the osmotic pressure data of Wijmans et al [3] for dextran T70 are used:

$$\Delta\pi = 37.5C_m + 0.752C_m^2 + 76.4 \times 10^{-4}C_m^3 \quad (9)$$

Diffusivity

Diffusion coefficients of dextran in water are available for 20°C [16]. Corrected for temperature and solvent viscosity the diffusion coefficients for dextran T40, T70 and T250 are 6.0×10^{-11} , 4.6×10^{-11} and 3.1×10^{-11} (extrapolated) m²/sec respectively

Viscosity

Dynamic viscosity of dextran solutions is correlated with temperature and concentration according to the following relationship [17]:

$$\ln(\mu) = a + b \ln(T - 273) \quad (10)$$

in which

$$a = -5.078 + 3.428 \times 10^{-2}C - 1.133 \times 10^{-4}C^2 + 2.298 \times 10^{-7}C^3,$$

$$b = -5.972 \times 10^{-1} - 2.409 \times 10^{-3}C + 1.583 \times 10^{-5}C^2 - 4.279 \times 10^{-8}C^3, \text{ and with } 0 \leq C \leq 300 \text{ kg/m}^3 \text{ and } 293 \leq T \leq 313 \text{ K}$$

Estimations of the viscosity of dextran T40 and T250 solutions are obtained by correcting

the viscosity for dextran T70 by means of the viscosity numbers (0.20, 0.27 and 0.47 for T40, T70 and T250 resp. [18])

Mass transfer coefficient

According to the osmotic pressure model the membrane concentration varies with the bulk concentration. Therefore the mass transfer coefficient k_m is not equal to the slope of the flux versus $\ln C_b$ plot (eqn 4, $C_p = 0$). The slope of the plot $\partial v / \partial \ln C_b$ should be corrected for the change in the membrane concentration in order to get a correct value of k_m [5]:

$$k_m = -\frac{\partial v}{\partial \ln C_b} \left(1 + \frac{R_m k_m}{r \Delta\pi} \right) \quad (11)$$

in which $\Delta\pi$ is assumed to be equal to (constant) $\times C_m^r$. According to the fit of the osmotic pressure data restricted to the range of the experimental membrane concentrations, r equals 2.7

The thus determined values of the mass transfer coefficients are compared with coefficients obtained in our laboratory by means of an electrochemical method [19] and by heat transfer measurements. The measurements were performed in cells that resemble the used membrane cell except for the presence of a membrane. In the electrochemical cell the membrane was replaced by a perspex bottom provided with circular nickel electrodes of the same shape as the two permeate sections in the membrane cell (see Fig 2). The heat transfer cell was supplied with a copper bottom that was cooled from underneath [20]. The Sherwood relations obtained with these measurements have the following form:

$$Sh = k_m^* d_c / D$$

$$= A Re^p Sc^{0.33} (\mu_b / \mu_w)^{0.14} \quad Re > 2000 \quad (12)$$

in which the Reynolds number $Re = \rho_b n d_s^2 / \mu_b$ and the Schmidt number $Sc = \mu_b / \rho_b D$. The coefficient in factor $(\mu_b / \mu_w)^{0.14}$ is obtained from

TABLE 1

Coefficients for the Sherwood relations for the inner and outer sections and the surface averaged Sherwood relation

	Inner	Outer	Surface averaged
<i>A</i>	0.14	0.29	0.23
<i>p</i>	0.73	0.70	0.71

the heat transfer measurements, the coefficient for *Sc* is taken from literature [21]. The values of the other coefficients in the right term of eqn. (12) are presented in Table 1. The cell used for the filtration of dextran is not divided in two permeate sections. Therefore the surface averaged Sherwood relationship is used to calculate the mass transfer coefficient k_m (Table 1).

Silica

Osmotic pressure

Dextran considerably alters the activity coefficient of water due to the strong interaction between dextran and water. Since silica is expected to show little interaction with water in this respect, it is assumed that the silica suspensions behave almost ideally. Calculation of the osmotic pressure for silica with the Van 't Hoff equation for ideal solutions shows that it is negligible (see also *Results*).

Gel concentration

At the end of each experiment the gel was removed from the membrane cell. To determine the gel concentration and the weight of silica present in the gel layer the gel was weighed before and after drying. The experimental gel concentrations will be presented in Table 4.

Diffusivity

To calculate the diffusion coefficient of the

silica particles the Stokes–Einstein equation is used

$$D = \frac{kT}{3\pi\mu'd_{\text{par}}} \quad (13)$$

Viscosity

Viscosities of silica suspensions were measured in the range of shear rates from 1 to 1600 sec^{-1} and concentrations from 7 to 100 kg/m^3 by means of a Rheometrics RFS-2. At low concentrations the viscosity was nearly independent of shear rate. Above 40 kg silica/m^3 the viscosity decreased with increasing shear rate up to a factor of 2. All measured viscosities are higher than expected from the volume fraction of particles. Volume fractions calculated from the relative viscosity on the basis of a virial series of the volume fraction of spheres [22] are ten times as high as the actual silica volume fractions. This is an indication for the presence of agglomerates. We will come back to this subject later.

The viscosity at the bulk concentration (7 kg/m^3) had a value of 1.1×10^{-3} Pa-sec. Viscosities at concentrations of 80 and 100 kg/m^3 seemed to be equal, values ranging from 1×10^{-2} Pa-sec at low shear rates to 0.5×10^{-2} Pa-sec at high shear rates. The equality of the viscosities at the highest concentrations is most likely due to deformation of the agglomerates, so we may expect that viscosity does not increase much on a further increase of concentration up to the measured gel concentrations in the order of 200 kg silica/m^3 . Based on this assumption an estimate is made for the factor $(\mu_b/\mu_w)^{0.14} = (0.1)^{0.14} = 0.7$ for use in eqn. (12). The value of this factor may be higher for the outer permeate section as a result of the high shear rates near the membrane in this section.

Diameter particles and mass transfer coefficient

The primary particle diameter of silica as provided by Degussa is equal to 12 nm. How-

ever, the degree of agglomeration of the silica in the suspension is unknown, which causes an uncertainty in the particle diameter. Therefore the diameter of silica is used as a fitting parameter for the gel-polarization model. The aim of the fit procedure is to predict correct values for the fluxes and the weight of silica present in the gel layer

Besides the particle diameter use is also made of k_m as fitting parameter. Due to the considerable unsteady behaviour during the experiments with silica it is not possible to derive a value for k_m from a flux vs. $\ln C_b$ -plot. First estimates of the values for k_{m1} and k_{m0} (the mass transfer coefficients of the inner and outer sections) are calculated from the experimentally determined Sherwood relations (Table 1). These relations are obtained by an electrochemical method and by heat transfer measurements as described in more detail under *Dextran*

Results

To illustrate the flux behaviour under unsteady-state conditions, first the transient permeate fluxes for batch ultrafiltration experiments with dextran will be presented. Henceforth the response of the permeate flux to a sudden pressure change is discussed. The experiments with silica will be described similarly

Dextran

Permeate flux during batch ultrafiltration

In Figure 4 the permeate flux is given as a function of time. Three types of dextran (T250, T70 and T40) were ultrafiltered at 200 kPa and a stirrer speed of 1.5 rps. Experimentally a sudden drop in flux compared to the PWF is observed at the beginning of the filtration of dextran. Afterwards the flux only decreases gradually. The solid lines in Fig 4 represent the

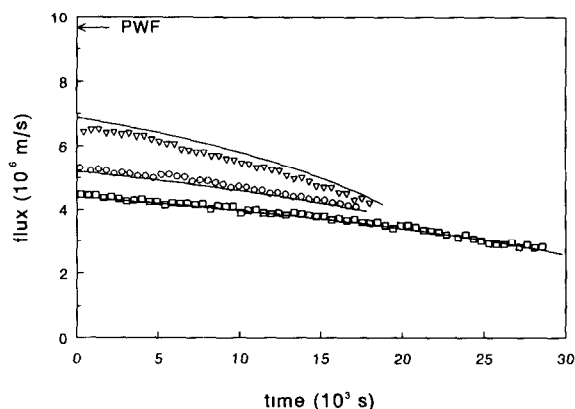


Fig 4 Plot of the flux versus time for dextran T40, T70 and T250. $\Delta P = 200$ kPa, $n = 1.5$ rps. (∇) Exp T40, (\circ) Exp T70, (\square) Exp T250, (—) OPM

calculated permeate fluxes according to the osmotic pressure model. Parameters for the model calculations are taken from the data described under *Model parameters*

The sudden drop in the flux at the beginning of the filtration of dextran is well described by the osmotic pressure model. According to the model calculations the build-up of the polarization layer takes less than one minute. The osmotic pressure model predicts a strong decline of the permeate flux during the formation of the polarization layer. As a result of the increase of the membrane concentration the osmotic pressure rises rapidly. A quasi-steady flux is reached which only alters due to changes in the bulk concentration. The change of the bulk concentration during the batch ultrafiltration is slow compared to the rapid formation of the polarization layer. Except for the period necessary to form the polarization layer the flux at each bulk concentration can be considered equal to the corresponding flux in steady situation (eqn 4, $C_p = 0$)

The experimental permeate fluxes depend on the molecular weight of the dextran. The fluxes calculated with the osmotic pressure model are in good agreement with the experimental fluxes. Lower molecular weight of the solute results in

TABLE 2

Comparison of mass transfer coefficients determined with the flux vs $\ln C_b$ plot and the surface averaged Sherwood relation

Dextran	n (rps)	k_m ($\mu\text{m}/\text{sec}$)	k_m^* ($\mu\text{m}/\text{sec}$)
T40	1.5	2.2	1.8
T70	1.5	1.6	1.4
T250	1.5	1.3	1.0

a higher permeate flux, because the back diffusion into the bulk is larger. Due to the higher diffusion coefficient the value for the mass transfer coefficient is higher (Table 2)

Comparison between k_m derived from the flux versus $\ln C_b$ plot and k_m^* calculated with the Sherwood relation shows that k_m is 15–25% higher. It should be noted that the values of Schmidt numbers under these conditions are more than an order of magnitude larger compared with the values at the experimental conditions under which the Sherwood relations were determined.

Response of permeate flux to sudden pressure change

An other example of the unsteady behaviour of the permeate flux is the response to a sudden pressure change. The pressure was increased from 100 kPa to 200 kPa and after ca. 3 hr changed back to 100 kPa. The solute used was dextran T250 (Fig 5). Experimentally it is found that the permeate flux immediately responds to the 100% pressure increase with a 40% increase in permeate flux. This flux behaviour is well predicted by the osmotic pressure model. The doubling of the pressure does not result in a doubling of the permeate flux, because the increase in pressure is partly counteracted by an increase in osmotic pressure. On account of analogue considerations the decrease of the pressure to 100 kPa does not lead to a 50% decrease of the permeate flux.

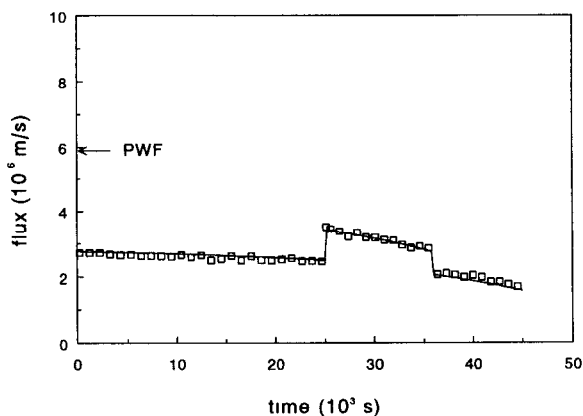


Fig 5 Plot of the flux versus time for dextran T250 $n = 1.5$ rps, pressure change $\Delta P = 100$ kPa, 200 kPa, 100 kPa (\square) Exp, (—) OPM

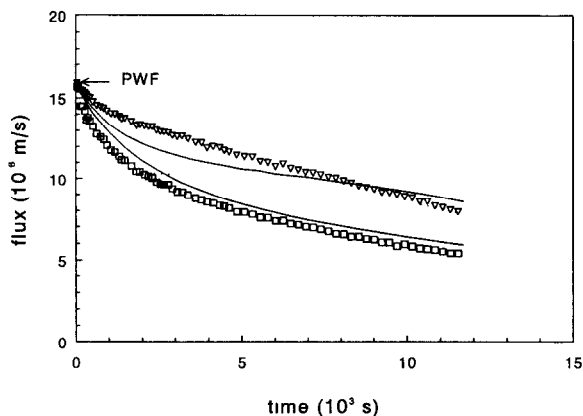


Fig 6 Plot of the flux versus time for silica (Si14) $\Delta P = 200$ kPa, $n = 1.5$ rps (\square) Inner section, (∇) outer section, (—) GPM, (---) quasi-steady flux

At both pressure changes the change of the concentration gradient at the membrane surface is very fast, so almost immediately the quasi-steady permeate flux corresponding to the actual bulk concentration under the new conditions is obtained. The gradual change in flux during the entire experiment is again due to the increase of the bulk concentration with time.

Silica

Permeate flux during batch ultrafiltration

Figure 6 shows that for both the inner and outer sections the flux during the filtration of silica decreases gradually, starting from the pure water flux (PWF). A gel layer is observed at the membrane surface. The distribution of the gel layer over the membrane surface is not uniform. At the edge of the membrane the gel thickness is lower than in the middle due to a higher mass transfer coefficient at the edge. Therefore the fluxes in the outer permeate section are higher than in the inner section. In Fig 7 a top view of the gel layer is presented. It shows a fan-shaped pattern of the gel layer. The solid lines represent the highest values for the gel thickness, in between the gel thickness is lower, superimposed on the already mentioned increase of thickness towards the centre of the membrane.

No clear relation between the gel concentration and the process parameters is found (see Table 4). The variation of the gel concentration might be ascribed to variations in the degree of break-up of the agglomerates. In experiment Sil6 with only one hour ultrasonic treatment the lowest gel concentration has been determined.

Before the experimental fluxes are compared to the flux calculations with the gel-polariza-

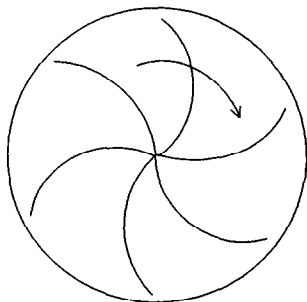


Fig 7 Top view of gel layer (→) rotation direction of stirrer

tion model a description of the fitting procedure will be given. If the k_m^* values calculated with the Sherwood relations were used model calculations show that it is only possible to predict either correct values for the fluxes or for the weight of silica present in the gel layer but not for both. Therefore it was decided to use silica experiments in which the two permeate fluxes were measured separately (Sil4, Sil5 and Sil6) to fit the mass transfer coefficients, k_{m_i} and k_{m_o} , for the inner and outer area respectively. The values of the mass transfer coefficients and the particle diameters that give the best fits are presented in Table 3. Moreover, the values for the mass transfer coefficients calculated with the Sherwood relations $k_{m_i}^*$ and $k_{m_o}^*$ are given.

Table 3 shows that the electrochemically determined $k_{m_i}^*$ and $k_{m_o}^*$ are 50–60% smaller than the fitted k_{m_i} and k_{m_o} . This difference is considerable larger than that for the dextran experiments where the surface averaged k_m^* is 15 to 20% smaller than k_m . The fitted particle diameters have values of 17.5 and 18.5 nm, which is larger than the primary particle diameter of 12 nm. This deviation might be attributed to the presence of agglomerates but it seems as likely to ascribe it to a compensation for porosity effects in the Kozeny–Carman relation (eqn. 8), since porosities of about 90% are extremely high for this relation. The presence of a double layer around the colloidal silica particles can also effect the diameter of the silica particle. The diffusion coefficient used in the Sherwood relation is based on the average value of $d_{par} = 18$ nm taken from Table 3. As already mentioned by Fane [23] repulsive forces between the colloidal particles can cause augmented diffusional transport. If a higher value of the diffusion coefficient would be used in the calculation of k^* , the difference between k^* and k becomes smaller. The discussion about the deviations between k^* and k will be extended at the end of

TABLE 3

Comparison of mass transfer coefficients determined by the fit procedure and by the Sherwood relations for the inner and outer sections

Exp	n (rps)	k_{m_i} ($\mu\text{m}/\text{sec}$)	$k_{m_i}^*$ ($\mu\text{m}/\text{sec}$)	k_{m_o} ($\mu\text{m}/\text{sec}$)	$k_{m_o}^*$ ($\mu\text{m}/\text{sec}$)	d_{par} (nm)
Sil4	1.5	1.7	0.9	3.1	1.4	18.5
Sil5	1.5	1.6	0.9	2.8	1.4	17.5
Sil6	1.5	2.1	0.9	3.5	1.4	17.5

TABLE 4

Experimental conditions and results Values of d_{par} from fit with mean values of k_{m_i} and k_{m_o} (1.8×10^{-6} and 3×10^{-6} m/sec resp)

Exp	ΔP (kPa)	T (K)	C_0 (kg/m^3)	C_g^b (kg/m^3)	M_{sil} (g)	V_{fin} (dm^3)	d_{par} (nm)
Sil1 ^a	200	298	2.5	$230 \pm 10\%$	3.11	0.175	13
Sil2 ^a	200	298	7	$230 \pm 5\%$	8.21	0.281	17
Sil3 ^a	200	318	7	$230 \pm 1\%$	8.75	0.220	15
Sil4	200	298	7	$250 \pm 1\%$	7.06	0.370	19
Sil5	100/200	298	7	$264 \pm 1\%$	5.21	0.555	18
Sil6	200/0/200	298	7	$198 \pm 1\%$	5.86	0.460	16.5

^aOnly one permeate stream

^bDensity silica = $2250 \text{ kg}/\text{m}^3$

this section after all experiments have been dealt with

The mean values for both k_{m_i} and k_{m_o} from exp Sil4, Sil5 and Sil6 are used to fit all experiments and the resulting values of the fitting parameter d_{par} are presented in Table 4 together with the experimental conditions and results. It is seen that the particle diameters found do not deviate much from the diameters according to the best fits.

The experimental fluxes of experiment Sil4 are compared with the model calculations in which the values of d_{par} and k_{m_i} from Table 3 are used. From Fig. 6 it is seen that the inner permeate flux is rather well described, the outer permeate flux is somewhat underpredicted. This might be explained by the presence of large

silica agglomerates (see additional remarks at the end of silica section).

According to the gel-polarization model the permeate flux decreases until quasi-steady flux is reached. The quasi-steady fluxes for the inner and outer permeate section, which only change due to the increasing bulk concentration, are represented by the dotted lines in Fig. 6. The figure shows that the experimental fluxes indeed decrease during the experiment until the quasi-steady flux is attained.

The long time to reach steady-state is in strong contrast with the time needed during the filtration of dextran. Under the experimental conditions the gradual decrease in unsteady permeate flux clearly indicates the formation of a gel layer.

Response of permeate flux to sudden pressure change

To study the influence of the pressure on the permeate flux the pressure was increased from 100 to 200 kPa during the filtration of a silica suspension (Sil5)

Experimentally it is found that for both the inner and outer permeate section the sudden pressure increase with 100% immediately results in an 100% increase of the permeate flux (Fig 8). This is in agreement with the flux behaviour predicted by the gel-polarization model, since the permeate flux is linearly dependent on the pressure for the same gel thickness. The effect of a sudden pressure increase on the permeate flux is strikingly different from the flux behaviour during the ultrafiltration of dextran (see Fig. 5) In that case no doubling of the flux is observed due to an increase in osmotic pressure (see *dextran*) Due to the pressure increase the convective flux of silica towards the membrane is higher than the back-diffusion flux So, immediately after the pressure rise the gel thickness will increase until the net silica flux becomes equal to zero (steady situation). The dotted lines in the figure represent the flux in steady situation at the *actual* concentration of the bulk solution for the inner and outer per-

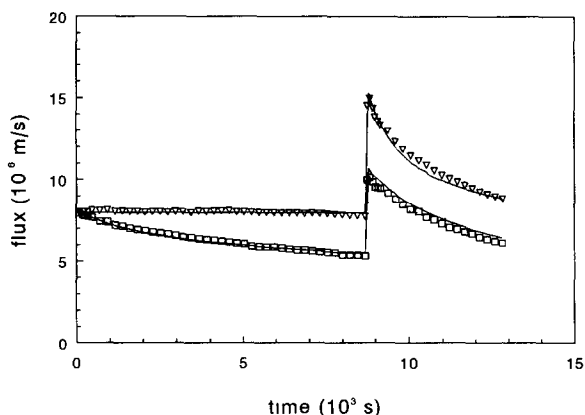


Fig 8 Plot of the flux versus time for silica (Sil5) Pressure change $\Delta P = 100$ kPa, 200 kPa (\square) Inner section, (∇) outer section, (—) GPM, (·) quasi-steady flux

meate section The decline in the quasi-steady flux is the result of the change in bulk concentration during the experiment. According to the gel-polarization model the steady flux is independent of the pressure (eqn 4, $C_m = C_g$). The gradual decrease in flux towards the quasi-steady flux as predicted by the model is really found experimentally (Fig 8). This gradual decrease in flux is a great contrast to the immediate change in flux during the filtration of dextran In that case only the polarization layer has to adjust itself to the new situation, which according to our calculations takes a few seconds (see *dextran*)

During the filtration at 100 kPa the permeate fluxes in the inner and outer permeate section behave different The flux in the inner permeate section decreases gradually from the PWF towards quasi-steady flux as usual On the other hand the flux in the outer permeate section is considerably lower than the quasi-steady flux. In this case the flux is not limited by gel formation but determined by the membrane resistance In other words no gel layer is formed on top of the outer permeate section.

Since the permeate flux in the outer permeate section is only determined by the membrane resistance the flux must be equal to the PWF According to eqn (4) the value for k_{mo} should at least be larger than $PWF / \ln(C_g / C_b) \cong 2.5 \times 10^{-6}$ m/sec. This indicates that the mass transfer coefficient is indeed larger than the one calculated with the Sherwood relation (Table 3) The fact that the flux equals the PWF confirms that the osmotic pressure of the silica suspension is negligible up to concentrations quite near to the gel concentration.

The absence of a gel layer in spite of the convective transport towards the membrane is a strong evidence for the existence of back diffusion into the bulk solution A cake layer model without back diffusion is not able to predict that phenomenon This conclusion is supported by experiment Sil6 in which after 2.5 hr of filtra-

tion the cell was depressurized for almost 21 hr while stirring was continued. When pressure was put on again the permeate flux was almost equal to the PWF, so silica seems to have diffused back into the bulk solution.

Before concluding this section we give some additional remarks about the deviations between k_m and k_m^* as presented in Table 3. Besides the already mentioned influence of repulsive forces on the diffusion coefficient the presence of agglomerates may also play a role in the deviations between k_m and k_m^* . The presence of agglomerates, that was deduced from the high values found for the suspension viscosities, implies that the actual concentration of the primary particles is lower than the total silica concentration. The fitted values for k_m would become lower – closer to the values of k_m^* – if the concentration of the primary particles would be used in the fitting calculations instead of the silica concentration. The above reasoning only holds if the aggregates do not deposit onto the gel layer. That this may be the case under certain conditions can be concluded from the lack of a change in the flux during the first part of experiment Si15 at 100 kPa. Since the agglomerates will show far less back-diffusion than the primary particles this behaviour must be attributed to lift forces in the non-uniform flow field near the membrane. This lift behaviour is typical for larger colloids. Attempts to measure the size of the aggregates by means of light scattering gave an indication of a size of about 500 nm. Fane [23] showed that capture efficiency for this particle size is low. The deposition of agglomerates is more likely to occur in the inner permeate section due to the comparatively lower shear forces exerted in this region. In experiment Si14 the outer permeate flux is probably underpredicted because in reality less material is deposited on the membrane due to the lift of the aggregates. If a lower concentration of primary particles is assumed, the shape of the flux curve can be rea-

sonably well predicted. In the inner section the flux is mainly determined by convective transport due to the low mass transfer coefficient and low shear forces.

Concluding we may say that lowering of the concentration of the primary particles might attribute to deviations between the fitted k_m and the electrochemical determined k_m^* in the silica experiments. Besides this also the irregular shape of the gel-layer surface will certainly increase the mass transfer coefficient compared with the one for a flat surface as has been shown for corrugated membranes [24].

Unsteady flux behaviour in relation to the presence of a gel layer

The presented results show a clear distinction in the unsteady flux behaviour between the case where only a polarization layer is build up (dextran) and the case where also the formation of a gel layer takes place (silica). This difference expresses itself in two ways:

- (1) The time to reach steady-state is much longer in case a gel layer is formed due to the larger layer thickness compared with the polarization layer.
- (ii) A sudden change in pressure results in a different steady flux due to the change in membrane concentration in case only a polarization layer is formed. On the other hand after a linear change with pressure the flux gradually decreases to the same steady flux in case a gel layer is present.

For the filtration experiments with dextran and silica a clear discrimination can be made between the presence or absence of a gel layer based on either (1) or (ii). However, the differences are not always as pronounced as in these cases. A restriction which should be made to (1) is the fact that the time to build up the gel layer strongly depends on its permeability. Illustrative in this respect are the results obtained by Chudacek and Fane [25]. They measured the

time to build up a gel layer of another type of silica: Syton X-30 ($d_{\text{par}} = 16 \text{ nm}$) by means of a droplet counter on the permeate outlet. According to the experimental flux measurements the formation of the gel layer lasts 20 to 60 sec, depending on bulk concentration and pressure.

If an estimated mass transfer coefficient is used (from the available flux vs. $\ln C_b$ plot) the flux during the formation of the gel layer can be well predicted by our model calculations. If we apply our model calculations to the flux vs. time curve presented by Chudacek and Fane it does not show the slight overprediction of the transient flux as predicted by their model curve. The reason for this difference is that in our model-description the change in diffusive flux during the build-up of the gel layer is taken into account, whereas Chudacek and Fane assumed it to be constant and equal to the diffusive flux in the steady-state situation.

The large difference in time to build up the gel layer for Syton X-30 and Aerosil 200 (used in this work) is a result from the large difference in specific resistances of the gel layers: $(5.5-16) \times 10^{14} \text{ m/kg}$ and $(3-5) \times 10^{13} \text{ m/kg}$ respectively. The surface-averaged gel layer thickness under steady-state conditions is $(5.5-18.8) \times 10^{-6} \text{ m}$ for Syton X-30 and $(1-2.5) \times 10^{-3} \text{ m}$ for Aerosil 200.

The higher specific resistance for Syton X-30 is mainly caused by its higher gel concentration (ca. 900 kg/m^3); the diameters of Syton X-30 and Aerosil 200 are almost equal. If Syton X-30 is filtered under identical conditions as used for Aerosil 200 the time required to form the gel layer would also be about one minute.

Summarized, one can only expect a considerable difference in the times to build up a gel layer and a polarization layer if the specific gel layer resistance is not too high.

Therefore no definite answer can be given to the question whether a gel layer is formed or not in case steady-state is reached quickly.

However, the response of the flux to sudden pressure changes can provide additional information which is indicative for the presence of only a polarization layer (see 11). If the measurements show that the steady-state flux changes due to the change in pressure, it is clear that only a polarization layer is present. However, if the flux has an equal value for both pressures it does not prove the presence of a gel layer. In that case it is still possible that only a polarization layer has been formed. In Fig 9 the steady-state flux vs. pressure is depicted in case only a polarization layer is formed (osmotic pressure model). At low pressures the flux indeed changes by changing the pressure. But at high pressures the flux turns out to be almost independent of pressure, because the change in osmotic pressure caused by the rise in the membrane concentration compensates the change in pressure. At which pressure the flux hardly changes with increasing pressure depends on how strong the osmotic pressure varies with the membrane concentration. The stronger the variation with the membrane concentration, the lower the pressure at which 'constant' flux is reached.

Summarized, in case only a polarization layer is build up one can just expect a considerable

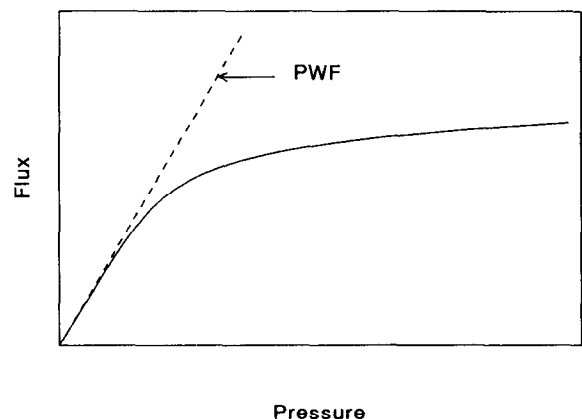


Fig. 9 Plot of the flux versus pressure according to osmotic pressure model

change in flux as a result of a sudden pressure change, if the osmotic pressure does not vary too much with membrane concentration.

So far only gel forming species have been considered which cause a negligible osmotic pressure. However, in other systems both osmotic pressure and gel formation may influence the flux. In that case the unsteady-state flux behaviour shows a combined effect. In the beginning of a filtration experiment a rapid drop in flux will occur during the build-up of the polarization layer due to the increase in osmotic pressure. After the gel concentration has been reached a gradual decrease in flux can be observed as a result of gel layer formation (if the permeability of the gel layer is not too high). During a sudden pressure increase the flux will not increase linearly with pressure as described for a gel layer without osmotic pressure, but with a factor $(\Delta P_2 - \Delta \pi) / (\Delta P_1 - \Delta \pi)$. Next, a gradual decrease in flux will occur (if the permeability of the gel layer is not too high) until the same steady flux is reached. The increase in pressure does not effect the osmotic pressure since the membrane concentration stays equal to the gel concentration at the retentate side of the gel layer. This gel concentration is most likely independent of the applied pressure, whereas the gel concentration at the membrane side may increase with increasing pressure due to compression.

In the previous discussion adsorption was not taken into account because according to PWF measurements dextran and silica did not adsorb on the membrane. If adsorption occurs it can greatly influence the characteristic unsteady-state flux behaviour. Due to adsorption the membrane permeability changes during filtration.

By preadsorption of the membrane the adsorption process may be separated from the filtration [26]. Assuming the adsorbed membrane permeability constant during filtration a discrimination between the presence and ab-

sence of a gel layer can be made on the grounds as described for the unadsorbed membrane.

Conclusions

The unsteady flux behaviour during ultrafiltration may differ considerably when either only a polarization layer or also a gel layer is formed as a result of the time needed to build up the layers. In certain situations the difference in unsteady flux can be so pronounced that measurement of the unsteady flux can be used for the discrimination between the presence or absence of a gel layer.

Under the experimental conditions dextran and silica show a clearly different flux behaviour. During the filtration of dextran only a polarization layer is build up, which takes less than a minute, whereas it takes hours before the gel layer of silica is formed. The osmotic pressure model (polarization layer) provides a good description of the flux for the experiments with dextran. If mass transfer coefficients are used which are higher than those electrochemically measured the transient flux for silica can be rather well predicted by the gel-polarization model.

Acknowledgements

Acknowledgements are made to IOP-membranes, AKZO, Gist-Brocades, Royal Dutch/Shell, Stork-Wafilm and Unilever for their financial support of this work. We thank Dr Ir I G Rácz for his suggestions with respect to the electrochemical measurements.

List of symbols

A	coefficient (eqn 12) (-)
A_j	virial coefficient, $j=1, 2, 3$ ($\text{Pa}\cdot\text{m}^3/\text{kg}'$)
C	concentration (kg/m^3)
D	diffusion coefficient (m^2/sec)

d	diameter (m)
GPM	gel-polarization model
k_m	mass transfer coefficient (m/sec)
M_{sil}	weight of silica in gel layer (kg)
MW	weight averaged molecular weight (Da)
n	stirrer speed (rotations per second) (sec^{-1})
OPM	osmotic pressure model
PWF	pure water flux (m/sec)
ΔP	transmembrane pressure difference (Pa)
p	coefficient (eqn 12) (-)
q	coefficient (eqn 12) (-)
R	resistance (m^{-1})
Re	Reynolds number (-)
r	coefficient (eqn. 11) (-)
Sc	Schmidt number (-)
Sh	Sherwood number (-)
T	temperature (K)
t	time (sec)
V_{fin}	final retentate volume (m^3)
v	permeate flux (m/sec)
x	coordinate perpendicular to the membrane (m)

Greek letters

δ	thickness (m)
ϵ	porosity (-)
Φ	volume fraction (-)
μ	dynamic viscosity (Pa-sec)
$\Delta\pi$	osmotic pressure (Pa)
ρ	density (kg/m^3)

Indices

b	bulk
c	cell
g	gel
i	inner permeate section
m	membrane
o	outer permeate section
p	permeate
par	particle

pol	polarization layer
s	stirrer
w	wall -membrane for OPM -gel layer surface for GPM
0	initial
*	calculated by eqn (12)
'	water

References

- 1 A A Kozinski and E N Lightfoot, Protein ultrafiltration a general example of boundary layer filtration, *AIChE J*, 18 (1972) 1030
- 2 R L Goldsmith, Macromolecular ultrafiltration with microporous membranes, *Ind Eng Chem, Fundam*, 10 (1971) 113
- 3 J G Wijmans, S Nakao, J W A van den Berg, F R Troelstra and C A Smolders, Hydrodynamic resistance of concentration polarization boundary layers in ultrafiltration, *J Membrane Sci*, 22 (1985) 117
- 4 W F Blatt, A David, A S Michaels and L M Nelsen, Solute polarization and cake formation in membrane ultrafiltration causes, consequences and control techniques, in J E Flinn (ed), *Membrane Science and Technology*, Plenum Press, New York, NY, 1970, p 47
- 5 G Jonsson, Boundary layer phenomena during ultrafiltration of dextran and whey protein solutions, *Desalination*, 51 (1984) 61
- 6 A G Fane, Factors affecting flux and rejection in ultrafiltration, *J Sep Proc Technol*, 4 (1983) 15
- 7 J G Wijmans, S Nakao and C A Smolders, Flux limitation in ultrafiltration osmotic pressure model and gel layer model, *J Membrane Sci*, 20 (1984) 115
- 8 D R Trettin and M R Doshi, Pressure independent ultrafiltration - is it gel limited or osmotic pressure limited?, in A F Turbak (Ed), *Synthetic Membranes*, ACS Symp Ser No 154, Vol II, American Chemical Society, Washington, DC, 1981, p 373
- 9 M Stakic, S Milonjic, V Pavasovic and Z Ilc, Ultrafiltration of silica sols, *Collect Czech Chem Commun*, 54 (1989) 91
- 10 Yu G Frolov, V V Ceskin, N A Shabanova, I A Donel'skii, V V Kandaryuk and A I Pavlov, Concentration of silica sols by ultrafiltration and properties of polymer membranes, translated from *Kolloidn Zh*, 40 (1978) 393
- 11 G van den Berg, Concentration polarization in ultrafiltration, Ph D Thesis, Twente University of Technology, Enschede, The Netherlands, 1988
- 12 P J Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953

- 13 P J A M Kerkhof and G H Schoutens, Membrane processing of industrial enzymes, in S Bruin (Ed), Preconcentration and drying of food materials, Elsevier, Amsterdam, 1988, p 87
- 14 H de Balmann and R Nobrega, The deformation of dextran molecules Causes and consequences in ultrafiltration, *J Membrane Sci* , 40 (1989) 311
- 15 A G Ogsten and N Preston, Macromolecular compression of dextran, *Biochem J* , 183 (1979) 1
- 16 K A Granath and B E Kvist, Molecular weight distribution analysis by gel chromatography on sephadex, *J Chromatogr* , 28 (1967) 69
- 17 F René and M Lalande, Momentum and mass transfer during ultrafiltration of dextran with tubular mineral membranes in turbulent flow regime, *J Membrane Sci* , 56 (1991) 29
- 18 M Schmidt and W Burchard, Moleküleigenschaften in verdünnten Lösungen, in W Burchard (Ed), Polysaccharide, Springer-Verlag, Berlin, 1985, p 154
- 19 J R Selman and C W Tobias, Mass transfer measurements by the limiting current technique, *Adv Chem Eng* , Vol 10, Academic Press, New York, NY, 1978, p 211
- 20 Unpublished results
- 21 J Marangozis and A I Johnson, A correlation of mass transfer data of solid-liquid systems in agitated vessels, *Can J Chem Eng* , 39 (1962) 231
- 22 C G de Kruif, The rheology of colloidal dispersions in relation to their microstructure, in J P Hulin et al (Eds), *Hydrodynamics of Dispersed Media*, Elsevier, Amsterdam, 1990, p 79
- 23 A G Fane, Ultrafiltration of suspensions, *J Membrane Sci* , 20 (1984) 249
- 24 M J van der Waal, S Stevanovic and I G Rácz, Mass transfer in corrugated-plate membrane modules II Ultrafiltration experiments, *J Membrane Sci* , 40 (1989) 261
- 25 M W Chudacek and A G Fane, The dynamics of polarisation in unstirred and stirred ultrafiltration, *J Membrane Sci* , 21 (1984) 145
- 26 W S Opong and A L Zydney, Hydraulic permeability of protein layers deposited during ultrafiltration, *J Colloid Interface Sci* , 142 (1991) 41