J. Membrane Biol. 27, 193–205 (1976)

Temporal and Local Concentration Changes in Diffusion Layers at Cellulose Membranes due to Concentration Differences between the Solutions on Both Sides of the Membrane

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Received 13 March 1975; revised 25 August 1975

Summary. By means of a laser-interferometrical method diffusion layers at the interface of a noncharged cellulose membrane are studied. These layers are induced by a concentration difference between the NaCl solutions separated by the membrane. The temporal and local shift of the NaCl concentration in the diffusion layers were measured. A steady-state concentration profile could be obtained for times of 121 sec$\leqq t_0 \leqq$484 sec. The concentration profiles at any time ($t_0 \leqq 900$) are not a linear function of the membrane surface, but could be fitted to a quadratic function. The thickness of the diffusion layers is also a function of time and its stationary value in this system is $(575 \pm 49) \times 10^{-6}$ m. The role of concentration polarization for the determination of phenomenological thermodynamic coefficients of membranes is discussed and a new method is suggested, which excludes the difficulties of the concentration polarization in the diffusion layers at the membrane.

Both in technical and biological membrane systems the phenomena of concentration polarization due to substance fluxes play a major role. Thus, in many papers it was concluded that under certain conditions, there are extensive diffusion layers at membranes, i.e., unstirred layers of increasing or decreasing concentration compared with the non-influenced interior of the solution (Dainty, 1963*a, b*; Barry & Hope, 1969*a, b*; Everitt & Haydon, 1969; Gitelson & Fish, 1969; Grigoryev & Ermishkin, 1970; Stehle & Higuchi, 1972; van Os & Slegers, 1973; Borisova, Ermishkin, Liberman, Silberstein & Trofimov, 1974).

By means of a laser-interferometrical method (Lerche & Wolf, 1974) current-induced diffusion layers could for the first time be proved directly in an optical way at cation-exchange membranes (Lerche & Wolf, 1971) as well as at biological epithelium layers (Lerche & Kott, 1973).

In the present paper we try to prove the existence of diffusion layers at a noncharged cellulose membrane by means of this method. The layers were induced by a NaCl-concentration difference between the solutions separated by the membrane. Moreover, the aim was to quantitatively prove the temporal and local change of substance concentration in this layer.

Theory

According to the papers of Bruner and Tolloczko (1900), Brunner (1904) and Nernst (1904) both in stirred and unstirred systems there exists a resting liquid film at a solid phase boundary. This film is also termed unstirred or convection-free layer. Following this idea, a system of an artificial membrane/electrolyte solution should have an unstirred layer as well[1]. All substances permeating the interface or chemically converted at the phase boundary, respectively, have to get through this convection-free layer by diffusion only (in case of ions, migration can also take part in the transport of substances). Under certain conditions, there are concentration changes during these transport processes in the unstirred layer. Such unstirred layers with a changing concentration compared with the interior of the solution is termed diffusion layer (Fig. 1). The distance between the membrane surface ($x=0$) and the point ($x=\delta$) of the diffusion layer where the concentration difference between this point and the noninfluenced electrolyte solution $[c(\delta)-c(+\infty)]$ is 1% of the concentration shift at the membrane surface $[c(0)-c(+\infty)]$ shall be defined as thickness δ of the diffusion layer (*see also* Dewhurst, 1960; Ibl, 1962). We will proceed only from the interface of membrane/solution II, since the analogous holds for the other side (Fig. 1).

If a concentration or a pressure difference between solutions I and II acts as driving force for the transport of substances through the membrane, then a diffusion layer is induced whenever the substance flux in the membrane resulting from the driving force exceeds the value of the diffusion flux in the convection-free layer. Assuming linear concentration courses, one gets as a condition for the shifting of concentrations on the side of solution II:

$$D_M \frac{c(-d)-c(0)}{d} + L_p\{\Delta p - RT\delta[c(-d)-c(+\infty)]\}\,\bar{c} > D_E \frac{c(0)-c(+\infty)}{\delta} \qquad (1)$$

where D_M and D_E are diffusion coefficients in the membrane and in the electrolyte solution, d is the thickness of the membrane, L_p is the hydraulic conductance, Δ_p is the (hydrostatic) pressure difference between the solutions, δ is the reflection coefficient, and $\bar{c}$ is the concentration in the membrane at the point $x=-0$. R and T have their usual meanings and the other symbols may be seen in Fig. 1.

In the steady state, the inequation (Eq. (1)) becomes an equation. If the first term of the sum in Eq. (1) is negligible, i.e., if the dissolved substance is completely excluded from the membrane, one will speak of a pressure- or osmosis-induced concentration polarization. This phenomenon should play a major role especially in technical reverse osmosis (Bressler, Wendt & Mason, 1971; Schlögl, 1971). It should be allowed for, however, also in the thermodynamic treatment of transport phenomena (Dainty, 1963*a*). If the first term of the sum in Eq. (1) plays the main role, it is termed a diffusion-induced concentration polarization. An example of this phenomenon is drug permeation through artificial lipid membranes (Lerche, Becker, Falk & Fürst, 1976). These polarization phenomena will play an important role whenever the coefficient of membrane permeability (P_M) is larger than that of the diffusion

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[1] Attention should be drawn to the fact that, in real systems, there is, of course, no clear-cut boundary between absolutely resting (unstirred) and well stirred liquid, because, due to finite viscosity in this layer, there is always also a finite gradient of streaming velocity (*cf.* Levich, 1952; Green & Otori, 1970).

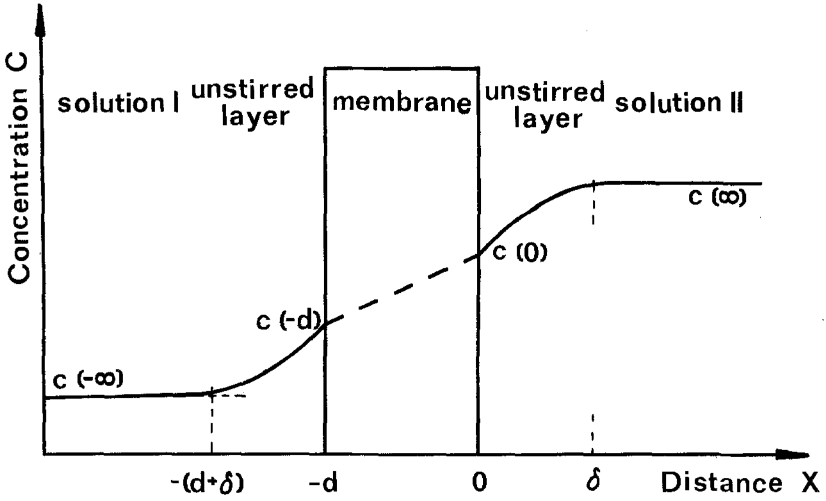

Fig. 1. Schematic course of concentration in the system of solution I/unstirred layer/membrane/unstirred layer/solution II. The concentration profile in the membrane depends on the membrane properties as well as on the type of substance transport and therefore has been entered only for the case of diffusion through a symmetric membrane (distribution coefficient $L=1$)

layer ($P_E = D_E/\delta$). As shown in Eq. (1), a negligible concentration polarization, however, cannot be inferred from the inequation $P_M < P_E$ as assumed by a number of authors (Dainty, 1963*a*; Liberman, Topaly, Silberstein & Oklobistin, 1971; Markin, Grigoryev & Ermishkin, 1971).

Experimental

In this paper diffusion layers in the system of NaCl solution I/cellulose membrane[2]/NaCl solution II were investigated by means of an interferometrical measuring method. The principle of this method (for detailed description *see* Lerche and Wolf, 1974) consists of bringing two coherent rays generated by a helium-neon laser to interference, after one of these rays has passed through the measuring cell tangential to the membrane surface. The formation of the diffusion layer is equivalent to a change of concentration and thus also of the refractive index of this layer compared with the noninfluenced electrolyte medium. The resulting shift of the interference bands (Fig. 2) in the diffusion layer represents a direct reflection of the concentration gradient perpendicular to the membrane surface. The concentration shift $\Delta c(x, t_0)$ can be calculated from the change of the refractive index (Δn) between the point of the diffusion layer to evaluated and the noninfluenced interior of the solution by means of Eq. (2):

$$\Delta c(x, t_0) = \frac{\Delta n(x, t_0)}{a} = \frac{f\lambda}{a l} \tag{2}$$

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[2] The cellulose membrane was produced following a procedure (Correns, Purz, Schwarz & Hagen, 1971) in a laboratory at the Institute for Polymer Chemistry in the Academy of Sciences of the GDR, by courtesy of Drs Purz and Schwarz, which is gratefully acknowledged.

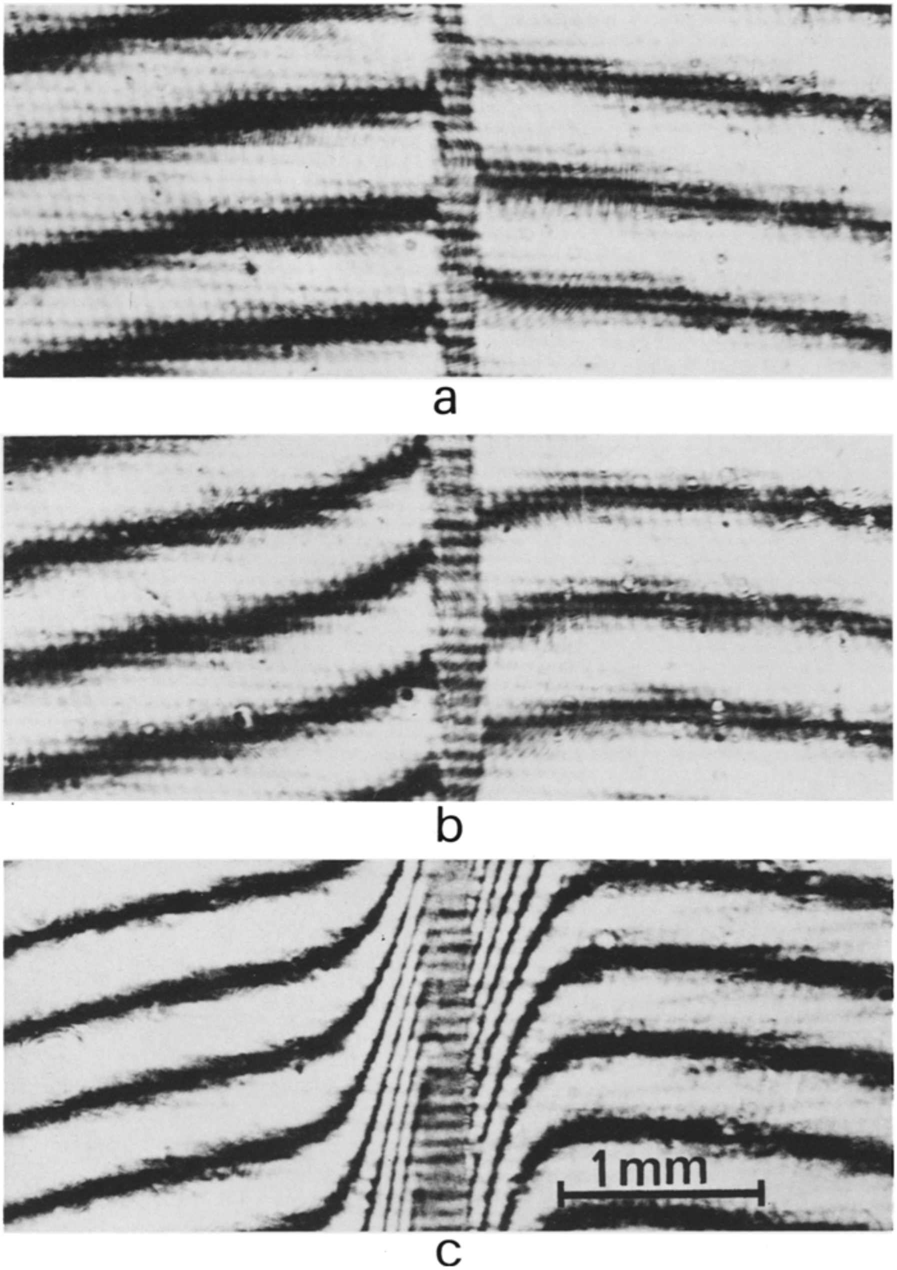

Fig. 2. Interference picture of the system of NaCl-solution ($100\,\mathrm{mol\,m^{-3}}$)/cellulose membrane/NaCl-solution. (*a*) Initial state of the system after the filling-in of the solution ($t=0$ sec); (*b*) Concentration of the NaCl-solution on the right side $135\,\mathrm{mol\,m^{-3}}$; duration of experiment 400 sec; (*c*) Concentration of the NaCl-solution on the right side $800\,\mathrm{mol\,m^{-3}}$; duration of experiment 121 sec. The nonhorizontal course of the interference lines outside of the diffusion layers is due to cuvette errors

where f is the quotient of band shift over band distance, a is the proportionality factor of refractive index and concentration, l is the depth of the cuvette and λ is the wavelength of helium-neon laser.

A glass cuvette (37.2 × 14.2 × 3.06 mm), halved vertically, served as measuring cell. The membrane ($d = (30-35) \times 10^{-6}$ m), which had been cut to fit the chamber cross-section, soaked in NaCl solution (100 mol m^{-3}) for about one hour before the experiment and used only once each, was vertically stretched in the measuring cell. The electrolyte solution was filled into both halves of the chamber at the same time. On side I NaCl concentrations of 100 mol m^{-3} and on side II of 140 mol m^{-3}, 200 mol m^{-3}, 500 mol m^{-3} and 800 mol m^{-3} were used. The cuvette was filled up to a height of 36.2 ($\pm$1) mm. Immediately after the filling ($t=0$) the initial state (Fig. 2*a*) was recorded photographically. The formation of the diffusion layer is continuously followed in the viewfinder of the camera within 900 sec and recorded at certain time intervals by photographs (Fig. 2*b*). The experimental temperature was 25.0 ($\pm$0.2) °C. The photographs of the type of Fig. 2*b* and *c* were quantitatively evaluated with a Schnellphotometer GII (VEB Carl Zeiss Jena, GDR). In each experiment, the shift of only one interference band was measured in discrete steps, proceeding from the membrane surface ($x=0$), at a height of 18 to 19 mm above the cuvette bottom.

By means of Eq. (2) the concentration shift was calculated for every point measured. The wavelength of the laser used was $6{,}328 \times 10^{-10}$ m, the cuvette depth was 3.06×10^{-3} m and the proportionality factor[3] between refractive index and concentration was 9.94×10^{-6} m^3 mol^{-1}. The experiments were repeated four times with various membrane pieces and the mean value and standard deviation were calculated for the concentration shifts determined according to Eq. (2) for the same points in the diffusion layer. Regression analyses, calculations of correlation as well as computer diagrams were performed with the Hewlett-Packard-Calculator 9810A (USA). Only concentration shifts of $\Delta c(x,t) >$ 0.2 mol m^{-3} were used.

Results

Phenomena of concentration polarization, i.e., the formation of diffusion layers which are directly detectable optically, could be observed at the cellulose membrane for NaCl concentration gradients from 1×10^6 mol m^{-4} to 2×10^7 mol m^{-4} (Fig. 2*b*, *c*). The amount of the concentration shift depends directly on the value of the concentration difference between the two solutions. The rate of the concentration change in the diffusion layer also strongly depends on the concentration gradient in the membrane. These qualitative data could also be observed in other systems (Lerche, 1974) and have been quantitatively confirmed in recent investigations (Lerche *et al.*, 1976).

A quantitative analysis of the interference pictures obtained was made on the dilution side of the system of NaCl solution (100 mol m^{-3})/cellulose membrane/NaCl solution (200 mol m^{-3}). The concentration course as a function of the membrane-surface distance x in the diffusion layer at the

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[3] This factor was taken from refractive-index measurements by Kruis (1936) for NaCl at various wavelengths and concentrations after linear interpolation on the wavelength and concentration (100 mol m^{-3}) used in this paper.

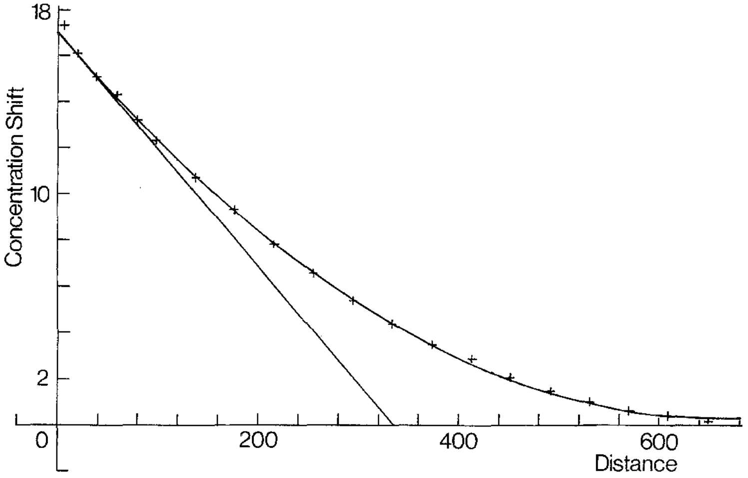

Fig. 3. Concentration shift in the diffusion layer on the side of dilution in the system of NaCl-solution (100 mol m^{-3})/cellulose membrane/NaCl-solution (200 mol m^{-3}) after 121 sec duration of experiment. The points entered correspond to the experimentally determined mean values of four individual measurements (maximum standard deviation ±2.3 mol m^{-3}). The line joining the measuring points is the compensatory curve fitted by means of parabolic regression (Eq. (3)). The Nernst diffusion-layer thickness δ' may be read off at the intersection of the straight prolongation of the concentration gradient at the membrane surface ($x=0$) and the abscissa. *Ordinate:* Concentration shift $|\Delta c(x)|$, (mol m^{-3}). *Abscissa:* Distance from membrane surface x, (10^{-6} m)

time (t_0) could be successfully fitted to a quadratic function (Eq. (3)) (see Fig. 3):

$$\Delta c(x, t_0) = a_2 x^2 + a_1 x + a_0 \qquad 0 \leqq x \leqq -\frac{a_1}{2a_2} \tag{3}$$

The a_0, a_1 and a_2 values determined for the various times t_0, the thickness δ of the diffusion layer, the number of measuring points evaluated and the measure of accuracy are listed in Table 1. Fig. 4 shows the concentration profiles after 25, 49, 121, 324, 676 and 900 sec. From Table 1 and Fig. 4 it may be clearly seen that a maximum concentration shift can be observed at the membrane surface (-17.2 mol m^{-3}) after 324 sec and a slight decrease of the concentration gradient in the diffusion layer begins if the experiment continues.

The time dependence of the amount of the concentration shift $\Delta c(x_0, t)$ at several selected points of support in the diffusion layer, i.e., at selected distance from the membrane surface in the direction of the x-coordinate, is represented in Fig. 5.

The formation of a steady state for times of 121 sec$\leqq t_0 \leqq$484 sec may be clearly seen both in Fig. 4 and Fig. 5. A compensating straight

Table 1. Parameters of osmosis-induced diffusion layers (100 mol m^{-3} : 200 mol m^{-3}) in dependence on the duration of experiment[a]

Parameters of diffusion layer (100 mol m^{-3} : 200 mol m^{-3})	Diffusion time (sec)									
	25	49	81	121	169	225	324	484	676	900
$-a_0$ (mol m^{-3})	7.7	10.6	14.1	16.3	16.8	17.0	17.2	17.0	15.7	14.6
$+10^{-4}\,a_1$ (mol m^{-4})	4.28	4.11	4.48	4.88	5.13	5.06	5.09	4.98	5.14	5.10
$-10^{-7}\,a_2$ (mol m^{-5})	6.30	4.09	3.67	3.80	3.99	3.83	3.76	3.65	4.32	4.54
R^2	0.9979	0.9991	0.9985	0.9987	0.9991	0.9997	0.9995	0.9997	0.9995	0.9991
n	13	17	19	18	18	20	19	18	19	18
$10^6\,\delta$ (m)	268	429	519	533	587	598	611	627	524	505

[a] The coefficients a_0, a_1, and a_2 were obtained after parabolic regression (Eq. (3)) of n-measuring points with the measure of accuracy R^2. δ corresponds to the experimentally determinable field of concentration shift.

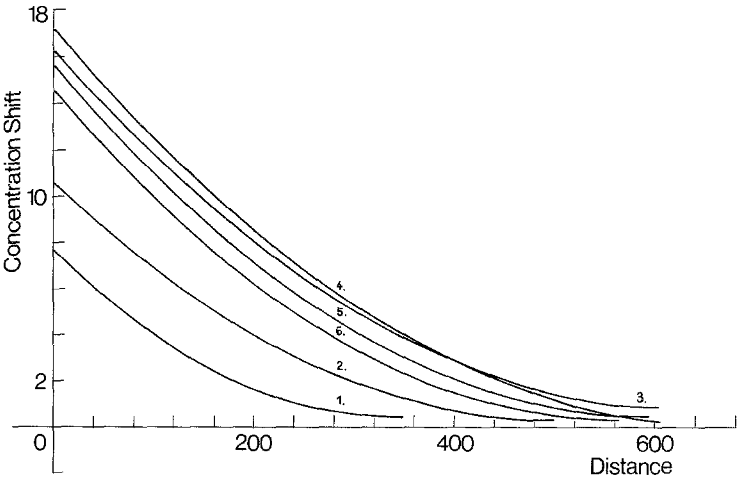

Fig. 4. Kinetics of the amount of concentration shift $|\Delta c(x, t_0)|$ on the side of dilution in the diffusion layer in the system of NaCl-solution (100 mol m^{-3})/cellulose membrane/NaCl-solution (200 mol m^{-3}), represented for several selected experimental times (curve *1* – 25 sec, *2* – 49 sec, *3* – 121 sec, *4* – 324 sec, *5* – 676 sec, *6* – 900 sec). The curves were entered with the regression coefficients a_0, a_1 and a_2 listed in Table 1 by means of the Hewlett-Packard Calculator in the range of $0 \leq x \leq \delta$. *Ordinate:* Amount of concentration shift $|\Delta c(x, t_0)|$, (mol m^{-3}). *Abscissa:* Distance from membrane surface x, (10^{-6} m)

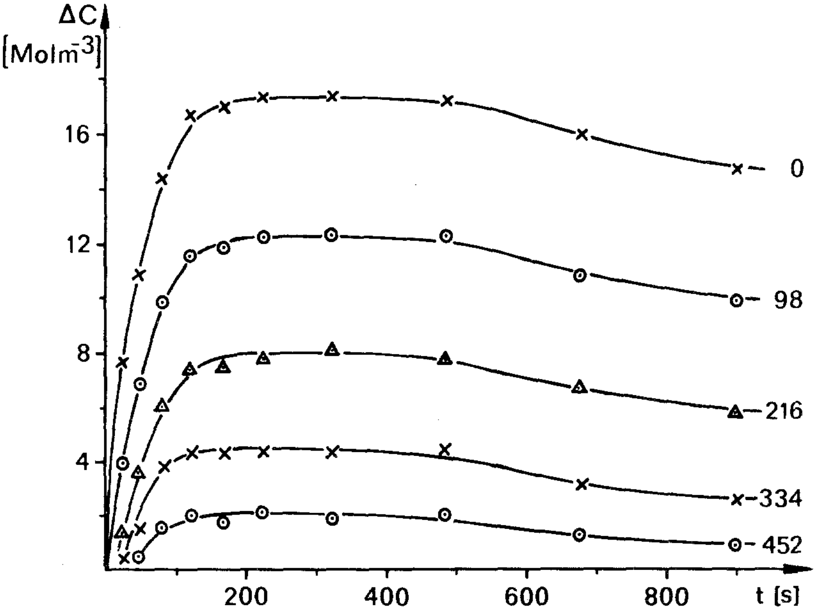

Fig. 5. Amount of concentration shift $|\Delta c(x_0, t)|$ on the side of dilution in the system of NaCl-solution (100 mol m^{-3})/cellulose membrane/NaCl-solution (200 mol m^{-3}) for several selected points in the diffusion layer in dependence on the duration of experiment. The numbers at the curves, multiplied by 10^{-6}, give the distance from the membrane surface in meters. The points entered are the mean values of four individual measurements (maximum standard deviation 1.1 mol m^{-3}). *Ordinate:* Amount of concentration shift $|\Delta c(x_0, t)|$, (mol m^{-3}). *Abscissa:* Duration of experiment t, (sec)

Table 2. Listing of the values[a] of concentration shift $c(x, t)$ in the diffusion layer at the cellulose membrane for the membrane-surface distances x in column 1 in steady state ($121\ \mathrm{sec} \leqq t_0 \leqq 484\ \mathrm{sec}$)

x (10^{-6} m)	$-A$ (mol m^{-3})	$-B$ (mol m^{-3} sec$^{-1/2}$)	$-\Delta\bar{c}(x,t) \mp s$ (mol m^{-3})
0	16.80	0.00112	17.1 ∓ 0.27
98	11.57	0.00188	12.1 ∓ 0.34
216	7.37	0.00129	7.7 ∓ 0.31
334	4.30	0.00021	4.4 ∓ 0.10
452	1.89	0.00021	1.9 ∓ 0.20

[a] Values are based on the results listed in Table 1. In columns 2 to 3, the regression constants of the straight line $\Delta c(x, t) = A + Bt$ are given for the above-mentioned time interval. The mean concentration shift $\Delta\bar{c}(x, t)$ with standard deviation s was listed in column 4 for the steady state.

line calculated at this time interval for the curves in Fig. 5 hardly shows any rise. The standard deviation of the mean concentration shifts for the corresponding x-values listed in Table 2 is also accordingly small.

For times of $t_0 \leqq 121$ sec, there is a direct proportionality between the concentration shift at the membrane surface $\Delta c(0, t)$ and the term $\sqrt{t}$. The straight line of regression calculated from the values in Table 1 shows a rise of $-1.5\ \mathrm{mol\ m^{-3}\ sec^{-1/2}}$ and intersects the ordinate at $0.5\ \mathrm{mol\ m^{-3}}$ ($R^2 = 0.996$; $n = 4$).

The time dependence of the thickness δ of the diffusion layer can be described for times of $t_0 \leqq 121$ sec by the following empiric relation:

$$\delta = 83 \times 10^{-6}\ \mathrm{m} + 44.2 \times 10^{-6}\ \mathrm{m\ sec^{-1/2}}\ \sqrt{t} \quad (R^2 = 0.937;\ n = 4). \tag{4a}$$

For longer experimental times, a quasi-stationary state develops for the thickness δ of the diffusion layer, which can be characterized by a straight line of regression with a slight negative rise:

$$\delta = 626 \times 10^{-6}\ \mathrm{m} - 1.00 \times 10^{-7}\ \mathrm{m\ sec^{-1}}\ t \quad (R^2 = 0.521;\ n = 6). \tag{4b}$$

The mean thickness δ of the diffusion layer for the quasi-stationary state ($169\ \mathrm{sec} \leqq t_0 \leqq 900\ \mathrm{sec}$) is $(575 \pm 49) \times 10^{-6}$ m.

Discussion

The results obtained clearly permit the conclusion that there is an extensive nonlinearity of the concentration profile in the diffusion layer at the cellulose membrane at the time interval investigated. By means of a quadratic approach (Eq. (3)), the experimental values can virtually be well fitted. Proceeding from a particular solution of the diffusion equation for the time t_0 (Lerche, 1974), the change of the membrane-surface concentration $c(0)-c(+\infty)=\Delta c(0,t)$ corresponds to the coefficient a_0. Moreover, the slope of the tangent of the concentration function $c(x,t_0)$ at the membrane surface at the time t_0 corresponds to the coefficient a_1. The nonlinearity of $\Delta c(x,t_0)$ is fitted by the term $a_2 x^2$ of the sum in Eq. (3). For small distances from the membrane surface, the influence of this term is slight and the concentration shift is largely determined by the linear term (cf. Fig. 3), as assumed by Nernst (1904) in his theory for the entire diffusion layer. A clear time dependence could be found for the concentration at the membrane surface $c(0)$. Interestingly the Sand equation (Vetter, 1961) derived for the galvanostatic transient in electrochemistry demands the same time behavior $(\Delta c \sim \sqrt{t})$. Therefore we may conclude that a constant volume flux permeates the membrane within the scope $(t_0 \leqq 121$ sec).

Eq. (3) allows to calculate the thickness δ of the diffusion layer (Table 1) as well as the intersection of the straight prolongation of the tangent of the function $\Delta c(x,t_0)$ at the point $x=0$ and the noninfluenced concentration of the solution (often termed Nernst diffusion-layer thickness δ'). Between both thicknesses, a relation δ'/δ of 0.59 ± 0.04 can be calculated. This relation agrees well with the calculation $(\delta'/\delta=0.57)$ by Ibl (1962) for vertical metal electrodes under the condition of natural convection. By means of natural convection, caused by the density gradients forming at the membrane, the decrease of the thickness of the diffusion layer as well as of the concentration difference in the diffusion layer with increasing time (Table 1) can be explained, too (*see also* Lerche, 1975).

From the investigations (Tables 1 and 2) it follows that the system is approximately in a steady state for experimental times of $121\text{ sec} \leqq t_0 \leqq 484$ sec. Values of the same order were observed by various authors for current-induced diffusion layers (Barry & Hope, 1969*b*; Lerche, 1974) and at osmosis-induced diffusion layers (Dainty, 1963*b*). Therefore the assumption of quickly adjusting steady state, as made for example by Gingras and Samson (1970), Miller (1972) or Sonin and Grossman (1972), should always be checked critically for the special system.

Phenomena of concentration polarization cause a shifting of the driving forces for substance transport across a membrane, as pointed out already by Dainty (1963*a*). As follows from Table 2, the concentration decrease in the membrane in our system amounts in the steady state (under these conditions the volume flux (J_v) and the diffusion flux (J_D) were measured) only to 65.8 mol m^{-3} (presupposing $|-\Delta c|=|+\Delta c|$) instead of 100 mol m^{-3}. If, in an isobaric system, the permeability coefficient is determined according to the diffusion flux, this coefficient will be underestimated by 34.2% under the conditions of concentration polarization mentioned above. Furthermore, from these investigations it follows that the amount of the concentration shift in the diffusion layer is sufficient only for small driving forces of a linear relation and approaches a limiting value with increasing concentration differences between the two solutions (Lerche, 1974; Lerche *et al.*, 1976). This nonlinear dependence of the "true" driving force (concentration difference between the membrane surfaces $c(0)-c(-d)$) on the concentration difference used between the solutions $c(+\infty)-c(-\infty)$ on both sides of the membrane could also be a reason for the concentration dependence of several thermodynamic coefficients partly observed in literature. Taking concentration polarization into account, the volume flux of the solution across the membrane should be calculated by Eq. (5) (*cf.* Dainty & House, 1966):

$$J_v = L_p \Delta p + L_{pD} RT[c(0) - c(-d)]. \tag{5}$$

In contrast to measurements of permeability at membranes where the diffusion layer also has to be assigned a fictitious permeability ($P_E = D/\delta$), in the case mentioned above only the "true" driving force is changed.

The concentration profiles determined interferometrically in steady state in principle allow to determine thermodynamic coefficients. From Eq. (1) a relation for the determination of hydraulic conductance or for ultrafilter coefficient can be derived.

$$L_p = \frac{L_{pD}}{\delta} = \frac{D_E}{\{\Delta p - \delta RT[c(0) - c(-d)]\}\,\bar{c}} \left(\frac{dc}{dx}\right)_{x=0} \tag{6}$$

The values $(c(0)-c(-d))$ and $(dc/dx)_{x=0}$ can be experimentally determined by means of a volume-flux-induced diffusion layer. To be sure, the determination of $\bar{c}$ presents difficulties. For $\delta \approx 0$ we obtain $\bar{c} = c(-d)$. If δ lies between $0<\delta<1$, a concentration between $c(-d)<\bar{c}<c(0)$ must be assumed. For the case $\delta \approx 1$ the $\bar{c}$ of Eq. (6) corresponds to the membrane-surface concentration $c(0)$. Under this condition Eq. (6) for $c(0)<0.5\,c(+\infty)$ and $dc/dx = \text{const}$ can be converted to an equation stated by Dainty (1963*b*) between the value of concentration polarization and a pure H_2O-flux across a membrane (Eq. 7):

$$c(+\infty) = c(0) \exp \frac{L_p\{\Delta p - \delta RT[c(0) - c(-d)]\}}{D_E} = c(0) \exp \frac{J_v \delta}{D_E}. \tag{7}$$

In the case of an isobaric system from a diffusion-induced layer, the diffusion or the permeability coefficient of the membrane can be determined for substances used according to the following equation (*cf.* Eq. 1):

$$P=\frac{D_M}{d}=\frac{D_E}{c(0)-c(-d)}\left(\frac{dc}{dx}\right)_{x=0}. \tag{8}$$

In the determination of P by Eq. (8), the influence of the unstirred layer as fictitious resistance (D_E/δ) as well as the change of the driving force due to polarization phenomena is excluded.

The author thanks Prof. Dr. R. Glaser and Dr. H. Wolf for inspiring discussions and for their active interest in these studies.

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