Membranes and Membrane Separation Processes, 4. Concentration Polarization and Membrane Fouling

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Even if the proper membrane for a certain mass separation task is available, various engineering aspects must be considered that can affect the economics of the process considerably, or even make it technically impossible. A major problem in all membrane separation processes is the decline of the membrane flux due to concentration polarization effects and the formation of cake or gel layers by feed solution constituents retained by the membrane. Equally devastating for the performance of a process is membrane fouling. Membrane fouling is a more general term. It may be the result of concentration polarization, or the consequence of adsorption of feed solution constituents at the membrane surface and, especially in microfiltration, also within the membrane structure. The control of concentration polarization and membrane fouling is a major problem in the design of membrane separation processes and equipment [1–3].

Concentration polarization occurs in all separation processes, but its consequences are especially severe in membrane processes. When in a mass separation procedure a molecular mixture is brought to a membrane surface, some components permeate the membrane under a given driving force while others are retained. This leads to accumulation of retained material and depletion of the permeating components in the boundary layers adjacent to the membrane surface. This phenomenon is referred to as concentration polarization. The causes and consequences of concentration polarization may differ in different membrane processes. Often the adverse effects of concentration polarization are intensified by adsorption of certain feed mixture constituents at the membrane surface. This phenomenon is referred to as membrane fouling. It is often observed when solutions containing biological materials such as proteins are processed, but inorganic materials, especially polyelectrolytes, can also cause severe fouling. In biofouling microorganisms accumulate at and attach to the membrane surface. The actual mechanism of biofouling is rather complex and involves the formation of a so-called conditioning film, which consists of organic polymeric material that then leaves the membrane surface within the biocompatible range for attachment of film-forming bacteria. Biofouling is especially severe in reverse osmosis of seawater and its control is crucial for the reliable operation of reverse osmosis desalination plants. Concentration polarization can be minimized by hydrodynamic means such as the feed flow velocity and the membrane module design. The control of

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membrane fouling, however, is more difficult. Membrane fouling is influenced by the chemical nature of the membrane material and the feed solution constituents. To avoid or control membrane fouling extensive feed water pretreatment and dosage of special chemicals may be required. The causes and consequences of concentration polarization and membrane fouling as well as necessary means to control them depend on the feed water composition and on the membrane process.

1. Concentration Polarization in Filtration Processes

The causes and consequences of concentration polarization in pressure-driven membrane processes such as reverse osmosis and ultra- and microfiltration have been studied extensively [4–6]. While the causes for concentration polarization are identical in all three processes the consequences are rather different. When water selectively permeates a reverse osmosis or ultra- and microfiltration membrane, the retained solutes are accumulated at the membrane – solution interface. Thus, a concentration gradient between the solution at the membrane surface and the bulk is established which leads to backtransport of the material accumulated at the membrane by diffusion and eventually other means. This phenomenon is referred to as concentration polarization. In reverse osmosis mainly low molecular weight materials are separated from a solvent such as water. The feed solutions often have a considerable osmotic pressure. For example seawater has an osmotic pressure of about 24 bar. In reverse osmosis concentration polarization leads to an increase in the osmotic pressure, which is directly proportional to the solute concentration at the membrane surface, and thus a decrease in the membrane flux at constant applied hydrostatic pressure. Furthermore, the quality of the filtrate is impaired since solute leakage through the membrane is also directly proportional to the solute concentration at membrane feed-side surface [7, 8].

In ultra- and microfiltration only macromolecules and particles are retained by the membrane. The osmotic pressure of the feed solution is generally quite low. However, the applied hydrostatic pressure is also low and in certain applications of ultrafiltration the osmotic pressure can not be neglected. Due to the rather high molecular weight of the components separated in ultra- and microfiltration their diffusion from the membrane surface back into the bulk solution is relatively slow. Therefore, the retained components often are precipitated and form a solid layer at the membrane surface [9]. This layer, which often exhibits membrane properties itself, can effect the membrane separation characteristics significantly by reducing the membrane flux and by changing the rejection of lower molecular weight components. This is especially problematic in the fractionation of materials of different molecular weight.

To describe concentration polarization in membrane filtration processes mathematically a relationship is needed which relates the solute concentration at the membrane surface to that in the bulk and permeate solution, the membrane flux, and the fluid flow conditions in the boundary layer between membrane surface and bulk solution. There are two basic approaches to this problem [10]:

- Application of the so-called film model with the appropriate mass transfer coefficients to describe solute transport into and out of the boundary layer.
- Solution of the transport equations for the fluid velocity field to obtain an expression for the local concentration at any point in the feed solution.

Concentration polarization without precipitation of solutes at the membrane surface can be described reasonably well as a function of the various hydrodynamic parameters and membrane and feed solution properties by the film model. The more rigorous treatment of concentration polarization is based on a material and momentum balance. The numerical solution of the transport equations for the fluid and the solutes is rather complex even after introducing certain simplifications such as complete solute rejection, concentration-independent transport coefficients, and no diffusive transport parallel to the membrane surface. Mathematical modeling is even more difficult when concentration polarization leads to precipitation of the solutes at the membrane surface. Here time-dependent effects such as densification of a formed gel or cake layer often influence flux and separation characteristics of the membrane.

1.1. Concentration Polarization without Solute Precipitation

The treatment of concentration polarization without solute precipitation by the film model assumes turbulent flow with fully developed velocity and concentration profiles in the boundary layer at the membrane surface. The description of concentration polarization in laminar flow is based on considerations analogous to heat transfer in laminar feed flow conditions and must consider entrance and exit effects in the development of the velocity and concentration profiles in the feed solution.

The film model assumes that, even with *turbulent feed flow*, at a certain distance from the entrance a constant laminar boundary layer is established adjacent to the membrane surface in which longitudinal mass transport is negligibly low, so that mass transport within the film can be regarded as one-dimensional in the direction perpendicular to the membrane surface. During the filtration process, a steady state is reached in which the convective transport of solutes to the membrane surface is counterbalanced by a diffusive flux of the retained material back into the bulk solution. Therefore, a constant concentration profile of the retained material in the laminar boundary layer is obtained. This is illustrated in the schematic diagram of Figure 1.

The material balance for the solute in the differential element of the film is given by:

$$J_{\mathrm{s}} = J_{\mathrm{s,con}} - J_{\mathrm{s,diff}} \tag{1}$$

where J_{s} is the solute flux through the membrane, $J_{\mathrm{s,con}}$ the solute flux toward the membrane by convection, and $J_{\mathrm{s,diff}}$ the solute flux from the membrane surface into the bulk solution by diffusion.

Furthermore:

$$J_{\mathrm{s}} = J_{\mathrm{v}} C_{\mathrm{s}}^{\mathrm{p}}, \; J_{\mathrm{s,diff}} = -D_{\mathrm{s}} \frac{\mathrm{d}\, C_{\mathrm{s}}}{\mathrm{d}\, z}, \text{ and } J_{\mathrm{s,con}} = J_{\mathrm{v}} C_{\mathrm{s}} \tag{2}$$

where J_{v} is the membrane volume flux, D_{s} is the diffusion coefficient, and $\mathrm{d}C_{\mathrm{s}}/\mathrm{d}z$ is the concentration gradient of the solute in the boundary layer solution.

Combination of Equations (1) and (2) and integrating with the boundary conditions $C_{\mathrm{s}} = C_{\mathrm{s}}^{\mathrm{w}}$ at $z = 0$ and $C_{\mathrm{s}} = C_{\mathrm{s}}^{\mathrm{b}}$ at $z = Z_{\mathrm{b}}$ leads to:

$$\frac{J_{\mathrm{v}} Z_{\mathrm{b}}}{D_{\mathrm{s}}} = \ln \frac{C_{\mathrm{s}}^{\mathrm{w}} - C_{\mathrm{s}}^{\mathrm{p}}}{C_{\mathrm{s}}^{\mathrm{b}} - C_{\mathrm{s}}^{\mathrm{p}}} \tag{3}$$

where Z_{b} is the boundary layer thickness, $C_{\mathrm{s}}^{\mathrm{p}}$ the permeate solute concentration, and $C_{\mathrm{s}}^{\mathrm{w}}$ and $C_{\mathrm{s}}^{\mathrm{b}}$ are the solute concentrations in the feed solution at the membrane wall and in the bulk.

The membrane rejection R relates the permeate concentration to the concentration at the membrane wall:

$$R = 1 - \frac{C_{\mathrm{s}}^{\mathrm{p}}}{C_{\mathrm{s}}^{\mathrm{w}}} \tag{4}$$

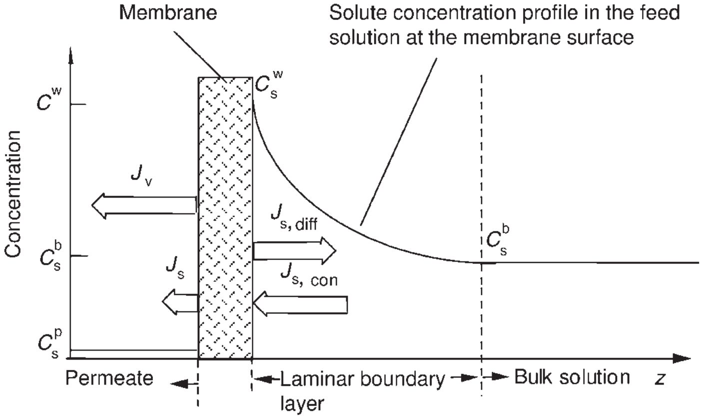

Figure 1. Schematic diagram illustrating the concentration profiles of a component retained by the membrane and the fluxes in the laminar boundary layer at the feed side surface of a membrane under steady-state conditions as assumed in the film model

Combination of Equations (3) and (4) leads to:

$$\frac{C_\mathrm{s}^\mathrm{w}}{C_\mathrm{s}^\mathrm{b}} = \frac{\exp\frac{J_\mathrm{v} Z_\mathrm{b}}{D_\mathrm{s}}}{R+(1-R)\exp\frac{J_\mathrm{v} Z_\mathrm{b}}{D_\mathrm{s}}} \tag{5}$$

In Equation (5) the concentration polarization is expressed as the ratio of the solute concentration at the membrane surface $C_\mathrm{s}{}^\mathrm{w}$ and that in the bulk solution $C_\mathrm{s}{}^\mathrm{b}$. It is a function of the membrane flux J_v, the thickness of the boundary layer Z_b, the diffusion coefficient of the solute in the boundary layer solution D_s, and the membrane solute rejection R.

To describe the concentration polarization under various feed flow conditions a solute mass transfer coefficient k_s is introduced. Assuming that the membrane flux is small compared to the feed flow parallel to the membrane surface the mass transfer coefficient can be expressed by:

$$k_\mathrm{s} = \frac{D_\mathrm{s}}{Z_\mathrm{b}} \tag{6}$$

where k_s is the solute mass transfer coefficient, D_s is the solute diffusion coefficient in the boundary solution, and Z_b is the boundary layer thickness.

Introducing Equation (6) into Equation (5) leads to:

$$\frac{C_\mathrm{s}^\mathrm{w}}{C_\mathrm{s}^\mathrm{b}} = \frac{\exp\frac{J_\mathrm{v}}{k}}{R+(1-R)\exp\frac{J_\mathrm{v}}{k}} \tag{7}$$

Equation (7) describes the concentration polarization as a function of the filtration rate, the membrane rejection, and the mass transfer coefficient. The filtration rate and the membrane rejection can easily be measured. The mass transfer coefficient is more difficult to determine. However, empirical correlations developed for various feed solution flow regimes under the assumption of steady-state conditions can be used to estimate the mass transfer coefficient as a function of the feed flow velocity and the filtration device geometry. These correlations may be expressed in a very general form by the Sherwood, Reynolds, and the Schmidt numbers [11]:

$$Sh = a\,Re^b\,Sc^c\left(\frac{d_\mathrm{H}}{L}\right)^d \tag{8}$$

where *Sh, Re*, and *Sc* are respectively the Sherwood, Reynolds, and Schmidt numbers, d_H is the hydraulic diameter or other characteristic dimension, L the length of the feed flow duct, which may be a channel or a tube, and *a, b, c*, and *d* are constants which are characteristic for different filtration system geometries and which must be experimentally determined.

The Sherwood number is given by:

$$Sh = k_\mathrm{s}\frac{d_\mathrm{H}}{D_\mathrm{s}} \tag{9}$$

where D_s is the diffusion coefficient.

The Schmidt number is given by:

$$Sc = \frac{\nu}{D_\mathrm{s}} \tag{10}$$

where ν is the viscosity.

The Reynolds number for turbulent flow in a tube or channel is given by:

$$Re = \frac{d_\mathrm{H} u}{\nu} \tag{11}$$

where u is the linear velocity.

In a stirred batch cell the Sherwood and the Reynolds numbers can be expressed by the cell diameter D_c, the stirrer speed ω, and the stirrer length d. Thus, in a well-stirred batch cell the Sherwood number is given by:

$$Sh = k_\mathrm{s}\frac{D_\mathrm{c}}{D_\mathrm{s}} \tag{12}$$

and the Reynolds number by:

$$Re = \frac{\omega\, d^2}{\nu} \tag{13}$$

When the film model is used to describe concentration polarization in turbulent flow regime, it is generally assumed that the flow is fully developed and entrance effects can be neglected. This can be done in most filtration systems that are used in large-scale industrial applications; therefore, exponent d in Equation (8) is 0. In laminar flow the situation is different, especially in modules consisting of relatively short thin channels. Here, the entrance length often covers the entire channel length.

Combination of Equations (5), (8), (10), (12), (13), gives a relation for the mass transfer coefficient in a well-stirred batch cell:

$$\frac{C_\mathrm{s}^\mathrm{w}}{C_\mathrm{s}^\mathrm{b}} = \frac{\exp\frac{J_\mathrm{v} D_\mathrm{c}}{a(D_\mathrm{s}\omega d^2)^{0.66}\nu^{-0.33}}}{R+(1-R)\exp\frac{J_\mathrm{v} D_\mathrm{c}}{a(D_\mathrm{s}\omega d^2)^{0.66}\nu^{-0.33}}} \tag{14}$$

where $C_s{}^w$ and $C_s{}^b$ are the solute concentrations at the membrane surface and in the bulk solution, D_s is the solute diffusion coefficient, D_c the diameter of the cell, d the stirrer length, ν the viscosity of the solution, ω the stirrer speed, J_v the membrane flux, R the membrane rejection, and a a constant which has a value between 0.1and 0.6 depending on the cell design.

Equation (14) shows that concentration polarization for a given feed solution and batch-cell geometry increases with increasing transmembrane flux and membrane rejection and decreases with increasing stirrer speed.

By introducing the appropriate relation for the hydraulic diameter and the length of the flow duct the concentration polarization can also be calculated for a rectangular channel and a circular tube. The hydraulic diameter is expressed in terms of the channel width w and the channel height h by:

$$d_H = \frac{2wh}{w+h} \tag{15}$$

where w is the channel width and h the channel height.

Thus, the concentration polarization in a rectangular channel is given by:

$$\frac{C_s^w}{C_s^b} = \frac{\exp\frac{J_v\left(\frac{wh}{w+h}\right)^{0.2}\nu^{0.47}}{a\,D_s^{0.66}u^{0.8}}}{R+(1-R)\exp\frac{J_v\left(\frac{wh}{w+h}\right)^{0.2}\nu^{0.47}}{a\,D_s^{0.66}u^{0.8}}} \tag{16}$$

where w is the channel width, h the channel height, and u the linear feed flow velocity.

The concentration polarization in a tubular membrane device can be calculated accordingly to:

$$\frac{C_s^w}{C_s^b} = \frac{\exp\frac{J_v r_t^{0.2}\nu^{0.47}}{a\,D_s^{0.66}u^{0.8}}}{R+(1-R)\exp\frac{J_v r_t^{0.2}\nu^{0.47}}{a\,D_s^{0.66}u^{0.8}}} \tag{17}$$

where r_t is the radius of the tubular membrane device.

The film model which pictures a laminar boundary layer at the membrane surface and a turbulent bulk solution can obviously not be applied to membrane devices with *laminar feed flow*. In laminar flow in thin-channel, tube, or capillary membrane modules the flow velocity is no longer constant over the cross section of the flow channel or capillary, and the velocity and concentration profiles develop over a much longer distance from the channel entrance than in turbulent flow. Therefore, entrance effects cannot be neglected in most commercially available membrane modules operated with laminar feed flow when the concentration polarization effects are described mathematically. Concentration polarization in laminar flow can be estimated with reasonable accuracy by describing the mass transfer in analogy to heat transfer in laminar flow by the Reynolds, the Schmidt, and the Sherwood numbers, taking the entrance length into account. The Sherwood number for laminar flow devices can be expressed by [12]:

$$Sh = a\left(ScRe\frac{d_H}{L}\right)^{0.33} \tag{18}$$

In filtration processes with laminar flow the concentration polarization can be calculated as a function of the flow velocity, the channel height, and the channel length by combination of Equations (5), (6), and (18).

Although the film model assumes several simplifications such as steady-state conditions, that is, no variations in the concentration profile with time, no mass transport parallel to the membrane surface due to concentration or density gradients, and fully developed velocity profile in the turbulent flow regime, it has proved to be quite useful for describing concentration polarization in reverse osmosis and ultrafiltration under various feed flow conditions as long as no solutes precipitate at the membrane surface. The same is true for the treatment of concentration polarization in membrane modules with laminar flow.

The characteristic constants for the calculation the concentration polarization in practically used membrane filtration modules with turbulent and laminar flow are summarized in Table 1.

Table 1. Mass transfer correlation for the constants *a, b, c*, and *d* under various hydrodynamic feed flow conditions

Flow regime	Module geometry	Hydraulic diameter d_H	Characteristic constants			
			a	*b*	*c*	*d*
Turbulent	channel	$\frac{2hw}{h+w}$	0.023	0.8	0.33	0
Laminar	channel	$\frac{2hw}{h+w}$	1.62	0.33	0.33	0.33
Turbulent	tube	r_t	0.023	0.8	0.25	0
Laminar	tube	r_t	1.86	0.33	0.33	0.33

r_t = tube radius, h = channel height, w = channel width.

The *rigorous analysis* of concentration polarization involves the solution of the general transport equations for fluid and solute (i.e., the mass balance of solute and solvent and the momentum balance). The solution of the coupled continuity and momentum equations is mathematically rather complex and it becomes even more complicated in the case of significant viscosity changes or precipitation of solutes at the membrane surface due to concentration polarization [10].

1.2. Concentration Polarization with Solute Precipitation at the Membrane Surface

In ultrafiltration and even more so in microfiltration the simple film model is no longer applicable because the feed solutions contain macromolecular components or suspended materials and the membrane fluxes are generally significantly higher than in reverse osmosis [13, 14]. Due to the relatively low diffusion coefficient of macromolecules or suspended particles, diffusive mass transport of components retained by the membrane from the membrane surface back into the bulk solution is slow and can not counterbalance the convective mass transport towards the membrane. Thus, the solute concentration at the membrane surface often exceeds the solubility of the feed solution constituents. This results in the precipitation of the feed solution components at the membrane surface and the formation of a dense solid layer on the membrane surface, which adds an additional hydrodynamic resistance to the membrane flux. When the membrane surface concentration reaches the solubility limit of the feed water constituents, the concentration difference between the membrane surface and the bulk solution and thus the diffusive transport from the membrane surface into the bulk solution reaches its maximum value. If the membrane flux and thus the convective solute transport towards the membrane is increased by increasing the hydrostatic pressure, more solutes are transported towards the membrane than can diffuse back. The additional solutes also precipitate and increase the thickness of the layer at the membrane surface and thus increase its resistance correspondingly, and in spite of an increase in the hydrostatic pressure driving force the membrane flux is not further increased. That means that in ultrafiltration and microfiltration of solutions containing high molecular components with limited solubility the membrane flux becomes independent of the hydrostatic pressure driving force as soon as these components precipitate and form a solid layer at the membrane surface. Typical results obtained in ultrafiltration of macromolecular solutions that precipitate at the membrane surface when a certain hydrostatic pressure or feed solution concentration is exceeded is shown in Figure 2. Here, membrane fluxes obtained when filtering hemoglobin solutions of different concentrations through an ultrafiltration membrane are shown as a function of the applied hydrostatic pressure and the hemoglobin concentration. The filtration apparatus is a stirred batch cell operated at constant stirrer speed. With pure water the membrane flux is directly proportional to the applied hydrostatic pressure. With the hemoglobin solution the membrane flux depends on the applied pressure only at very low pressures and approaches a constant, pressure-independent value at higher pressures. This value is a function of the hemoglobin concentration and is lowest at the highest concentration. Similar membrane flux – pressure relations are obtained in all filtration tests with feed solutions that contain macromolecular or particulate components which have low diffusivities and thus tend to precipitate at the membrane surface.

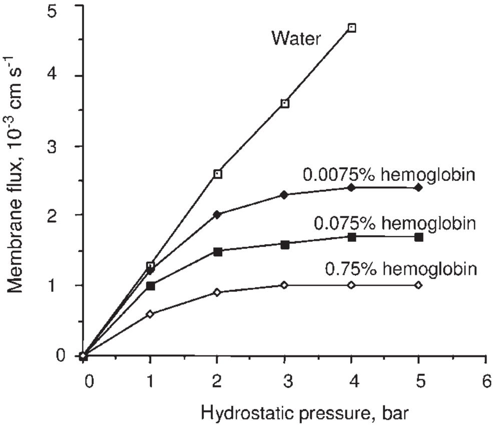

Figure 2. Ultrafiltration fluxes of water and hemoglobin solutions of different concentrations determined as a function of the hydrostatic pressure in a stirred batch cell at constant stirrer speed of 1800 rpm

Under conditions of precipitation-layer formation at the membrane surface the membrane flux can only be increased by a decrease in the boundary layer thickness or the bulk solution concentration. The boundary layer in membrane separation processes depends on hydrodynamic conditions of the system and depends on the degree of mixing, that is, on the Reynolds number achieved in the feed solution in turbulent flow or the channel height or capillary diameter under laminar flow conditions. The flux decline due to the formation of a precipitate layer also depends on the feed water constituents. Some components, such as proteins, dextrans, and metal oxides, form rather dense layers that affect the membrane flux significantly, while other materials, such as rigid particles, have a lesser effect on the flux.

The effect of the boundary layer thickness on the membrane flux has been demonstrated in several studies [15, 16]. Figure 3 shows the ultrafiltration flux of 1 % bovine albumin ($M =$ 69 000) and 1 % dextran 110 ($M = 110\ 000$) as a function of the stirrer speed determined in a batch cell at 5 bar hydrostatic pressure [17]. With increasing stirrer speed, that is, decreasing boundary layer thickness, the membrane flux increases.

The experimental results show that in the case of precipitation of solute at the membrane surface, as in ultrafiltration and more so in cross-flow microfiltration, the hydrodynamic resistance to membrane flux is not only a function of the membrane properties but is also strongly affected by the gel or cake layer formed by the retained solutes at the membrane surface. A simpler approach to describe the membrane flux in case of formation of a gel or a cake layer is to assume that the osmotic pressure of the feed solution in micro- and ultrafiltration can be neglected and express the flux in terms of the resistances of the membrane and the layer in series [18, 19]:

$$J_{\mathrm{v}} = A \frac{1}{R_{\mathrm{m}} + r_{\mathrm{l}} \Delta z_{\mathrm{l}}} \Delta p \tag{19}$$

where J_{v} is the membrane flux, R_{m} the hydrodynamic resistance of the membrane, r_{l} the specific resistance of the layer, Δz_{l} the thickness of the layer, Δp the hydrostatic pressure driving force, and A the membrane area.

Formation of a gel or cake layer in micro- and ultrafiltration is illustrated in Figure 4. This figure shows schematically a membrane, the gel layer at its surface, and the concentration and hydrostatic pressure profiles in the bulk solution, the laminar boundary layer, the gel layer, and the membrane. When the concentration of the retained solute at the membrane surface $C_{\mathrm{s}}^{\mathrm{w}}$ reaches the gel layer concentration $C_{\mathrm{s}}^{\mathrm{g}}$, maximum diffusive transport of retained components from the membrane surface back into the bulk solution is attained. In the description of concentration polarization in terms of the film model it is assumed that diffusion is the only mechanism in the laminar boundary layer for the transport of components from the membrane surface to the bulk solution, and that in the steady state diffusive transport is just counterbalanced by the convective transport towards the membrane. This means that an increase in the hydrostatic pressure will lead only to short-term increase of the membrane flux and convective transport of solutes towards the membrane surface. Since diffusive transport from the membrane into the bulk solution is independent of the applied hydrostatic pressure, and additional components transported towards the membrane surface will precipitate and lead to an increase in gel layer thickness, the overall cake layer resistance will increase until the membrane flux has dropped back to its original value. This means that the membrane flux in ultra- or microfiltration is independent of the applied hydrostatic pressure when a gel layer is formed due to precipitation of the retained

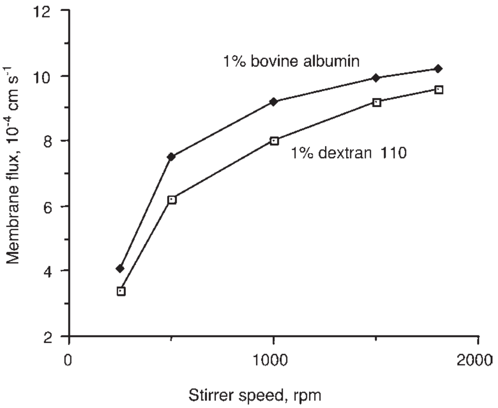

Figure 3. Membrane flux determined in a stirred batch cell with 1 % solutions of dextran 110 and bovine albumin at different stirrer speeds and constant hydrostatic pressure of 5 bar

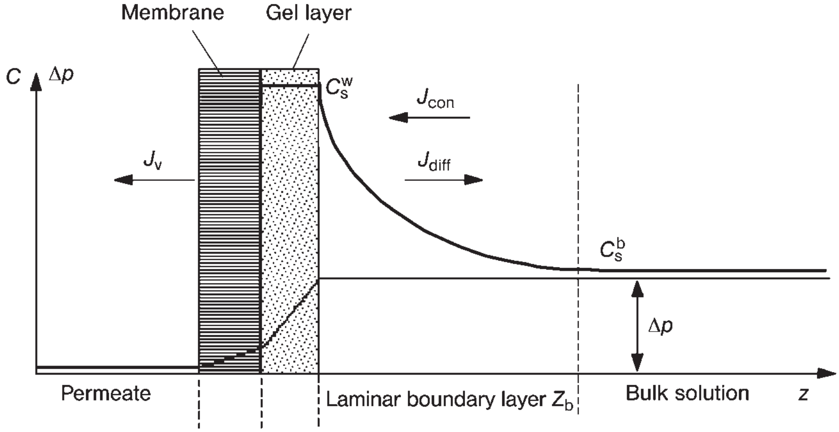

Figure 4. Schematic illustrating concentration polarization with the solutes forming a gel or cake layer at the membrane surface ($C_s{}^b$ and $C_s{}^w$ are the solute concentrations in the bulk solution and at the membrane wall, Δp is the pressure difference between the permeate and the feed, and J_v the filtrate rate)

components at the membrane surface and it depends only on the transport of these components back into the bulk solution.

Under conditions of precipitation of retained components at the membrane surface the membrane flux can only be increased by increasing the backtransport of the retained components into the bulk solution. This can be done, for example, by decreasing the boundary layer thickness or decreasing the bulk solution concentration, as can be seen from Equations (20) and (21), which describe the mass transport in the laminar boundary layer in a filtration device with turbulent bulk flow. For simplicity it is assumed that the dissolved components are completely retained by the membrane (i.e., $R = 1$):

$$\frac{C_s^w}{C_s^b} = \exp\frac{J_v Z_b}{D_s} \tag{20}$$

where $C_s{}^b$ and $C_s{}^w$ are the solute concentrations in the bulk solution and at the membrane surface, which is identical to the gel layer concentration $C_s{}^g$ and constant for a given temperature and pressure. With $C_s{}^w = C_s{}^g$ = const. the flux is determined according to Equation (20) only by the bulk solution concentration and the boundary layer thickness. For certain mass transfer conditions and bulk solution concentration it is given by:

$$J_v = \frac{D_s}{Z_b}\ln C_s^b = k_s \ln C_s^b \tag{21}$$

Figure 5 shows the membrane flux obtained for three different feed solution concentrations in the filtration of solutions with constituents that precipitate at the membrane surface as a function of the applied hydrostatic pressures, as calculated by Equation (21). The flux versus pressure curves in Figure 5 show the same general pressure – flux relation as the experimental data obtained in ultrafiltration experiments with hemoglobin solutions of different concentrations (Fig. 2). The flux of pure water increases linearly with the applied pressure. The flux of a solution also increases linearly with pressure until a certain flux is attained. A further increase in pressure does not lead to a permanent increase in flux since the concentration of the retained solutes at the

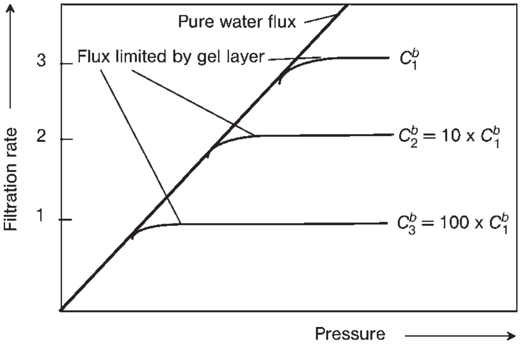

Figure 5. Schematic showing the permeate flux as a function of the applied pressure for the filtration of gel-layer-forming feed solutions of different concentrations

membrane surface has reached the solubility limit and precipitation occurs. The precipitated solute forms a dense layer which grows in thickness and in hydrodynamic resistance when, due to an increase in the applied pressure, the flux through the membrane is increased for a short time period and then reaches its former value again. The gel or cake layer at the surface of a micro- or ultrafiltration membrane not only impairs the membrane flux, but it can also influence separation properties of the membrane by acting as a permeable membrane which retains lower molecular weight materials not rejected by the membrane [9]. Especially in fractionation of biological fluid mixtures such as blood the formation of a gel layer impairs the entire process and can make a separation of different molecular weight components impossible.

With the formation of a gel or cake layer during filtration of macromolecular or particulate solutions or suspensions with high-flux membranes, mathematical modeling of the process becomes significantly more complex, because the specific resistance of the gel layer depends on the layer-forming components and can be very different for different components. While some rigid materials such as latex balls form layers that resemble the packing of spheres, other materials such as certain proteins form gel-type layers. Many gel layers change their structure with time and their resistance often increases with time.

Furthermore, because of the low diffusivities of macromolecules and particles, diffusion can no longer be the only means of transportation of the components retained by the membrane in micro- and ultrafiltration. Grossly simplified, the process can be described as a three-step procedure (Fig. 6). In the gel layer the material retained by the membrane is more or less solidly integrated in a structure. The strength of this structure will depend on the intrinsic properties of the material but also on the hydrostatic pressure and eventually on the "age" of the gel layer. The first step in the process of bringing the material back into the bulk solution therefore is to release it from the structure into the solution at the boundary layer. If the material is in solution it can diffuse or be transported by other means such as convection into the bulk solution. Steps 2 and 3 of the transport process are in parallel, while steps 1 and 2 or 3 are in series.

In parallel processes, the fastest is the overall rate-determining step, and in consecutive processes the slowest is rate-determining. In ultra- and microfiltration with gel layer formation it is quite likely that the first step, that is, the release of the material from the gel layer structure, is the rate-determining step, and of the two parallel steps convective transport is fastest.

In many ultrafiltration tests a flux decline with time is observed even when all other operating parameters are kept constant. The original membrane flux can usually be restored when the membrane has been cleaned thoroughly with a proper solution. This is demonstrated in Figure 7, which shows schematically the results of a typical filtration test.

The flux decline with time when all operating parameters are kept constant, as shown in Figure 7 and observed in many practical ultrafiltration tests, is difficult to explain with flow condition arguments only. It can, however, be rationalized by the assumption that the rate-limiting step for the transport of the material retained at the membrane surface into the bulk solution is the release rate of the material from the gel structure. This rate may well decrease with time when the

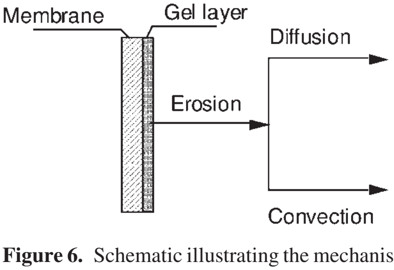

Figure 6. Schematic illustrating the mechanism of the transport of components retained by the membrane and accumulated in a gel layer from the membrane surface back into the bulk solution

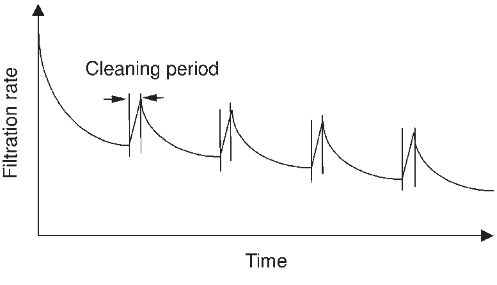

Figure 7. Membrane flux obtained during ultrafiltration of cheese whey at constant operating conditions but with daily cleaning periods as function of time (schematic)

gel structure ages and becomes more compact under pressure [20].

Modeling the mass transport at the membrane surface in micro- and ultrafiltration mathematically in terms of the hydrodynamic feed flow conditions, with inclusion of all phenomena observed in practical separation problems, is rather difficult when a gel layer has formed and the mass transfer at the membrane surface is no longer just a function of the diffusion coefficient and boundary layer thickness. Many mathematical models use fitting parameters and can be applied only to very specific conditions of membranes, feed solutions, and process parameters. A general model that fits all feed solutions and process parameters seems to be too complex to be of practical value.

2. Membrane Fouling and its Causes

In the literature the term “membrane fouling” is often used to describe a long-term flux decline caused by accumulation of certain materials at the membrane surface. The consequences of membrane fouling are obvious, but its causes are often not very clear [20, 21, 23]. Formation of a gel or cake layer is one cause of membrane fouling. Gel or cake layers can be formed by a variety of materials including inorganic precipitates such as $CaSO_4$, $Fe(OH)_2$, and other metal hydroxides; organic materials such as proteins, humic acids, and other macromolecular materials; and biological components such as microorganisms and their metabolic products. Membrane fouling can also occur without concentration polarization (i.e., direct transport to the membrane surface as in any mass separation process). The attachment of the substances to the membrane surface may be caused by adsorption due to hydrophobic interactions, van der Waals forces, or electrostatic forces. The fouling layer itself can be porous and thus permeable to aqueous solutions, as in the case of some inorganic precipitates, or highly impermeable when the layer consists of films of mineral oils or hydrophobic surfactants. The fouling mechanism also depends on the membrane process. In electrodialysis fouling is caused mainly by precipitation of polyelectrolytes or sparingly soluble salts such as $CaSO_4$ or $CaCO_3$. Membrane fouling in electrodialysis affects mainly anion-exchange membranes because most of the colloidal and macromolecular polyelectrolytes present in natural waters (e.g., humic acids and proteins) are negatively charged. In ultra- and microfiltration of biological solutions, but also in reverse-osmosis seawater desalination, biological fouling is a severe problem affecting the economics of the processes. In biomedical applications protein adsorption and protein denaturation at the membrane surface often impair the performance of the membranes.

The difference between concentration polarization and membrane fouling or scaling is illustrated schematically in Figure 8. Concentration polarization is a reversible process based on diffusion and takes place over a few seconds; it can be described adequately by a simple mathematical model and easily controlled by proper process design. Fouling is generally irreversible and the flux decline takes place over many minutes, hours, or even days. A constant flux is generally not reached. Membrane fouling is more difficult to describe and to control by experimental means. Membrane fouling is determined by a variety of different parameters including the feed solution constituents and their concentration, membrane material, and the fluid-dynamic system design. Membrane fouling can be caused by simple precipitation of insoluble materials or by reversible or irreversible adsorption of components at the membrane surface and within the membrane pores.

The means of preventing or at least controlling membrane fouling are as heterogeneous as the different materials and mechanisms causing the fouling [22, 23]. The main procedures to avoid or control fouling involve:

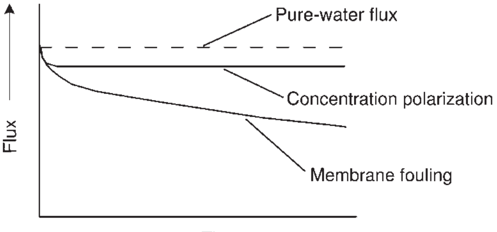

Figure 8. Schematic illustrating the difference between the flux decline due to concentration polarization and due to membrane fouling

- Pretreatment of the feed solution
- Membrane surface modifications
- Hydrodynamic optimization of the membrane module
- Membrane cleaning with appropriate chemical agents

Pretreatment of the feed solution can include chemical precipitation, prefiltration, pH adjustment, chlorination, and carbon adsorption. In some membrane module designs, for instance, hollow-fiber modules, the elimination of all particulate materials is of great importance for the proper function of the membrane.

Membrane surface modifications include the introduction of hydrophilic moieties or charged groups in the membrane surface by chemical means or plasma deposition.

Increasing the shear rate imposed by the feed solution on the membrane surface will in many cases reduce membrane fouling. High feed flow velocities and proper module design are efficient tools in controlling membrane fouling.

When, in spite of an adequate membrane and module design, the membrane flux decreases with operating time to an unacceptably low value it is necessary to clean the membrane to restore the flux in part or completely. Typical cleaning agents are acids and bases such as HNO_3 and NaOH, complexing agents, enzymes, and detergents. Another very effective method to minimize the effects of membrane fouling in microfiltration is backflushing, in which the applied pressure is reversed and the permeate pushed through the membrane to lift off fouling material precipitated on the feed side membrane surface and wash it out of the filtration device. Backflushing is done at certain time intervals for a few seconds.

3. Concentration Polarization in Other Membrane Separation Processes

In other membrane separation processes of technical relevance concentration polarization is of lesser significance than in reverse osmosis or ultrafiltration. It can generally be controlled and its detrimental effects be minimized by proper process design.

3.1. Concentration Polarization in Dialysis

In dialysis, concentration polarization is an accepted phenomenon. There is always depletion of the components in the boundary layer at the membrane surface facing the feed solution and accumulation at the membrane surface facing the dialysate (Fig. 9). However, the differences between the concentrations at the membrane surfaces and in the bulk solutions is low, because dialysis membranes are rather thick compared to the laminar boundary layers at their surfaces, and the transport in the

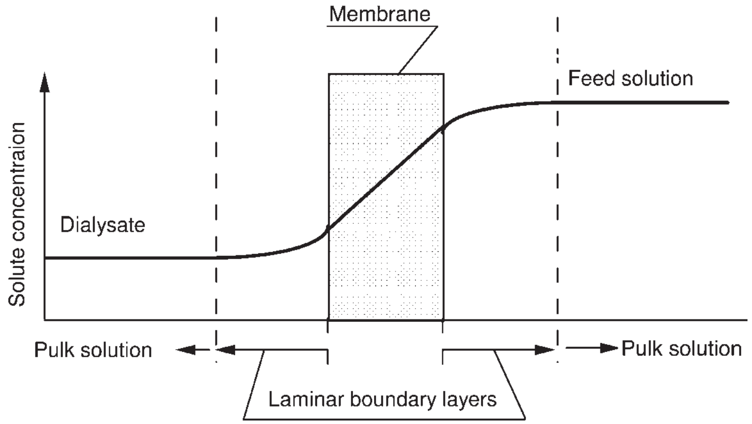

Figure 9. Schematic illustrating the effects of concentration polarization in dialysis

membrane is rate-limiting for the overall mass transfer from the feed to the dialysate bulk solution. Thus, in dialysis concentration polarization effects are small.

3.2. Concentration Polarization in Electrodialysis

In electrodialysis, concentration polarization decreases the ion concentration at the membrane surface facing the diluate cell and increases the concentration at the membrane surface facing the concentrate cell of the electrodialysis stack. The concentration increase may lead to a precipitation of salts. The concentration decrease lowers the limiting current density. Since the required membrane area is inversely proportional to the limiting current density, concentration polarization in electrodialysis has direct consequences for the overall process economics. It is controlled by using cell design and the flow velocities in the system to minimize the thickness of the laminar boundary layers at the membrane surfaces.

3.3. Concentration Polarization in Pervaporation

In pervaporation, concentration polarization can occur on both sides of the membrane. As in dialysis the boundary layer at the membrane surface facing the feed solution is depleted of the preferentially permeating components, which are then enriched at the membrane surface facing the permeate [24]. In pervaporation, concentration polarization is generally controlled by decreasing the laminar boundary layer thickness through hydrodynamic measures. This can lead to problems when high-flux thin-film composite membranes are used. At the permeate side the laminar boundary layer is always as thick as the porous substructure, and severe concentration polarization and capillary condensation may occur on the permeate side of the membrane. If the solubility of the permeating component in the feed solution is low the boundary layer at the feed side of the membrane may be depleted of the permeating component and the membrane flux and separation efficiency may be severely impaired. This, for example, is the case when organic solvent – water mixtures of limited solubility are treated.

3.4. Concentration Polarization in Gas Separation

In the separation of gases by solution-diffusion membranes, concentration polarization is of lesser importance and has generally little effect on the overall efficiency of the process. The reason is that the diffusivity of gases in the gas phase is much higher than in a solid polymer phase. Therefore, the transport rates in the boundary layer are comparatively high and there is less accumulation or depletion of components at the membrane surface. Nevertheless, concentration polarization in gas separation can not in all cases be neglected and must also be controlled by proper system design and flow conditions of the gases on the feed and permeate side of the membrane.

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