DIALYSIS EXPERIMENTS WITH ASYMMETRIC CELLULOSE ACETATE MEMBRANES

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Cellulose acetate membranes for ultrafiltration produced by phase inversion have an asymmetric structure in the cross-section. In spite of this asymmetry it is possible to characterize such membranes by dialysis. The asymmetry has no influence on the permeability for solute poly(oxyethylene). The membrane structure was varied systematically by annealing. The influence of solution concentration, dialysis time and temperature was also investigated. Statements are made on the annealing influence. A relationship between diffusion permeability and the true rejection is discussed.

Cellulose acetate membranes for ultrafiltration and reverse osmosis, which are produced according to a method developed by Manjikian[1], have a typical asymmetric structure in the cross-section. The active layer on the membrane surface, responsible for the separation properties flux and rejection, is very thin and is supported of an essentially thicker porous layer. Determinations of the active layer porosity yield average diameters from 2 to 5 nm for cellulose acetate ultrafiltration membranes[2] and from 1·3 to 1·5 nm for reverse osmosis membranes[2,3].

The asymmetric structure of phase-inversion membranes is an essential premise for their performance in the pressure-driven process. The properties of membranes can be varied not only by a change of the conditions of their production but also by a later modification. A thermal treatment, the so-called annealing, leads to a thickening of cellulose acetate membranes and these membranes become suitable for reverse osmosis.

In contrast with these asymmetric membranes, preferably used for ultrafiltration, there are membranes which are used for dialysis. They must show a symmetric cross-section structure. The driving force of dialysis is a concentration difference. The dissolved substances diffuse with different rate through the membrane according to the molecular size and they are transported from the higher to the lower concentrated compartment. But, in addition, the concentration of solutions can be changed, because the osmosis overlaps the dialysis.

The determination of diffusion permeability is important especially in connection with the development of membranes for haemodialysis. Substances such as urea and creatinine have been in the foreground of investigations since long ago and till the present time. Electrolytes, e.g. NaCl, and proteins, e.g. albumine and haemoglobine, have also been applied. The use of poly(oxyethylene) was also described for the characterization of dialysis properties[4,5]. Poly(oxyethylenes) (POE) are available in a wide molecular weight range ($\overline{M}_w$ from 250 to 20 000). They are therefore suitable as test substances for the membrane characterization. A change of the substance class is not necessary and interaction effects between membrane and permeand are nearly constant.

The aim of this work has been to find out whether the dialysis is also suitable as a characterization method for typical asymmetric cellulose acetate membranes for ultrafiltration. Suitable test conditions were to be worked out. The membranes were investigated previously in a pressure-driven process and were also characterized by electrochemical measurements[6,7]. An attempt was made to find correlations between membranes permeability and filtrate flux or rejection. The cellulose acetate membranes were modified by annealing, because of a better differentiation of membrane properties.

EXPERIMENTAL

The cellulose acetate membrane UF 40 from VEB ZZW Wittenberge (G.D.R.) was modified by thermal treatment at 50, 60, 70, 80, 85, and 90°C. The annealing was carried out 10 min in water.

Samples of poly(oxyethylene) (POE) with graduated molecular weight and NaCl were used for the permeability measurements. The dialysis experiments were carried out using the batch principle in a cell described by Schauer[8]. Molecular weights ($\overline{M}_w$) and molecular diameters (nm) of POE used: 275 (1·13 nm), 400 (1·31 nm), 1 420 (2·22 nm), 2 205 (2·92 nm), 4 655 (4·15 nm), 9 300 (5·52 nm). The dialysis cell contains two compartments separated by the membrane and equipped with a stirrer in each case. The concentration of the aqueous solutions was determined with a differential refractometer (Waters Model R4, U.S.A.). The diffusive permeability was measured at 25 ± 0·5°C.

RESULTS AND DISCUSSION

The dialysis results were computed according to a relation by Farrel[9], also used by Schauer[10]:

$$P = \frac{\ln(\Delta c_1/\Delta c_2)}{at(1/V_1 + 1/V_2)}, \qquad (1)$$

where P is permeability coefficient (cm s^{-1}), Δc_1 is measured concentration difference, Δc_2 is concentration difference between the compartments before (1) and after (2)

the dialysis experiment, a is membrane area (9·62 cm^2), V_1 and V_2 are volumes of cell compartments (55 ml), and t is time.

The reciprocal value of the membrane permeability is the membrane resistance ($1/P = W$). If the membrane resistance and the molecular weight of the test substance concerned are plotted in the double-logarithmic coordinates, a straight line results, whose parameters A_w and B_w can be easily determined by regression calculation[9]:

$$\ln W = A_w + B_w \ln M . \qquad (2)$$

Systematic Investigation of Dialysis

Before the characterization of the annealed membranes could take place, suitable test conditions had to be found. For this reason, different influences on the membrane permeability were investigated: membrane asymmetry, concentration of test solutions, time of dialysis, temperature of the test solutions.

At first, it was necessary to determine whether the asymmetry of membrane structure influences the diffusion permeability. The necessary dialysis experiments were carried out with a membrane annealed at 70°C. During the dialysis experiments in one case the active layer of membrane ((+)-orientation) and in the other case the supporting layer ((−)-orientation) were directed to the test solution compartment. The results in Table I show, that the asymmetric structure of the membrane cross-section has no influence on permeability. If the mean values of the parameters A and B of the linear regression are calculated (Table II), then variation coefficients that result are of about 3%. A significant influence on the membrane permeablity can not be proved. The membrane orientation in the dialyzer has obviously no effects on the measured permeability values.

The driving force of the dialysis process is a concentration difference. Higher concentrations lead to higher diffusion velocities. The concentration 5 g l^{-1} used was favourable for technical reasons. It was necessary to examine, however, how a concentration change influences permeability. The data in Table III demonstrate that the permeability coefficient is not influenced by concentration; in spite of varied driving force the permeability is constant. The values make possible an evaluation of the reproducibility of measurements on one membrane. The variation coefficient amounts to 2·5% for repeated permeability measurements.

The time needed for one experiment is decisive for the efficiency of a characterization method. Therefore, dialysis time was varied between 7·5 and 180 min in one experimental series with the membrane UF 40 annealed at 60°C. Each experiment was carried out with a new solution of POE 275 having concentration of 5 g l^{-1}. The permeability coefficient decreases in the period up to 45 min and the coefficient is approximately constant after that (Table IV). The variation coefficient of P yields 3·2% in the range 45 min to 180 min; the variation of the permeability coefficient

is not significant in this time range and 60 minute dialysis time leads to reliable and representative results.

The absolute mass of permeated POE is linear by dependent on the dialysis time (Table IV). The decrease in the solution compartment is described by the following correlation:

$$m = 7{\cdot}83 \,.\, 10^{-4} + 2{\cdot}48 \,.\, 10^{-4} t \,.$$

$$(k = 0{\cdot}9933)$$

Likewise, a time dependence is obtained if the solute flux, J_s, is calculated. At first the solute flux decreases rapidly, but it becomes quasi-constant after 60 min (Table IV). This analogy with the permeability coefficient results from the relationship of

TABLE I

Permeability coefficient in both membrane orientations (25°C, 60 min). Annealing temperature (T_a) of membranes M 1 and M 2 was 70°C

Test substance 5 g l^{-1}	$P \,.\, 10^5$, cm s^{-1}		
	(+)-orientation		(−)-orientation
	M 1	M 2	M 2
NaCl	—	20·73	20·56
POE 275	8·56	—	—
POE 400	6·52	6·13	6·35
POE 1420	—	2·72	2·45
POE 2205	2·09	—	1·82

TABLE II

Parameters A_w and B_w calculated from Eq. (*2*) for a membrane annealed at 70°C. Symbols: s average deviation, v_c variation coefficient, k correlation coefficient

X	M 1(+)	M 2(+)	M 2(−)	$\bar{X}$	$s(\bar{X})$	$v_c, (\bar{X}), \%$
A_w	5·59	5·91	5·73	5·74	0·16	2·9
B_w	0·67	0·63	0·67	0·66	0·02	3·5
k	0·9999	1·0000	0·9987	—	—	—

both quantities. In both cases a linearization of the time dependence is possible by a double-logarithmic plot of the data.

The influence of temperature on the membrane permeability was investigated in the range from 20 to 30°C. The permeability coefficient increases with increasing temperature. A linear correlation exists between permeability and temperature. The temperature dependence of the permeability coefficient was calculated for both molecular

TABLE III

Influence of concentration (c) on the permeability coefficient (25°C, 60 min) of membrane ($T_a = 60$°C)

c, g l^{-1}	$P \cdot 10^5$, cm s^{-1}	c, g l^{-1}	$P \cdot 10^5$, cm s^{-1}
POE 275[a]		POE 1 420	
2·5	8·98	2·5	2·85
5·0	9·65, 9·15, 9·60	5·0	2·75
7·5	9·25	7·5	2·65

[a] For c 5·0 g l^{-1}, $\bar{P} = (9{\cdot}5 \pm 0{\cdot}25) \cdot 10^{-5}$ cm s^{-1}; for c 2·5 to 7·5 g l^{-1}, $\bar{P} = (9{\cdot}35 \pm 0{\cdot}27) \cdot 10^{-5}$ cm s^{-1}.

TABLE IV

Influence of the dialysis time (t) on the permeability coefficient (25°C) of membrane ($T_a = 60$°C). Solute: POE 275, $c = 5$ g l^{-1}. Symbols: m mass decrease of POE in the solution compartment, J_s solute flux

t min	$P \cdot 10^5$ cm s^{-1}	m g	$J_s \cdot 10^5$ g cm^{-2} min^{-1}
7·5	12·4	0·003	4·2
15	11·3	0·005	3·5
30	10·6	0·009	3·1
45	9·6	0·013	3·0
45	9·7	0·013	3·0
60	9·65	0·015	2·6
60	9·2	0·016	2·8
60	9·6	0·017	2·95
90	9·1	0·022	2·5
120	9·3	0·031	2·7
180	8·9	0·043	2·5

weights (an index at P denotes the molecular weight of POE):

$$P_{275} = 1{\cdot}925 \,.\, 10^{-5} + 2{\cdot}95 \,.\, 10^{-6}T,$$
$$(k = 0{\cdot}9113)$$
$$P_{1\,420} = -4{\cdot}3 \,.\, 10^{-6} + 1{\cdot}3 \,.\, 10^{-6}T.$$
$$(k = 0{\cdot}9912)$$

All dialysis experiments for the membrane characterization at constant temperature were carried out at 25°C. An accepted temperature variation of ± 1 K results in a deviation of the permeability coefficient from 3 to 4%. It has the same order of magnitude as the deviation of values obtained by repeated measurements. The *W–M* relations were calculated for 20 and 25°C:

$$\ln W_{20} = 5{\cdot}12 + 0{\cdot}77 \ln \overline{M}_w,$$
$$\ln W_{25} = 5{\cdot}08 + 0{\cdot}74 \ln \overline{M}_w.$$

Only small differences exist between the coefficients of linear regression.

The following conclusions are drawn from the systematic experiments: (i) The membrane orientation does not influence the permeability under experimental conditions used. (ii) A significant influence on the membrane permeability was not observed in the concentration range from 2·5 to 7·5 g l^{-1}. Small variations in the concentration of test substances are without effect on the result of dialysis. (iii) One hour dialysis time is sufficient. (iv) Larger variations respectively deviations of temperature from the set point influence the experimental results; The temperature must be constant.

Permeability of Differently Annealed Membranes

From characterization experiments in the pressure-driven process ultrafiltration it is known that the membrane is thickened by annealing. From this fact we have that the water flux decreases significantly while the rejection for solutes increases. In Table V the structure characterizing parameters of the differently annealed membranes are listed[6]. In the pressure-driven process all characterization parameters change significantly in depenence on the annealing temperature.

The results of dialysis experiments with the different annealed membranes are summarized in Table VI. An annealing effect on the membrane's permeability behaviour is observed first with temperatures starting from 70°C. For each membrane the correlation (*2*) was calculated (Table VII)) with the data listed in Table VI, on the one hand including NaCl permeability and on the other, for poly(oxyethylenes) only.

The permeabilities for two molecular weights ($\overline{M}_w$ = 1 000 and 4 000) were calculated with the A_w- and B_w-data from Table VII. These values are listed in Table VIII. Such calculated permeabilities are the starting point for further discussion.

The change of the membrane permeability is not linear in dependence on the annealing temperature. The plot of P and T in the double-logarithmic coordinates shows a discontinuous alternation. This graph is in a good agreement with the graph of specific number of pores vs annealing temperature (Fig. 1; data from Table V). From this a quasi-linear correlation follows between permeability and the specific number of pores in the membrane surface, also proved in Fig. 2.

TABLE V

Water flux, (J_w, at 0·3 MPa), average pore diameter ($\bar{d}_0$), specific number of pores (n), and surface porosity (ε) of annealed membranes (from ultrafiltration experiments)

T_a °C	J_w l h^{-1} m^{-2}	$\bar{d}_0$ nm	$n \cdot 10^{-9}$ cm^{-2}	$\varepsilon \cdot 10^4$
20[a]	42·9	2·2	9·2	3·48
50	26·8	1·8	9·8	2·61
60	21·4	1·7	9·9	2·25
70	16·1	1·6	8·9	1·79
80	10·7	1·5	7·8	1·31

[a] Unannealed.

TABLE VI

Membrane permeability coefficients, $P \cdot 10^5$ (cm s^{-1}), of different annealed membranes (25°C)

Substance	Annealing temperature, °C						
	20[a]	50	60	70	80	85	90
NaCl	22·8	23·2	23·0	20·7	17·6	11·0	8·0
POE 275	9·2	10·0	9·5	8·6	6·35	4·0	1·3
POE 400	6·9	7·4	6·9	6·3	4·55	3·8	—
POE 1420	3·3	3·4	2·75	2·7	1·5	—	—
POE 2205	2·4	2·9	2·25	2·1	—	—	—
POE 4655	1·0	1·2	—	—	—	—	—

[a] Unannealed.

The surface porosity, ε, is correlated with the size of membrane pores, $\bar{r}$, and the specific number of pores, n:

$$\varepsilon = n \,.\, \pi \bar{r}^2 \,. \tag{3}$$

Between the surface porosity defined in this way and the permeability measured in dialysis experiment there exists the following correlation:

$$P = A_p + B_p/\varepsilon \,. \tag{4}$$

TABLE VII

Parameters of the correlation (*2*) for membranes annealed at different temperatures (T_a)

T_a °C	POE + NaCl			POE		
	A_w	B_w	k	A_w	B_w	k
20[a]	5·63	0·665	0·9940	5·17	0·727	0·9892
50	5·63	0·650	0·9903	5·23	0·704	0·9862
60	5·59	0·664	0·9964	5·30	0·709	0·9977
70	5·84	0·639	0·9986	5·64	0·670	0·9986
80	5·55	0·751	0·9930	4·75	0·876	0·9877
85	6·78	0·579	0·9901	—	—	—
90	4·69	1·168	—	—	—	—

[a] Unannealed.

TABLE VIII

Permeability coefficients of membranes (different annealing temperature, T_a), for molecular weights ($\overline{M}_w$) 1 000 and 4 000; calculation with the parameters from Table VII (POE considered only) using Eq. (*2*)

T_a °C	$P_{1000} \cdot 10^5$ cm s^{-1}	$P_{4000} \cdot 10^5$ cm s^{-1}
20[a]	4·09	1·77
50	4·14	1·56
60	3·73	1·39
70	3·47	1·37
80	2·09	0·6

[a] Unannealed.

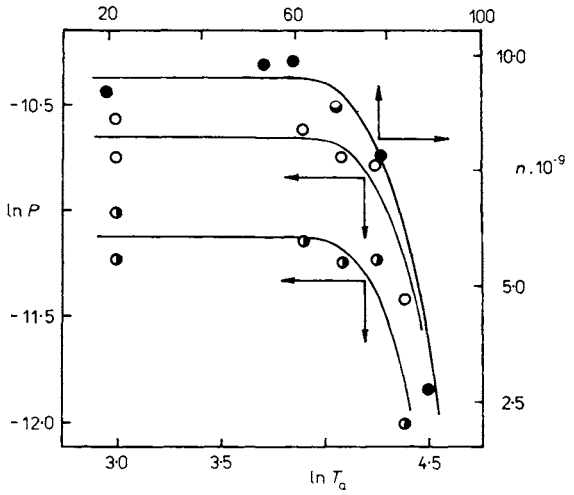

FIG. 1

Correlation between permeability coefficient, P, or specific number of pores, n (cm^{-2}), and annealing temperature, T_a, respectively, of cellulose acetate membranes UF 40. Molecular weight, $\overline{M}_w$, of solutes: ○ 2 000, ◑ 4 000

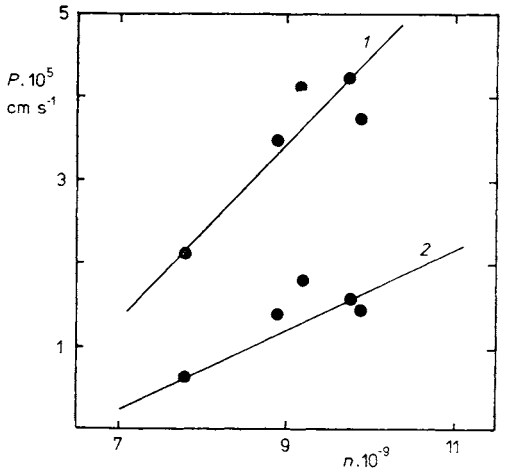

FIG. 2

Relationship between the permeability coefficient, P ($cm\,s^{-1}$), and specific number of pores, n (cm^{-2}) for two molecular weights ($\overline{M}_w$) of POE: *1* 1 000, *2* 4 000

Parameters A_p and B_p were calculated for two molecular weights of POE:

$\overline{M}_w$	A_p	B_p	k
1 000	$5{\cdot}635 \cdot 10^{-5}$	$-4{\cdot}372 \cdot 10^{-9}$	0·9567
4 000	$2{\cdot}477 \cdot 10^{-5}$	$-2{\cdot}337 \cdot 10^{-9}$	0·9662

Thus, the diffusion of solutes is significantly influenced by an interaction between pore dimension and pore number on the membrane surface.

A relatively simple relationship can also be proved between the water flux of membrane in the pressure-driven process (Table V) and the permeability coefficients of solutes (Table VIII). A linear correlation exists by analogy with the surface poro-

TABLE IX

Distribution parameters of the separation curves of membranes ($p = 0$) for different annealing temperature (T_a)

T_a °C	μ_M^0	σ_M^0
20[a]	3·15	0·36
50	2·99	0·59
60	2·87	0·62
70	2·81	0·72

[a] Unannealed.

TABLE X

Parameters of the correlation $u(\log M) = A_e + B_e \log P$; T_a annealing temperature of a membrane

T_a °C	A_e	B_e	k
20[a]	−20·627	−4·605	1·0000
50	−10·536	−2·407	1·0000
60	−9·855	−2·273	1·0000
70	−8·971	−2·071	0·9999

[a] Unannealed.

sity between P and the reciprocal value of the water flux:

$$P = A_f + B_f \, 1/J_w \,. \tag{5}$$

$\overline{M}_w$	A_f	B_f	k
1 000	$5{\cdot}075 \,.\, 10^{-5}$	$-2{\cdot}989 \,.\, 10^{-4}$	0·9604
4 000	$2{\cdot}179 \,.\, 10^{-5}$	$-1{\cdot}6 \,.\, 10^{-4}$	0·9712

The examples demonstrate that the unambiguous quantitative relationships exist between structure and permeability properties of membranes.

Relationship Between Diffusion Permeability and True Rejection

Dialysis experiments, which basically are carried out under pressure-free conditions, give permeability coefficients depending on the molecular weight of the disolved components. The permeability coefficients can be calculated for any molecular weight with the parameters given in Table VII and on using Eq. (*2*).

On the other hand separation curves are obtained in ultrafiltration experiments. The basis of this separation curves are the true rejection, R, and also the molecular

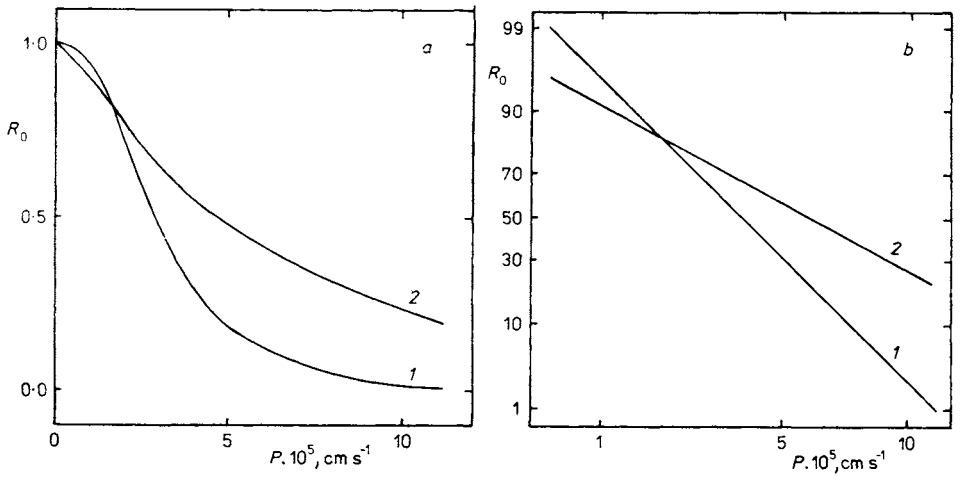

FIG. 3

Relationship between the true membrane rejection, R_0, from ultrafiltration test and the diffusion permeability coefficient, P (cm s^{-1}), from dialysis experiment for membranes: UF 40, unannealed (*1* 20°C) and annealed (*2* T_a = 70°C): *a* normal plot, *b* log-probability paper

weight of the solutes. The true rejection results from the relation between the filtrate concentration and the concentration at the membrane surface. In ultrafiltration experiments the true rejection can be determined only by extrapolation[11]. From the pressure dependence of the separation curves the distribution parameters, μ_M^0 and σ_M^0, describing the pressure-free state of these curves, can be obtained by extrapolation on $p = 0$ (refs[2,12]). The distribution parameters are summarized in Table IX.

By inversion of the separation curve calculation, the true rejection can be determined from μ and σ for any molecular weight:

$$\mu = -A_d/B_d \quad \text{and} \quad \sigma = 1/B_d\,, \tag{6a, b}$$

$$u(\log M) = A_d + B_d \log M\,, \tag{7}$$

where u is the inverse function of normal distribution, $R(\log M)$ (ref.[12]). A plot of the true rejection as a function of diffusion permeability yields curves which can be linearized ideally in the log-probability paper. The R-values must be transformed according to $u(M^*) = \mathrm{F}^{-1}(R)$ with $M^* = \log M$ before carrying out the linear regression. Both graphic variants are shown in Fig. 3. The abscissa in the probability paper is divided logarithmically and the ordinate is divided according to the Gaussian integral. The parameters of the straight lines in the probability paper are listed in Table X. Both parameters change systematically in dependence on the annealing temperature of modified membranes. Very good correlations can be established for the annealing temperature:

$$A_e = -4{\cdot}237 - 327{\cdot}1\,.\,(1/T_a)\,,$$

$$(k = 0{\cdot}9995)$$

$$B_e = 1{\cdot}046 - 71{\cdot}02\,.\,(1/T_a)\,.$$

$$(k = 0{\cdot}9994)$$

Correlations between the true rejection and the diffusion permeability are especially remarkable, because here a combination is used of fictive membrane data with data actually measured in an experiment. The true rejection of a membrane for $p = 0$ is accessible only by extrapolation and is a purely theoretical value. But the permeability is obtained directly in the dialysis experiment.

Further investigations should show whether quantitative information on membrane porosity can be obtained by measurements of diffusion permeability only.

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