EFFECT OF THE STRUCTURE OF CELLULOSE ACETATE MEMBRANES ON THEIR PERMEABILITY, ELECTRICAL CONDUCTIVITY AND REJECTION

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Ultrafiltration cellulose acetate membrane can be transformed by annealing into reverse osmosis membranes (RO type). Annealing brings about changes in structural properties of the membranes, accompanied by changes in their permeability behaviour and electrical properties. Correlations between structure parameters and electrochemical properties are shown for the temperature range 20—90°C. Relations have been derived which explain the role played by the dc electrical conductivity in the characterization of rejection ability of the membranes in the reverse osmosis, i.e. $r_{RO} = (1 + \exp(A - B))^{-1}$, where $\exp A$ and $\exp B$ are statistically significant correlation functions of electrical conductivity and salt permeation, or of electrical conductivity and water flux through the membrane, respectively.

Changes in the properties of asymmetrical membranes made from cellulose acetate due to annealing have been reported[1-4]. At higher annealing temperatures the membrane becomes more compact, and its permeability to salt and water decreases. The results of investigation of ultrafiltration were used to derive quantitative relations between the annealing temperature and structure parameters[1]. Dialysis experiments brought evidence about changes in the diffusion permeability to dissolved compounds, i.e. NaCl and poly(oxyethylene)[2]. Measurements of the electrical properties of the membranes, i.e. of the concentration potential and the dc resistance or conductivity also demonstrated a distinct dependence on the annealing temperature[3,4]. In this study, earlier measurements have been completed and the results have been interpreted in order to elucidate the role of electrical conductivity in the evaluation of the rejection ability of asymmetrical membranes.

EXPERIMENTAL

Cellulose acetate membranes, type UF 40 (ZZW Wittenberge, G.D.R.), were annealed at 50 to 90°C as reported earlier[1-4]. The number and the mean pore diameter and the surface porosity were determined by the method of separation curves using ultrafiltration data[1]. Water flux

through the membranes was measured at 0·3 MPa. Permeability of the membrane was measured with NaCl (5 g l^{-1}) and calculated according to Farrel and Babb[5]. The electrical resistance (conductivity) was measured by direct current (dc) in a 0·1M-KCl solution using the source of constant stabilized current and a four-electrode arrangement[4].

RESULTS AND DISCUSSION

Structure parameters (characterization of porosity), permeability and electrochemical properties of the starting cellulose acetate ultrafiltration membrane and of the corresponding membranes after annealing are summarized in Table I. The effect of membrane thickness is implicitly included in its permeability and areal electrical conductivity, so that these properties are related to the membranes themselves and not to the material from which they are made. This is advantageous just for asymmetrical membranes in which such properties form a gradient, and it cannot be decided, therefore, what part of membrane thickness is the decisive one.

The pore number, n, and the membrane permeability to NaCl, P, vary similarly with the annealing temperature, and a very good linear correlation was found for the relation between both parameters:

$$P = 9·74 . 10^{-3} \ln n - 0·21591 \quad (r = 0·986) . \tag{1}$$

With increasing annealing temperature the mean pore diameter, $\bar{d}_0$, decreases within the whole temperature range, while the permeability of NaCl decreases only

TABLE I
Properties of annealed (10 min) asymmetrical cellulose acetate membranes. Symbols: T annealing temperature, n number of pores per cm^2, $\bar{d}_0$ mean pore diameter, ε surface porosity, P permeability of membrane to NaCl in dialysis, J_w water flux intensity at 0·3 MPa, L_A areal electrical conductivity of the membrane, R_A areal electrical resistance of the membrane

T °C	$n . 10^{-9}$ cm^{-2}	$\bar{d}_0$ nm	$\varepsilon . 10^4$	P J_w 10^{-3} m h^{-1}		R_A Ω cm^2	L_A mS cm^{-2}
20[a]	9·2	2·2	3·48	8·208	42·9	3·11	321·5
50	10·5	1·8	2·66	8·352	26·8	3·58	279·4
60	9·9	1·7	2·25	8·280	21·4	3·42	292·4
70	8·9	1·6	1·80	7·452	16·1	4·01	249·4
80	8·0	1·5	1·32	6·336	10·7	7·19	139·1
85	6·6	1·4	1·02	3·960	8·0	12·87	77·7
90	5·6	1·3	0·74	2·880	5·4	28·31	35·3

[a] Starting (unannealed) membrane.

at temperatures above 60°C. An analogy can be seen in a comparison between the surface porosity, ε, and permeation of NaCl (Fig. 1). This is why significant P vs $\bar{d}_0$ and P vs ε dependences exist only for the range of annealing temperatures $60-90°C$:

$$\ln P = -1\cdot0910 - 6\cdot1488\bar{d}_0^{-1} \quad (r = 0\cdot9822) \tag{2}$$

$$P = 1\cdot086 \cdot 10^{-2} - 6\cdot213 \cdot 10^{-7}\varepsilon^{-1} \quad (r = 0\cdot9785). \tag{3}$$

These relations characterize structural changes in the membranes caused by annealing.

The areal electrical (dc) membrane resistance, R_A (below, only electrical resistance) begins to change at the annealing temperature 70°C, while increasing progressively above this value. This is a consequence of the change in porosity, undoubtedly connected with the glass transition temperature of cellulose acetate (about 69°C). For correlations between R_A and n, and between R_A and ε the following relations have been derived,

$$\ln R_A = 83\cdot248 - 3\cdot566 \ln n \quad (r = 0\cdot9706), \tag{4}$$

$$\ln R_A^{-1} = \ln L_A = 6\cdot544 - 2\cdot178 \cdot 10^{-4}\varepsilon^{-1} \quad (r = 0\cdot9903), \tag{5}$$

where L_A denotes the areal electrical (dc) conductivity of the membrane (below, electrical conductivity). The electrical conductivity decreases with increasing pore diameter, and below the glass transition temperature of cellulose acetate assumes a limiting value about $3\,\Omega\,cm^2$. At this resistance, also the membrane permeability does not vary any more (Fig. 2). Using relations (4), (5) and R_A vs $\bar{d}_0$ (Fig. 2), the membranes can be characterized by electrical resistance measurement, which is easier than the ultrafiltration and dialysis measurements.

All the relations given above justify the assumption that a good correlation does exist between the electrical conductivity and diffusion permeability of the membrane to NaCl, and between the electrical conductivity and water flux intensity through the membrane at 0·3 MPa. Of course, the finding that the electrical conductivity increases both with the increasing salt permeability and with membrane permeability to water, J_w, impedes the use of conductivity in order to express the ability of the membrane to reject selectively the dissolved compounds. The different shape of curves for the L_A vs P and L_A vs J_w dependence (Fig. 3) suggests, however, that such generalization is feasible. Let us use for this purpose the solution-diffusion model, whence we have, among other things, that in reverse osmosis the flow of water through the membrane depends on pressure, while the permeation of salt does not. Rejection of the dissolved compound, r_{RO}, is defined by
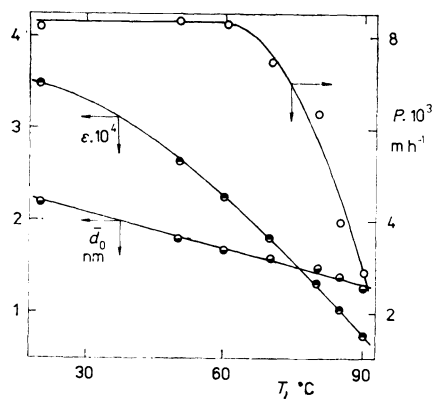
$$r_{RO} = (c_s' - c_s'')/c_s', \tag{6}$$

FIG. 1

Changes in the mean pore diameter $(\bar{d}_0)$, surface porosity (ε), and membrane permeability $(P$, to NaCl) with annealing temperature
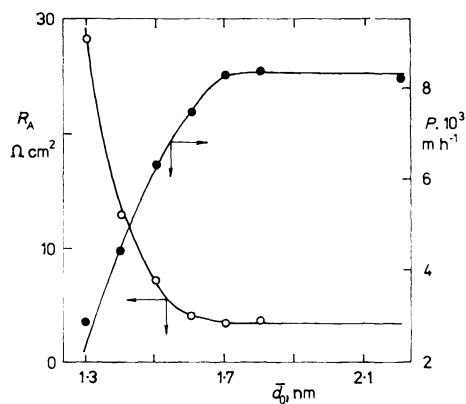
FIG. 2

Dependences of electrical resistance (R_A) and membrane permeability $(P$, to NaCl) on the mean pore diameter of the membrane $(\bar{d}_0)$
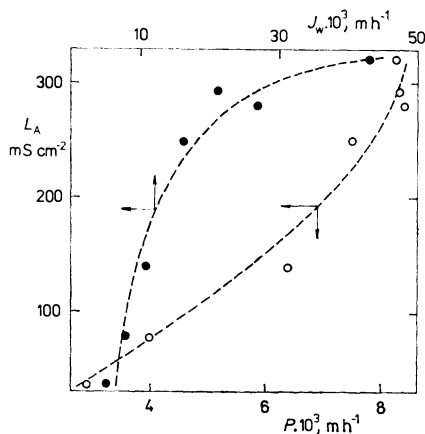
FIG. 3

Dependences of electrical conductivity (L_A) on membrane permeability $(P$, to NaCl) and on the water flux intensity through the membrane at 0·3 MPa (J_w)
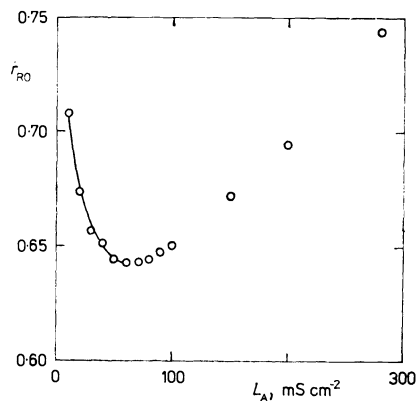
FIG. 4

Salt rejection of the membrane in reverse osmosis (r_{RO}) at various electrical conductivity values of the membrane (L_A) according to relations $(11)-(13)$. The curve indicates the range of validity of the solution-diffusion model

where c_s' is the salt concentration on the feed side, c_s'' is the salt concentration on the permeate side. The ratio between the concentrations of salt and water on the permeate side of the membrane equals that of the respective fluxes:

$$c_s''/c_w'' = J_s/J_w \,. \tag{7}$$

The salt flux intensity, J_s, in the solution-diffusion model is given by permeability of the membrane and by the concentration gradient. Permeability of the membrane according to Farrel[5] involves the diffusion coefficient (D_s), the partition coefficient (K_p) and the membrane thickness (Δx): $P = D_s K_p/\Delta x$. For the salt flux intensity we have, therefore,

$$J_s = P(c_s' - c_s'') \,. \tag{8}$$

Substitution for J_s from Eq. (7) into Eq. (8) gives

$$c_s' = c_s'' + (J_w c_s'')/c_w'' P \,. \tag{9}$$

By combining Eqs (6), (9) and rearrangement we obtain

$$r_{RO} = J_w/(c_w'' P + J_w) \doteq J_w/(P + J_w) \,. \tag{10}$$

The concentration of water in the permeate, c_w'', may be regarded as unity $(c_w'' \doteq 1)$, and for the sake of simplicity it need not be considered: even if $1{\cdot}0\text{M-NaCl}$ appeared in the permeate, c_w'' would be $0{\cdot}98$.

Values in Table I allow the correlations P vs L_A and J_w vs L_A to be derived:

$$P = \exp\left(0{\cdot}5011 \ln L_A - 7{\cdot}6416\right) = \exp A \quad (r = 0{\cdot}990) \tag{11}$$

$$J_w = \exp\left((1{\cdot}0445 - 0{\cdot}1274 \ln L_A)^{-1} - 6{\cdot}9078\right) = \exp B \quad (r = 0{\cdot}991) \,. \tag{12}$$

By combining Eqs (10), (11), and (12) we obtain a relation which elucidates the role played by the electrical conductivity of the membrane (measured by direct current) in the characterization of the rejection of cellulose acetate membranes:

$$r_{RO} = \exp B/(\exp A + \exp B) = (1 + \exp(A - B))^{-1} \,. \tag{13}$$

Combined equations (9), (11), (12), (13) and rearrangement give an equation for the salt concentration in the permeate:

$$c_s'' = c_s'/(1 + \exp(B - A)) = c_s'(1 - r_{RO}) \,. \tag{14}$$

The procedure used in deriving Eqs (13) and (14) suggests that these relations hold only for membranes in which the solution-diffusion transport mechanism is valid, i.e. for reverse osmosis membranes. Furthermore, it is evident that the model holds for various pressures if the correlation function B is known, and for various salts and feed concentrations, if the correlation function A is known. Validity of the model can be checked: if L_A 35·3 mS cm^{-2} is substituted from Table I into Eq (11) and (12), we obtain r_{RO} 0·652. In the experimental reverse osmosis with the same type of membranes the measured r_{RO} value at 0·5 MPA was 0·610 (feed 10 g NaCl in one litre of solution)[6]. At the more usual pressure, 3·0 MPa, the r_{RO} value was 0·913 and J_w was 0·0215 m h^{-1}. By substituting the latter value and P 0·00288 m h^{-1} from Table I into Eq. (10) we obtain r_{RO} 0·882. Thus, basically, the model is adequate. On the other hand, however, it does not reflect the interaction between the fluxes of water and salt and the effect of the so-called concentration polarization in the reverse osmosis. Although the model may help in a preliminary estimate of the rejection of various membranes of the same type on the basis of their electrical conductivities, its meaning mainly consists in the explanation of the relation between r_{RO} and L_A: The r_{RO} vs L_A dependence expressed through Eq. (13) has a minimum at L_A 60 mS cm^{-2} (Fig. 4). Hence, towards lower L_A values, i.e. in less porous membranes, the salt rejection increases with decreasing electrical conductivity. This case involves membranes typical of reverse osmosis, with the diffusion-solution transport model being operative. In the field of membranes annealed below 80°C the electrical conductivity is more affected by porosity than by permeation of the salt. The minimum on the curve according to Eq. (13) (Fig. 4) arises due to the different course of relations (11) and (12).

CONCLUSIONS

1. The cause of the increased rejection of membranes made from cellulose acetate due to annealing consists in the changed porous structure.

2. Although the electrical conductivity of the membranes increases both with increased permeation of the salt and with increased water flux through the membrane under pressure, which are opposite phenomena with respect to rejection, a model has been constructed which adequately describes the role of electrical conductivity as of the only parameter in the evaluation of the ability of the membrane to retain ions from the solutions.

3. The dependence of salt rejection on the electrical conductivity of the membrane according to the model has a minimum. The salt rejection increases or decreases with increasing conductivity of the membranes depending on the position of the minimum (in typical RO membranes the rejection decreases).

4. The minimum arises due to the different shape of the correlation functions of

electrical conductivity of the membranes vs salt permeation, and vs the pure water flux through the membrane under pressure.

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