

Review

Diffusional phenomena in membrane separation processes*

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(Received June 25, 1991, accepted in revised form April 6, 1992)

Abstract

Nowadays membrane filtration processes are used industrially as an alternative to conventional separation methods. Membrane separation methods can be divided into classes according to their separation characteristics: (i) separation by sieving action, (ii) separation due to a difference in affinity and diffusivity, (iii) separation due to a difference in charge of molecules, (iv) carrier-facilitated transport, and (v) the process of (time-) controlled release by diffusion. In all these cases diffusion processes play an important role in the transport mechanism of the solutes. Various mechanisms have been distinguished to describe the transport in membranes: transport through bulk material (dense membranes), Knudsen diffusion in narrow pores, viscous flow in wide pores or surface diffusion along pore walls. In practice, the transport can be a result of more than only one of these mechanisms. For all of these mechanisms models have been derived. The characteristics of a membrane, e.g. its crystallinity or its charge, can also have major consequences for the rate of diffusion in the membrane, and hence for the flux obtained. Apart from the diffusion transport processes in membranes mentioned above, other important diffusion processes are related to membrane processes, viz. diffusion in the boundary layer near the membrane (concentration polarization phenomena) and diffusion during membrane formation. The degree of concentration polarization is related to the magnitude of the mass transfer coefficient which, in turn, is influenced by the diffusion coefficient. The effect of concentration polarization can be rather different for the various membrane processes. The phase inversion membrane formation mechanism is determined to a large extent by the kinetic aspects during membrane formation, which are diffusion of solvent and of non-solvent and the kinetics of the phase separation itself.

Keywords: diffusion, theory, review

Introduction

Membrane filtration processes nowadays are

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

used industrially as an alternative to conventional separation methods such as distillation, centrifugation and extraction. Since the first asymmetric reverse osmosis membranes became available in the early sixties membrane technology has developed enormously. This is expressed in the vast amount of research that has gone into developing the right membrane type and module for different kinds of separa-

tion processes, developing new processes and the best possible circumstances for separation. These efforts have resulted in the present day commercialization of ultrafiltration (UF), microfiltration (MF), reverse osmosis or hyperfiltration (RO), gas separation (GS), pervaporation (PV), (kidney-) dialysis and electro dialysis (ED).

A membrane separation process can be generally represented as in Fig 1.

The various membrane separation methods can be divided into three classes according to their separation characteristics:

(i) UF and MF use the size of the solutes to separate particles by sieving action, with a pressure difference as the driving force, the membranes used in UF can have pores from 1 to 50 nm, while for MF the pore range is from 0.05 to 10 μm .

(ii) RO, gas separation and pervaporation, which are associated with (partly) dense membrane structures (pores < 1 nm), make use of a difference in affinity between several feed components and the membrane, and of a difference in diffusivity through the membrane, the driving force is a pressure difference in case of RO and gas separation, and in case of dialysis and pervaporation the driving force is a concentration gradient.

(iii) Electro dialysis uses anion- and cation selective membranes to separate charged molecules from uncharged ones. The ions are transported by a diffusional mechanism, as a result of an applied potential difference.

Some other membrane processes are under development at the moment, for instance, facilitated transport by liquid and fixed site car-

rier membranes. Carrier-facilitated transport can also be determined by diffusion only, which depends for example on the kind of membrane applied. Furthermore, the technique of controlled release of drugs from (biodegradable) reservoirs is a process that is mainly determined by diffusion.

Applications of already commercialized techniques include:

- Food industry: whey processing (RO and UF), concentration of milk for cheese production (UF), clarification and/or sterilization of various fluids such as wine, vinegar and apple juice (MF) and whey desalting (ED)
- Water treatment: production of high resistivity ($> 18 \text{ M}\Omega\text{-cm}$) water for the electronics industry (MF and RO) and production of clean boiler feedwater, potable water and clean waste water (RO and ED)
- Others: oil-water separation (UF and MF), recovery of paint and latices from waste water effluents (UF), hemodialysis, membrane electro dialysis and recovery of gases (GS)

The membranes used in the various membrane processes can be very different, both the material and the configuration (modules) offer several possibilities. A membrane can be made out of a polymeric or inorganic material. Well known polymer materials are polysulfone, cellulose-acetate, polycarbonate, polypropylene and polyacrylonitrile. A large variety of polymeric membranes are produced to optimize their permeability and separation characteristics. Inorganic membranes (usually MF-type) can be made from e.g. $\alpha\text{-Al}_2\text{O}_3$ or silica (SiO_2) eventually supplied with a less porous $\gamma\text{-Al}_2\text{O}_3$ top layer.

Membranes can be subdivided in symmetric and asymmetric membranes. Symmetric membranes can be dense, or can have straight or sponge-like pores. Polymeric asymmetric membranes, usually made by the phase-inversion method, consist of a thin dense skin layer (0.1-1 μm thickness, containing pores or not) on top of a much more porous sublayer. The thinness of the skin layer results in a low resis-

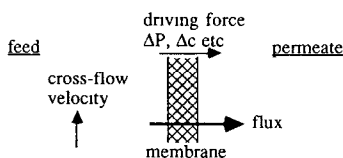


Fig 1 Schematic representation of a membrane process

tance for transport through the membrane. Another example of an asymmetric membrane is a composite membrane, which is usually made of a very permeable UF membrane into which a thin dense layer, often of another polymer type, is applied and which is chosen for its high selectivity.

Apart from the diffusion processes mentioned above, that determine the actual membrane separation, other important diffusion processes are related to membrane processes, viz diffusion in the boundary layer near the membrane (concentration polarization phenomena) and diffusion during membrane formation: the inflow and outflow of solvents and non-solvents during the phase inversion process determine the structure of the membrane to be formed.

The various diffusion processes that can occur during processes in which membranes are involved are summarized in Table 1.

The aim of this paper is to show the importance of diffusion related to membrane separation processes. A description of the different diffusion processes will be given in the paragraphs to come.

1. Diffusion in membranes

When describing transport in membranes various possible mechanisms can be distin-

guished in relation to membrane structure

- transport through bulk material (dense membranes),
- Knudsen diffusion, in narrow pores,
- viscous flow, in wide pores,
- surface diffusion, along pore walls

In practice, the overall transport can be the result of more than only one of these mechanisms, this is for example the case in an asymmetric membrane, as shown in Fig 2.

It is not possible to define fixed pore-dimensions coupled to the various transport mechanisms that occur. Apart from the case in which there are no pores at all (dense membranes in which sorption and diffusion of the permeants occurs), transport will be a combination of the various mechanisms mentioned. In general, the transport can be considered to be mainly of the Knudsen diffusion type when the pore radius r is smaller than 10^{-8} m (=10 nm) at ambient pressures, and it will be mainly viscous (Poiseuille) flow when r is larger than 10^{-5} m (=10 μ m). These values also depend on the applied pressure and temperature. In between these pore sizes the flow is a combination of Knudsen and Poiseuille flow [1].

1.1 Transport in dense membranes

In the literature usually one of the following three theories/models are used to describe the

TABLE 1

Survey of the various areas where diffusion occurs

1	In membranes	(a) in dense membranes (gas separation, pervaporation)
		(b) in porous membranes
		-gases
		-liquids
		-facilitated transport (liquid membranes)
		-solutes (controlled release)
		-electrodialysis
2	In the boundary layer near the membrane	
3	During membrane formation	

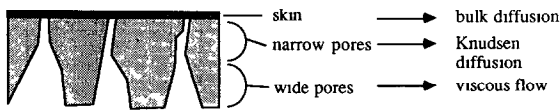


Fig 2 Transport in an asymmetric membrane can be the result of various mechanisms

transport in dense membranes [2,3]:

- I –thermodynamics of irreversible processes (TIP),
- II –preferential sorption capillary flow model (PSCF),
- III –solution–diffusion model (SD)

Since diffusion is the only possible transport mechanism in dense membranes a diffusion coefficient appears, directly or indirectly, in the three models mentioned above

- (TIP): diffusion coefficients are incorporated via the frictional coefficients,
- (PSCF) after (preferential) sorption, surface diffusion occurs at the walls of the ‘pores’,
- (SD): the transport in the membrane is determined by both the sorption and the diffusion of the permeants

1 1 1 Thermodynamics of irreversible processes

Since transport phenomena are due to non-equilibrium conditions and thermodynamics deal with equilibrium systems, the classical theory of thermodynamics is in principle less appropriate to describe transport processes. We assume firstly that simultaneously occurring processes can be clearly separated into non-interacting mechanisms of change in the system, and secondly that the steady state irreversible flows affect only each of the processes separately. At near equilibrium conditions of the irreversible processes, the thermodynamic treatment may be applied by dividing the system in

small subsystems in which a local equilibrium exists or is approached.

Equations for transport rates (fluxes), retention and other membrane related parameters can be derived using general thermodynamic equations. For example, the flux for each component, J_i , is described as [4]

$$J_i = \sum_{k=1}^n L_{ik} F_k$$

where the phenomenological coefficients, L_{ij} , are often complex functions of composition and concentration. The driving forces, F_i , which are chemical potential gradients, are given by

$$F_i = - \left(v_i \frac{dP}{dx} + \frac{d\mu_i^c}{dx} \right)$$

in which the first term indicates the gradient due to a pressure difference and the second term expresses the concentration related gradients. According to the friction model, the generalized force acting on solute i in the membrane is balanced by the frictional force between solute i and the membrane, and that between solute i and solute j

$$F_i = \sum f_{ij} (u_i - u_j) + f_{im} u_i$$

where u_i and u_j are the linear velocities of solute i and j in the membrane. In practice the friction coefficients, f_{im} , are always larger than the ‘free friction coefficients’, f_{ij} , which are related to diffusion coefficients by

$$f_{ij} = RT / (N_{av} D_{ij})$$

where D_{ij} is the ‘free’ diffusion coefficient, in a

binary solution f_{ij} can be described by, e.g. Stokes' relation:

$$f_{ij} = 6\pi\eta R_s$$

in which R_s is the Stokes' radius of the solute. Of course it is quite a problem to get quantitative values for the various friction coefficients, especially f_{im} values.

1.1.2 The preferential sorption capillary flow model [5,6]

If the pores in a dense membrane are small enough one should consider the transport phenomena taking place at the pore walls. Surface diffusion, or surface flow, can take place when the residence time of a molecule at the pore wall is larger than zero. Depending on the migration energy and the surface diffusivity a molecule can move along a pore wall. Because of differences in energies and diffusivities a certain selectivity in transport rate can be the result.

For component i the flux, N_{S_i} , due to surface diffusion can be described as:

$$N_{S_i} = -C' D_{S_i} (dC_{S_i}/dp) \nabla P$$

where C' is a geometrical parameter that depends on the pore system, and (dC_{S_i}/dp) can be determined from the adsorption isotherm. The surface diffusion coefficient D_{S_i} is a function of the temperature as is given by

$$D_{S_i} = D_{S_{0i}} \exp(-E/RT)$$

while $D_{S_{0i}}$ depends on the mean surface free-path length, the jump frequency and the surface concentration (especially at low surface concentrations). The activation energy for surface diffusion (migration energy) E is assumed to be a fraction of the differential heat of adsorption q .

$$E = q/m'$$

where $m' = 1, 2$ or 3 , which depends on the type of surface binding. Now it can be derived that

$$N_{S_i} = -C' D_{S_{0i}} \exp(-q/m' RT) (dC_{S_i}/dp) \nabla P$$

From experiments it appeared that the surface diffusion coefficients can be described very generally without taking the influence of the surface concentration into consideration as [6]:

$$D_{S_i} = 1.6 \times 10^{-6} \exp(-0.45q/m' RT)$$

Though the existence of pores seems to be contradictory to the tightness of dense membranes, this surface diffusion model can be used to describe transport in dense membranes: the intermolecular voids are considered to be the 'pores'. For the description of transport in RO membranes the situation is thought to be as described in Fig. 3 [7].

Furthermore, the surface diffusion approach can also be used in combination with other models. For instance, Jonsson et al. [8] described the flux as a result of a combination of diffusional surface flow and viscous flow through the 'pores' of a RO membrane.

1.1.3 The solution-diffusion model

This model, which in practice is most widely used for dense membranes, describes the transport by permeability = sorption \times diffusion [9]. This can be seen in the general expression for the flux J_i ,

$$J_i = -D_i c_i^m d(\mu_i^m/RT)/dx$$

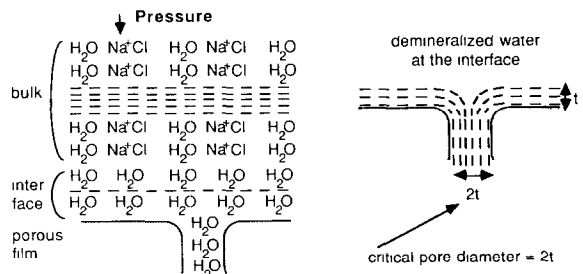


Fig. 3 Schematic representation of the preferential sorption capillary flow model. The dimension of the critical pore diameter is two times the thickness of the adsorbed water layer.

where the gradient in the chemical potential across the membrane $d(\mu_i^m)/dx$ is the driving force. The concentration c_i^m in the membrane can be calculated using, e.g., the Flory-Huggins equation

In the absence of strong interaction effects between the permeating components, the permeability constants P of the pure components can be used to describe the selectivity

$$\alpha_{A/B} = P_A/P_B = (S_A/S_B) \times (D_A/D_B)$$

where the preferential sorption is expressed by S_A/S_B and the ratio of the mobilities by D_A/D_B .

Both the sorption and the diffusion are dependent on the characteristics of the membrane material and the permeants. In the literature many examples can be found attempting to describe the permeation selectivity as a function of the sorption and/or the diffusion coefficient. Both in experimental and theoretical papers the solution-diffusion model has been used. For instance, Lee et al. [10] showed that, during pervaporation of organics from dilute aqueous solutions, the product of independently measured distribution (sorption ratio) and diffusion coefficients correlated reasonably well with the measured permeability coefficients.

On the other hand, also more basic theoretical descriptions have been given, as can be found below. For both sorption and diffusivity a number of (modified/improved) relations have been derived, this is quite understandable because of the many assumptions that had to be made to derive the most simple equations. In this survey only a limited number of relevant equations will be given.

(a) The *sorption* of the permeants in the polymer matrix can be described by, for instance, the Flory-Huggins equation because a swollen membrane may be considered to be a homogeneous liquid mixture of polymer and permeants: the partial molar free energy of

mixing of a solvent and a polymer is [2]

$$F_s^{\text{mix}} = RT[\ln \Phi_s + (1 - 1/m) \Phi_p + \chi \Phi_p^2]$$

where χ is the Huggins' parameter, m is the molar volume ratio of polymer and solvent, and Φ_p and Φ_s are the volume fractions of the polymer and the solvent, respectively, from which the concentration c_i^m can be calculated. Huggins' parameter χ depends on the solubility parameters of solvent and polymer, among other things.

In case of gas separation a different model is frequently used: the dual-mode sorption model. This model combines Henry's law with a Langmuir isotherm. The latter reflecting the sorption of a gas in voids that are assumed to exist in a glassy polymer membrane. For comparison, the solubilities of gases in rubbery polymers above the T_g often are described by Henry's law only. The resulting descriptions of the sorption equilibria are [11]

$$T > T_g \quad C = k_D p$$

$$T < T_g \quad C = k_D p + (C'_H b p) / (1 + b p)$$

where k_D is Henry's law solubility coefficient, C'_H is the Langmuir capacity constant and b is an affinity constant.

(b) The *diffusive transport* can be described by the (modified) Maxwell-Stefan (M-S) equation, whereas the (modified) Vigne equation can be used to calculate the necessary mixture diffusivities. The M-S equation

$$\frac{c_i \text{grad}(\mu_i)}{RT} = \sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_i N_j - x_j N_i}{D_{ij}}$$

uses the binary M-S diffusivities, D_{ij} , of i in a mixture of i and j , which are not equal to the Fickian diffusion coefficients (though in binary gases and dilute solutions they are about equal). It has been observed that these diffusivities vary considerably with composition and concentration, although much less than Fickian diffusion coefficients do. Therefore a mod-

ified M-S equation (MM-S) has been derived, no longer assuming a frictional force that is independent of concentration and composition [12]

$$\frac{c_i \text{grad}(\mu_i)}{RT} *D_{im} = \sum_{\substack{j=1 \\ j \neq i}}^n (x_j N_j - x_i N_i)$$

The MM-S equation uses the coefficients of self diffusion, $*D_{im}$, of a species i in a mixture. In all the equations mentioned above the membrane can be considered to be one of the components of the mixture. The self diffusion coefficients, $*D$, in a multicomponent mixture can be described by a Vigne equation, which read originally $\ln(D_i) = x_i \ln(\infty D_{ii}) + x_j \ln(\infty D_{ji})$, modified to

$$\ln(*D_{im}) = x_i \ln(*D_{ii}) + \sum_{\substack{j=1 \\ j \neq i}}^n x_j \ln(\infty D_{ij})$$

where ∞D_{ij} is the diffusivity of i in j at infinite dilution of i .

The crystallinity of a membrane can also have major consequences for the rate of diffusion in the membrane, and hence for the flux. The diffusion coefficient as a function of the crystallinity can be described as follows:

$$D_i = D_{i,0} \frac{\Psi_c^n}{B}$$

where Ψ_c is the fraction crystalline polymer, B is a constant and the exponent $n \leq (\ll) 1$. The effect can be a hundredfold increase in diffusion resistance, Fig 4 [12]

The influence of the molecular weight (hence size) of the components on the diffusion is shown in Fig 5. To emphasize the influence of the rubbery/glassy state of the polymer the diffusion in water, natural rubber (rubbery state) and polystyrene (glassy state) are given [13]. The drawn lines have been obtained from a large number of experimental data. The difference in value for the diffusion coefficient in

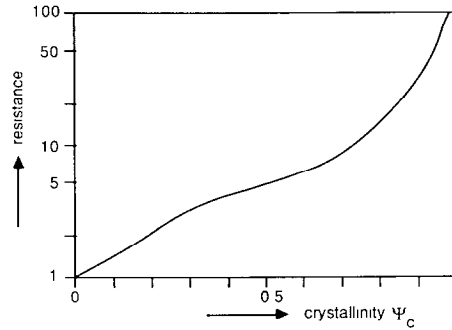


Fig 4 Possible effect of crystallinity on diffusion resistance. Taken from Ref [12]

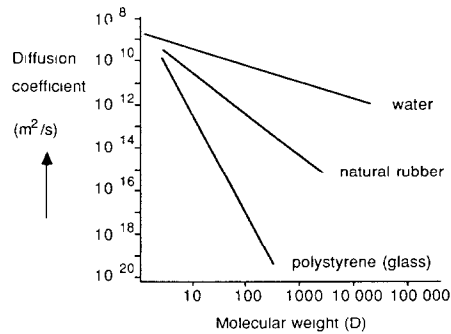


Fig 5 Diffusion coefficients, in water, in natural rubber and in glassy polystyrene, as a function of the molecular weight of the diffusing particle

these different media is shown to be several orders of magnitude for an average size molecule.

When selectively permeable materials are incorporated in a dense membrane, both the selectivity and the flux can be positively changed. Cussler [14] showed that in flake-filled membranes the selectivity and the relative flux can be greatly enhanced. An optimum ratio of the diffusion coefficient in the polymer and the diffusion coefficient in the flakes can be calculated using variable flake fractions in the membrane and variable flake-width/thickness ratios.

1.2. Transport in porous membranes

As stated in the introduction transport through bulk material (dense membranes), will

be different from the transport phenomena in more porous membranes. Knudsen diffusion in narrow pores and viscous flow in wide pores are more likely to occur in porous membranes. The various possibilities to consider are transport phenomena of gases, solutes and liquids, facilitated transport, solutes in controlled release and electrodialysis. These subjects will be described in the next paragraphs.

1.2.1 Knudsen diffusion in narrow pores

Knudsen diffusion occurs when the pore diameter is much smaller than the mean free path lengths, λ , of the (gas) molecules to be separated. λ is defined as:

$$\lambda = \frac{3\eta}{\rho_g} \sqrt{\frac{\pi M_A}{8RT}}$$

where the viscosity η and the density ρ are functions of T and ΔP . The flux due to Knudsen diffusion in straight pores can be described by

$$J_A = \frac{4r}{\sqrt{2\pi kT}} \frac{1}{\sqrt{M_A}} \frac{dP}{dx}$$

or by

$$J_A = \frac{2}{3} \pi n_k r^3 \frac{\Delta P}{\delta} \frac{\bar{v}_A}{RT}$$

\bar{v}_A is the average molecular velocity; it is normally represented by:

$$\bar{v}_A = \sqrt{(8RT/\pi M_A)}$$

From the first flux equation the selectivity α can be derived, as

$$\alpha_{A/B} = \sqrt{(M_B/M_A)}$$

The second equation shows the relation to diffusion. The Knudsen diffusion coefficient in a pore with diameter d_p , or radius r , can be calculated as

$$D_{KA} = \frac{1}{3} \bar{v}_A d_p \left(\frac{2-f}{f} \right)$$

(in which f is the fraction diffuse reflection which the pore wall); this is roughly equal to $\frac{2}{3} \bar{v}_A r$ when f equals about unity.

The importance of Knudsen diffusion relative to molecular diffusion, which is given by the number of collisions with the wall compared to the number of mutual collisions, can be described for hard spheres of pure component A as [15]:

$$\frac{D_{KA}}{D_{AA}} = \frac{d_p}{\lambda}$$

For example, for N_2 at a pressure of 0.1 MPa and pores of $d_p = 5$ nm, more than 90% of the collisions will be collisions with the wall and so Knudsen diffusion mainly determines the transport.

The importance of surface diffusion relative to Knudsen diffusion has been described in literature as well. Keizer et al. [1] found that the observed permeability of CO_2 was larger than could be calculated from the permeability of N_2 and ascribed the additional transport to surface diffusion (Fig. 6).

Uhlhorn et al. [16], using silica modified γ -alumina membranes, found much higher selectivities for condensable gases than Knudsen diffusion could account for. The modification of the γ -alumina membranes with silica con-

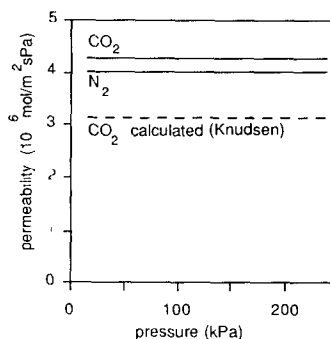


Fig. 6 The permeabilities of CO_2 and N_2 as a function of pressure for the separation (top-) layer of ceramic membranes [1]. The dashed line is the expected value for CO_2 if only Knudsen diffusion occurs.

sisted of a silica layer of approximately 30 nm thickness, with pores smaller than 1 nm, on top of the membrane and probably some filling of the pores with silica as well. From permeability experiments it could be concluded that transport of inert gases, e.g. helium and nitrogen, was determined by Knudsen diffusion only. However, for condensable gases the transport was greatly enhanced, the permeabilities were dependent on the applied pressure and surprisingly high permselectivities could be observed. These phenomena were attributed to surface diffusion.

In a further study a γ -alumina membrane was impregnated with magnesia, introducing more strong-base sites and fewer weak-base sites. This resulted in stronger bonding of CO_2 , at about equal amounts, and less surface diffusion (the surface diffusion accounts for approximately 30% of the CO_2 transport on unmodified γ -alumina membranes, see Fig. 6) [17].

1.2.2 Viscous flow in wide pores

The average velocity of a liquid medium in a pore is described by the Hagen-Poiseuille relation:

$$\langle v \rangle = \frac{\Delta P}{32\delta} \frac{d_p^2}{\eta}$$

from which the flux J can be calculated.

$$J = \frac{n_k A_{\text{pore}}}{A_{\text{membrane}}} \langle v \rangle = \epsilon \langle v \rangle = \text{constant} \times r^4$$

In this equation no molecule-related quantities are left, from which it can be easily concluded that Poiseuille flow will not result in any selectivity. Furthermore, it can be observed that now the flux is proportional to r^4 , which was r^3 for Knudsen flow. So in a matrix consisting of very small pores few large pores can have great impact on α .

The afore-mentioned transport of combined Knudsen and Poiseuille flow has been described by Schofield et al. [18]. They described

the flux in the Knudsen-Poiseuille transition range by

$$J = a (P/P_{\text{ref}})^g \Delta P$$

where a is the membrane constant and g is a measure of the extent of the Poiseuille flow. The parameter g increases with increasing molecular weight of the gas and with increasing membrane pore size.

Until now the examples on the performance of the membrane were mainly determined by the pore size of the membrane. Obviously, the nature of the membrane also determines the separation characteristics. An example is the description of a diffusion-reaction in a multi-membrane containing urease. The equilibrium reaction $\text{NH}_2\text{CONH}_2 + 2\text{H}_2\text{O} \leftrightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-}$ is strongly affected when one of the membranes in the cell is switched from a neutral cellulosic membrane to an anion-exchange membrane. The outward transport of the reaction products and so the conversion are greatly reduced because of the nature of the membrane [19].

1.2.3 Facilitated transport in liquid and fixed site carrier membranes

Liquid membranes (LM) were developed because of the relatively small transmembrane flux of polymer membranes. A liquid membrane is a fluid or quasi-fluid phase which separates two other phases that are immiscible with the liquid membrane. Various types of liquid membranes exist, e.g. bulk-, emulsion- and supported liquid membranes.

Because of the nature of the facilitated transport, in which a carrier is used for the selective transport of e.g. an ion, the transport in the liquid membrane is mainly determined by the diffusion of the carrier in the membrane phase. Transport of the ion can even take place against its own concentration gradient. This is possible because of the phenomenon of coupled transport, i.e. a different ion of equal charge is

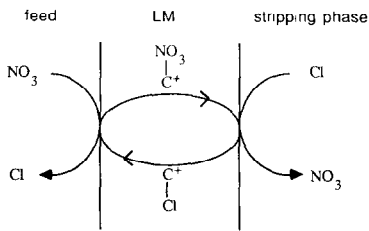


Fig 7 The (supported liquid membrane) separation with a countertransport mechanism for the removal of nitrate ions

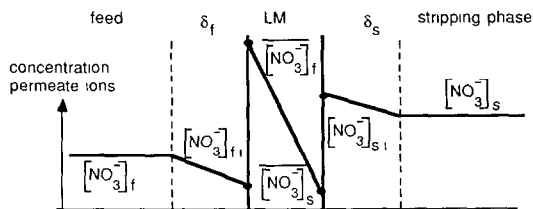


Fig 8 Ideal concentration profile for transport of permeating NO_3^- ions through a liquid membrane. NO_3^- stands for the carrier-ion complex

transported back. This ion can be provided with a large chemical potential gradient. Mostly cations are transported although also anion transport has been realized, e.g. the removal of nitrates from ground water [20] (Fig. 7). In this process the following steps of the permeate ion can be observed:

- diffusion of the ion to the membrane surface,
- chemical reaction (complexation) at the surface with a carrier molecule,
- diffusion of the carrier bounded ion through the LM-phase,
- chemical reaction at the surface with the stripping phase (decomplexation),
- diffusion of the ion to the bulk of the stripping phase

The expected concentration profile of the ion is shown in Fig. 8. In the most simple representation of the process the flux of the anion can be represented by Fick's law like $J = \Delta CD / \delta$ and so it will be a linear function of the diffusion coefficient of the complex in the LM. The dif-

fusion coefficient of the carrier-anion complex is usually calculated using the Stokes-Einstein equation. $D = kT / (6\pi\eta_0 r)$. Other diffusivities can play a role as well; e.g. the diffusion of the anion in the stagnant film at both sides of the membrane or the back-diffusion of the carrier. However, in case of nitrate removal the simple Fick's law can be applied.

Noble [21] developed a model for transport in fixed-site carrier membranes (the complexing agents are cast directly into the polymer films). This model yields a dual-mode sorption kind of description in the case of diffusion-limited transport. The diffusion in this case is determined by the diffusion coefficient of the solute-carrier complex. This implies that the transport is morphology dependent. Furthermore, it was shown that the change in mobility caused by changes in morphology may result in a percolation limit.

1.2.4 Solute transport in controlled release (CR) [22]

The release of a drug (e.g. the contraceptive steroid levonorgestrel) from a CR-membrane, which is usually a microporous hollow fibre membrane, can be described in two ways depending on the tightness of the skin.

(a) One way of release is described as a solution-diffusion mechanism, i.e. the steroid dissolves into the (dense) polymeric skin, diffuses through the polymer and finally partitions into the receiving fluid surrounding the hollow fibre. On the assumption that drug dissolution is not rate-limiting for such a mechanism two extreme conditions may exist. (1) the rate-controlling step is formed by diffusion of the steroid through the hollow fibre skin (membrane-controlled permeation process), or (11) by diffusion of the steroid from the hollow fibre into the receiving fluid (diffusion layer-limiting partition-controlled process).

In case (1) the transport is proportional to the diffusion coefficient of the steroid in the

polymeric skin D_{sp} , proportional to the concentration difference between the concentration in and outside of the fibre and inversely proportional to the thickness of the skin layer:

$$dM_t/dt = k_1 D_{sp} \Delta C / d_m$$

In case (11) (diffusion layer-limiting partition-controlled process) the transport is proportional to the diffusion coefficient D_{sr} and the solubility C_r in the receiving fluid, and inversely proportional to the thickness of the diffusion boundary layer d_h .

$$dM_t/dt = k_2 D_{sr} C_r / d_h$$

(b) When the asymmetric (hollow fibre) membrane contains a microporous skin a pore-diffusion mechanism can be imagined. The steroid release rate, into the liquid-filled pores, is then described as follows

$$dM_t/dt = k_2 D_{sr} (\epsilon/\tau) C_r / d_m$$

where d_m is the thickness of the microporous skin, and ϵ and τ are the porosity and the tortuosity of the membrane wall, respectively

1.2.5 Electrodialysis [23]

The separation of ions by electrically charged membranes under the influence of the driving force ΔE is schematically represented in Fig 9

The transport during electrodialysis is determined by two processes in which diffusion plays an important role

(a) the transport through the membranes that causes the actual separation of anions and cat-

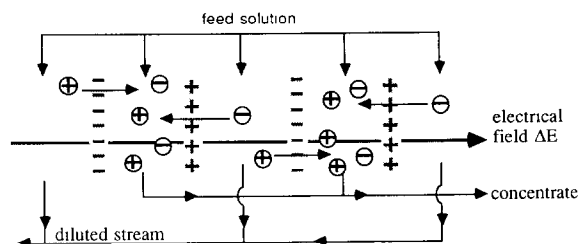


Fig 9 Schematic representation of the electrodialysis membrane separation process

ions. The diffusion involved is diffusion of ions in swollen polymers, and

(b) the transport through the inevitable concentration polarization boundary layer. In this case the diffusion is diffusion of an ion in the solvent

Usually concentration polarization phenomena influence the electrodialysis process to a large extent, which results in the observation that the transport is mainly determined by the diffusion process of the ions in the boundary layers near the membrane. For instance, Tanaka [24] has shown that ion-exchange electrodialysis of NaCl results in concentration polarization boundary layers on both the anion and the cation exchange membranes. Due to the diffusion coefficient of Cl^- ions being larger than the diffusion coefficient of the Na^+ ions, the concentration near the cation exchange membrane will rise considerably. As can be expected the concentration near the anion exchange membrane will drop compared to the bulk concentration. However, this is only the case when the convective flow rate towards the membrane stays below a critical value, if not, a concentration equal to the bulk concentration can be expected.

In practice, the concentration polarization problem can be reduced considerably by introducing the electrodialysis reversal mode in which the polarity of the electrodes is reversed periodically, typically every 15 min [25]

2. Diffusion in the boundary layer near the membrane (concentration polarization related phenomena) [26]

The description of concentration polarization phenomena during membrane separation processes can be generally divided into two groups (Fig 10).

-cake filtration, which is used for membrane processes that involve large particles, like in MF and sometimes UF, and

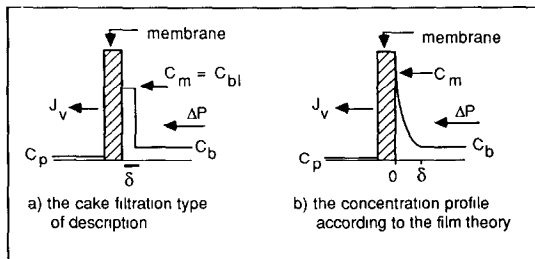


Fig 10 The concentration profiles due to concentration polarization phenomena according to the cake-filtration type of description (a) and the film theory (b)

-film theory description, which is used for all processes that separate liquids, ions and small particles. Examples are pervaporation (L-L), ED (ions), RO (small molecules) and often UF (macromolecules)

In most concentration polarization equations a flux expression like $J = k \times f(C_b, C_p, \dots)$ is used, e.g. the well known equation

$$J_v = k \ln \left\{ \frac{(C_m - C_p)}{(C_b - C_p)} \right\}$$

where k is the mass transfer coefficient, and $k = D/\delta$, in which δ is the thickness of the boundary layer. The diffusion coefficient of the solute in the solution that has to be used in this equation is usually taken to be independent of concentration. However, some researchers have shown that a concentration dependent diffusion coefficient can describe the process much better [27]. The effect of concentration polarization can be rather different for the various processes (see Table 2)

For ultrafiltration a number of different models have been described in literature, both for dead-end and for crossflow filtration. A model that appeared to be able to predict fluxes accurately during dead-end ultrafiltration of proteins is the Boundary Layer Resistance model [28,29]. Mainly using characteristics of the proteins, like sedimentation coefficient and specific volume, the flux behaviour could be calculated numerically. For instance, the concentration profiles after various periods of fil-

TABLE 2

The influence of concentration polarization on various membrane separation processes

Process	Influence of concentration polarization	Reason
Reverse osmosis	moderate	k large
Ultrafiltration	strong	k small
Microfiltration	strong	k small
Gas separation	(very) low	k very large/ J small
Pervaporation	low	k large/ J small
Dialysis	low	J small
Electrodialysis	strong	

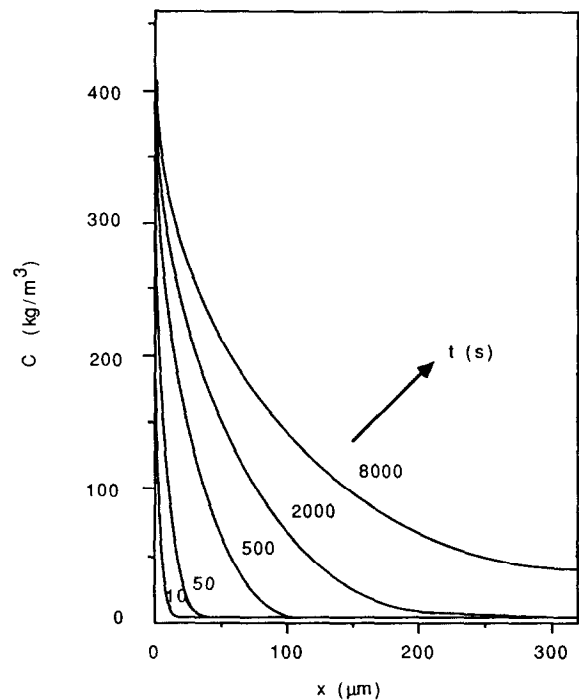


Fig 11 Simulated concentration profiles near the membrane interface for ultrafiltration of the protein BSA, as a function of time and distance from the membrane, using $D = 6.9 \times 10^{-11} \text{ m}^2/\text{sec}$

tration of a BSA solution are reproduced in Fig 11 [29]

The influence of the value of the diffusion coefficient on the build-up of the concentration profile was also calculated (Fig 12). The figure

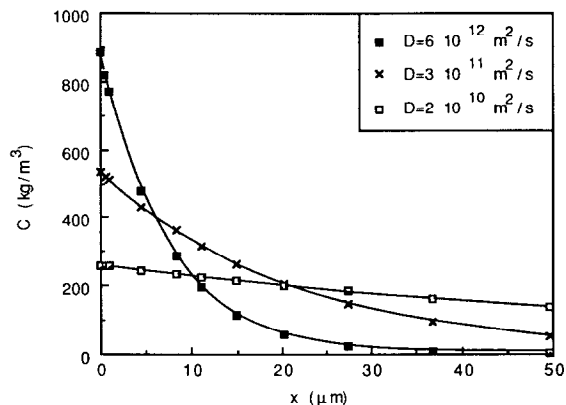


Fig 12 The calculated concentration profiles after 1000 sec ultrafiltration of BSA using various values of the diffusion coefficient

clearly shows the increasing concentration near the membrane with decreasing diffusion coefficient, this phenomenon will result in an increased resistance of the concentrated boundary layer near the membrane, while the separation characteristics are also affected strongly

3. Diffusion during membrane formation [30]

The most important preparation technique for polymeric membranes is the phase inversion method. This method results in various types of membranes by precipitation from a polymer solution using a non-solvent that diffuses into a film of polymer solution. Both symmetric and asymmetric membranes can be formed, with porous or dense top layers, depending on the membrane formation mechanism. Frequently used polymers are polysulfone, polyacrylonitrile, polypropylene, cellulose-acetate and polyamide.

The preparation technique is based on precipitation after immersing the polymer solution in a non-solvent bath, resulting in the name 'immersion precipitation'. Instead of immersing the polymer solution in pure non-solvent, a

mixture of solvent and non-solvent can also be used as the coagulation bath

The membrane formation mechanism by phase separation is determined by. (a) thermodynamic equilibria in the polymer/solvent/non-solvent system, and (b) the kinetic aspects during membrane formation, which are (b1) diffusion of solvent (out) and non-solvent (into the polymer film) and (b2) kinetics of the phase separation itself. Usually the phase behaviour of the three component system polymer/solvent/non-solvent is represented in a phase diagram. The changing composition during membrane formation will determine which type of membrane will be developed. Two possible composition paths (leading to either aggregate formation or L-L demixing) during coagulation determine the type of membrane that will be formed. These diffusion determined processes are represented in the phase diagram (Fig. 13).

The calculation of the composition profile is done using: (a) ternary diffusion equations, (b) the appropriate boundary conditions, and (c) concentration dependent diffusion coefficients. The fluxes of the various components are depicted in Fig 14

The ternary diffusion equations are for the polymer solution:

$$\partial(\phi_i/\phi_3)/\partial t = \partial/\partial t [v_i \phi_i \sum L_{ij} (\partial \mu_j / \partial m)]$$

$$(i = 1, 2, 3)$$

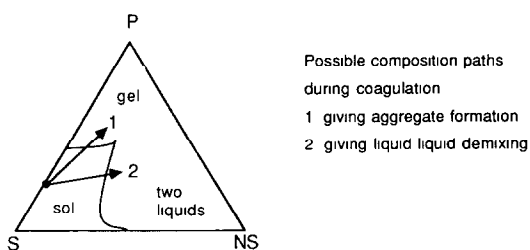


Fig 13 Phase diagram of the three component system solvent (S)/non-solvent (NS)/polymer (P) and the possible composition paths during coagulation

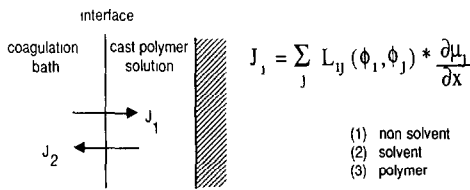


Fig 14 The situation during membrane formation

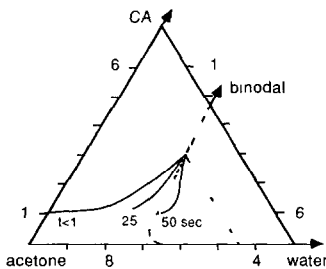


Fig 15 Approximated change of the composition path at different immersion times for a 10 vol % cellulose acetate (CA) solution immersed into a pure water bath

and in the coagulation bath

$$\partial \phi_i / \partial t = \partial / \partial t [D(\phi_i) \partial \phi_i / \partial x] \quad (i=1, 2)$$

The phenomenological coefficients L_{ij} can be obtained from solvent-non-solvent diffusion coefficients and the sedimentation coefficient of polymer in solvent.

Different experimental circumstances can be simulated also. In Fig 15 the influence of the time of immersion in the coagulation bath on the composition path is represented [30]. From the figure it will be clear that in this case a certain time is needed before liquid-liquid demixing will occur. During this delay-time a dense surface layer is formed by loss of solvent from the polymer solution, resulting in an asymmetric membrane structure. Consequently the kinetics of demixing determine the type of membrane that is formed.

4. Conclusions

Diffusion processes play an important role in membrane separation processes apart from the

diffusional transport processes in membranes, diffusion in the boundary layer near the membrane (concentration polarization phenomena) and diffusion during membrane formation are of high interest. The different diffusion processes are described by one of the numerous models.

Various mechanisms have been distinguished to describe the transport in membranes: transport through bulk material (dense membranes), Knudsen diffusion in narrow pores, viscous flow in wide pores, or surface diffusion along pore walls. In practice, the transport can be a result of more than only one of these mechanisms.

The characteristics of a membrane, e.g. its crystallinity or its charge, can also have major consequences for the rate of diffusion in the membrane, and hence for the flux obtained.

The effect of concentration polarization can be rather different for the various processes, which is mainly determined by the mass transfer coefficient, and thus by the diffusion coefficient.

The phase inversion membrane formation mechanism is determined to a large extent by the diffusion of solvent and of non-solvent.

List of symbols

a	membrane permeability constant (kg/m ² -sec-Pa)
A	surface area (m ²)
b	affinity constant (1/atm)
B	constant (-)
c_i	concentration of i (kg/m ³)
C	amount of sorbed gas per amount of polymer [m ³ (STP)/m ³]
C'	geometrical parameter (-)
C_b	concentration in the bulk (kg/m ³)
C'_H	Langmuir capacity constant (m ³ (STP)/m ³)
C_p	concentration in the permeate (kg/m ³)
C_r	solubility in receiving fluid (kg/m ³)

C_{S_i}	concentration of i at the surface (kg/m ³)	N_{S_i}	molar flux due to surface diffusion (mol/sec-m ²)
d_h	thickness of the diffusion boundary layer (m)	r	pore radius (m)
d_p	pore diameter (m)	p	relative pressure (Pa)
D_{ij}	diffusion coefficient of i in j (m ² /sec)	P	(hydraulic) pressure (Pa)
${}^\infty D_{ij}$	diffusivity of i in j at infinite dilution of i (m ² /sec)	P_A	permeability constant of the pure component A (m ³ /m ² -sec-Pa-m)
$*D_{im}$	coefficient of self diffusion of i in a mixture (m ² /sec)	P/P_{ref}	pressure within the membrane/reference pressure (-)
D_{S_i}	surface diffusion coefficient (m ² /sec)	q	differential heat of adsorption (J/mol)
D_{sp}	diffusion coefficient of steroid in the polymeric skin (m ² /sec)	R	gas constant (J/mol-K)
D_{sr}	diffusion coefficient of steroid in receiving liquid (m ² /sec)	R_s	Stokes' radius (-)
E	activation energy for surface diffusion (J/mol)	T	temperature (K)
ΔE	potential difference (V)	T_g	glass-rubber transition temperature (K)
f	fraction diffuse reflection at the pore wall (-)	u_i	velocity of i in a membrane (m/sec)
f_{ij}	friction coefficient (J-sec/m ²)	u_A	average molecular velocity (m/sec)
F_i	driving force (N)	v_i	partial specific volume (m ³ /kg)
F_i^{mix}	partial molar free energy of mixing (J/mol)	x_i	(molar) fraction (-)
g	exponent in Schofield's equation (-)	α	selectivity (-)
J_i	flux of component i (m/sec)	δ	thickness (m)
J_v	volume flux (m/sec)	ϵ	porosity (-)
k	mass transfer coefficient (m/sec)	η	viscosity (Pa-sec)
k_D	Henry's law solubility coefficient [m ³ (STP)/m ³ -atm]	μ_i	chemical potential, μ_i^c is concentration dependent part of μ_i (J/kg)
k_n	constant (m ²)	λ	mean free path length of (gas) molecules (m)
L_{ij}	phenomenological coefficient (kg-sec/m)	ρ	density (kg/m ³)
m	molar volume ratio of polymer and solvent (m)	τ	tortuosity (-)
m'	factor depending on type of binding (-)	ϕ_i	volume fraction of component i (-)
M_A	molecular weight (kg/kmol)	Φ_p	volume fraction of the polymer (-)
M_t	mass (kg)	Φ_s	volume fraction of the solvent (-)
n	exponent (-)	χ	Huggins' parameter (-)
n_k	number of pores (-)	Ψ_c	fraction crystalline polymer (-)
N_{av}	Avogadro's number (1/mol)		
N_i	molar flux (mol/sec-m ²)		

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