ORIENTATION DEPENDENT CONCENTRATION POTENTIALS OF ASYMMETRICAL CELLULOSE ACETATE MEMBRANES

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Orientation dependent (asymmetrical) membrane potentials were observed on both reverse osmosis and ultrafiltration cellulose acetate and polymer sulfone membranes in contact with electrolyte solutions. It was shown that this phenomenon can be observed only on asymmetrical membranes with a gradient of fixed charge molality in the active layer (skin), provided that the activity of the more concentrated solution is comparable with or higher than the fixed charge molality in the active layer. This holds also for partly hydrolyzed reverse osmosis membranes. The origin of the orientation dependence of the membrane potential can be explained by means of an analysis of Donnan potentials in given conditions. Diffusion potentials cannot play the decisive role. The asymmetry of osmotic fluxes observed only on reverse osmosis (annealed) membranes does not contribute to the orientation dependence of the membrane potential, because the asymmetrical dilution effect is compensated by the arising streaming potential.

For separation processes like ultrafiltration (UF) and reverse osmosis (RO), cellulose acetate membranes have been widely used up to the present day. Satisfactory separation properties require an appropriate combination of the asymmetric structure of these membranes with a certain content of acetyl groups in the polymer. Unfortunately, in media with a pH beyond the range between 4 and 8 the selectivity of cellulose acetate membranes often decreases with time. This effect caused by hydrolytic decomposition[1] limits their appplicability. The influence of the cellulose acetyl content on the separation properties of cellulose acetate membranes is well known[2-4]. Orientation dependent flux measurements on partly hydrolyzed (hydrolytically aged) cellulose acetate membranes gave further insights into the relations between chemical and morphological variations in the active layer (skin) during this process[5]. Such variations influence the mobility of solutes through the membrane and, hence, the rejection capability. Determination of ion mobility in a concentration cell with transference from the concentration potential, E_c, carried out using a membrane between two compartments of a cell filled with solutions of the same electrolyte at different concentrations, is a common way to obtain information on the physico--chemical nature of the membrane–solution interface, responsible for the separation behaviour.

On asymmetrical membranes or asymmetrical membrane systems, various orientation dependences of the measured E_c (asymmetrical membrane potentials) were observed already some years ago[6-9]. These experiments were carried out with extremely low-conductive non-acetate membranes. In contrast, asymmetrical cellulose acetate membranes for UF and RO have medium or high conductances and papers can be found dealing with E_c of these membranes where no orientation dependence is mentioned[10,11], or even a relationship between E_c and fixed charge density is sought as it is usual with ion-exchange membranes[12]. However, the existence of a concentration potential dependent on the orientation of the skin of a RO membrane towards the higher or lower concentrated solution was shown by Pusch[13]. He explains the orientation dependence as a manifestation of diffusion potentials due to a special concentration profile in the porous sublayer of asymmetrical cellulose acetate membranes for RO, this profile being a consequence of orientation dependent flows across the membrane. It is noteworthy that potentials measured in[13] in KCl and NaCl solutions did not differ essentially, although the respective differences in the ion mobilities in the porous sublayer can be expected to resemble those in a bulk solution. Therefore, the difference between diffusion potentials in KCl and NaCl ought to be comparable with that in liquid junction potentials.

By continuing the investigations[4,5], we tried to obtain information on variations of the membrane properties during the hydrolytic ageing of cellulose acetate membranes by means of E_c measurements. The application range of the method was extended to include membranes of the UF type, and attention was paid to the elucidation of orientation dependent E_c^0, taking into account the morphological structure not only of the sublayer, but also of the active layer (skin) of asymmetrical cellulose acetate membranes. In this paper, we try to show that orientation dependent concentration potentials, E_c^0, are not limited to reverse osmosis membranes, but appear also on porous, partly hydrolyzed reverse osmosis cellulose acetate membranes and on UF (unannealed) membranes; furthermore, that the origin of E_c^0 can be simply explained by an analysis of Donnan potentials arising on weakly charged asymmetrical membranes in contact with two electrolyte solutions, the molality of one of them approaching or exceeding the fixed ion molality in the membrane and, finally, that the asymmetrical osmotic flow arising on reverse osmosis membranes influences E_c^0 only insignificantly.

EXPERIMENTAL

Measurements were carried out in a two-compartment thermostated cell (Fig. 1) made of organic glass. Each part of the cell is provided with a double jacket for thermostating on its whole circumference. The design makes possible the insertion of a membrane and of a pair of calomel or other standard electrodes, thermometers and platinum or glass electrodes. Turbulences in conical chambers facilitate stirring with magnetic stirrers. The small effective membrane area (0·126 cm^2) guarantees a low influence of ion diffusion on the result. Potentials were measured

with saturated calomel electrodes connected to the solutions *via* salt bridges filled — if not stated otherwise — with a saturated KCl solution. The electrode dipped into the more concentrated solution was always connected to the positive input jacket of the electrometer Keithley 610, input impedance 10^{13} ohms, or of the digital voltmeter Meratronik V 544 (Poland), input impedance 10^{10} ohms. Asymmetrical potentials of the calomel electrodes were compensated by commuting them in solutions in contact with the membrane and taking the mean value from the two measurements in both positions of electrodes as the concentration potential. The standard deviation of potential measurements was better than 0·04 mV in all cases. Results in tables are the mean values from measurements on at least two samples.

Membrane 1 was prepared by casting from a 16% (by weight) cellulose acetate solution in acetone and formamide 3 : 2 on a glass plate, evaporation period 30 s, annealing temperature 90°C during 10 minutes. Membrane 4 was cast on a technological equipment from a 18% solution under analogous conditions[14]. Membrane 14 was cast from a 15% acetone solution on a glass plate and evaporated only 15 s, unannealed. Membranes in Table III were prepared analogously to the membrane 4. The phase inversion was carried out in all cases at 5°C, in water. Conditions of the hydrolysis follow from Table I. The UF membrane of the polymer sulfone "polysulfone" PL-15, Union Carbide, Table IV, was prepared in the Research Institute LIKO, Bratislava. Electron micrographs (made in IPOC, G.D.R.) showed that membranes 1—13 as well as polymer sulfone membranes had a typical spongelike asymmetrical structure, whereas membrane 14 had a more homogeneous cross section with unconnected microvoids, but its top layer (skin), being 30% of the total membrane thickness, was free of microvoids and other structural elements.

The content of acetyl groups in membranes was determined by back titration after complete hydrolysis. Osmotic experiments were carried out with a saturated NaCl solution and distilled water at room temperature. All reagents were *p.a.* grade and were used without further purification. KCl and NaCl solutions were prepared from degassed distilled water and kept free of CO_2. The pH of solutions for potential measurements was adjusted to $6·5 \pm 0·1$ by means of equimolar KOH, NaOH, and HCl solutions. The orientation of a membrane with the skin adjacent to the more concentrated solution is designated as positive (+).

FIG. 1

Two-jacket cell for measurements of concentration potentials. The inlets and outlets of thermostating liquid are in a plane situated at 30 degrees to the plane of the above depicted sectional view
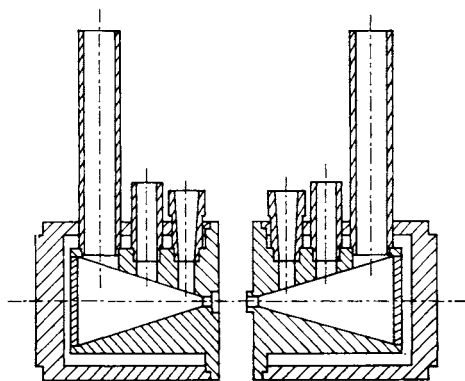
RESULTS AND DISCUSSION

In general, the concentration potential, E_c, is negative, *i.e.*, cellulose acetate behaves as a weak cation exchanger. It follows from Table II that potentials measured in NaCl solutions tend to less negative values in KCl, no doubt because of higher diffusion potentials in membranes in contact with NaCl solutions. Moreover, potentials in NaCl solutions with the hydrolyzed sample 2 are strongly influenced by liquid junction potentials as in this case the electrode and bridge filled with KCl was used. The orientation dependence of the potentials remains unchanged, however. Additionally, the results with sample 3 show that the choice of filling in the salt bridge and electrode is without any influence on the tendency of the results. The E_c values of reverse osmosis (RO) membranes are higher than those of more porous hydrolyzed or unannealed (UF) membranes.

An orientation dependent concentration potential, E_c^0, was observed both on hydrolyzed and on untreated samples (Table II). These potentials were always less negative in the positive orientation than in the negative one. The absolute values decrease with decreasing content of acetyl groups in the membranes. Investigations of the separation behaviour of stepwise hydrolyzed cellulose acetate membranes have led us to the conclusion that the hydrolysis enhances the dimensions of transport paths through the membrane skin[5]. In order to answer the question whether chemical or morphological modifications during hydrolysis are responsible for the observed behaviour, measurements of differently annealed membranes were carried out: An increasing annealing temperature diminishes the dimensions of transport paths in the skin of the membrane, whereas the chemical composition remains constant. The respective results are given in Table III. The orientation dependence of the

TABLE I

Conditions of the hydrolysis of cellulose acetate membranes. Symbols: C_s concentration of casting solution, C_A content of acetyl groups

Membrane	C_s wt.%	C_A wt.%	Hydrolysis conditions
1	16	39·2	Untreated
2	16	36·1	17 days; pH 10; 20°C
3	16	35·1	30 days; pH 10; 20°C
4	18	39·1	Untreated
5	18	36·4	4 days; pH 10; 20°C
6	18	18·3	24 min; 1% sol. NaOH; 20°C

measured concentration potentials occurs at all degrees of annealing, and also — which is surprising and was not known — on ultrafiltration membranes. The tendency of the orientation dependence is the same as that found with other membranes just mentioned. The E_c value increases with decreasing dimensions of transport paths in the skin. Consequently, morphological changes cannot be excluded in the case of hydrolytic ageing of cellulose acetate membranes, in consistence with our earlier results[5].

In order to determine whether the orientation dependence is an inherent property of cellulose acetate or a consequence of the asymmetric structure of a membrane, E_c^0 was measured also on membrane 14 and on the polymer sulfone membrane (Table IV). Whereas the orientation dependence is preserved in the case of the

TABLE II

Oriented concentration potentials (E_c^0, mV) of partly hydrolyzed reverse osmosis cellulose acetate membranes as a function of solute molality and membrane orientation

Membrane	Electrolyte	0·1/0·01 (+)	0·01/0·1 (−)	0·1/0·001 (+)	0·001/0·1 (−)
1	KCl	−9·5	−17·4	−38·0	−47·0
2	KCl	−3·1	−14·0	−12·1	−37·7
		−3·8	−12·4	−18·0	−37·0
		−2·4	−13·8	−11·4	−42·0
	NaCl[a]	+4·4	−10·2	+18·5	−9·4
		+3·0	−8·9	+17·6	−14·0
		+5·0	−10·6	+17·3	−9·5
3	KCl	−4·1	−6·3	−19·5	−32·6
		−4·4	−6·0	−18·1	−24·0
		−7·2	−9·0	−17·2	−25·0
	NaCl[b]	−0·3	−9·0	−7·2	−28·2
		−1·5	−5·8	−7·2	−18·2
		−1·7	−5·8	−8·7	−20·2
4	KCl	−7·1	−19·6	−20·2	−44·0
		−5·4	−14·8	−21·4	−42·0[c]
5	KCl	−3·9	−11·9	−14·6	−42·0
		—	—	−4·3	−20·9[c]
				−3·5	−18·0[c]
6	KCl	+2·0	−1·6	−2·2	−2·7
		—	—	+1·0	−10·7[c]

[a] Measured with a satd. KCl solution filled calomel electrode; [b] measured with a satd. NaCl solution filled calomel electrode; [c] digital voltmeter was used.

polymer sulfone asymmetrical membrane, it vanishes for sample 14 which has not such a pronounced morphological asymmetry. Hence, the orientation dependence of E_c^0 is related to the morphological asymmetry of the membranes. Now, to explain the origin of the orientation dependence of E_c^0, one must know the nature of the concentration potential measured. This can be a diffusion potential, a difference of Donnan potentials or a streaming potential. First, we exclude the dominant role of the diffusion potential, because Cl^- has a higher mobility than both K^+ and Na^+, and the diffusion would form an excess of negative charges on the side of the membrane adjacent to the less concentrated solution, in contradistinction to the experi-

TABLE III

Oriented concentration potentials (E_c^0, mV) on differently annealed cellulose acetate membranes as a function of KCl molality and membrane orientation. Concentration of the casting solution was 18 wt. %; T_a is the annealing temperature

Membrane	T_a °C	0·1/0·01 (+)	0·01/0·1 (−)	0·1/0·001 (+)	0·001/0·1 (−)
7	20	−1·8	−9·2	−7·4	−32·7
8	20	−1·5	−5·3	−3·0	−18·7
9	20	−1·6	−6·7	−6·1	−23·7
10	75	−2·1	−7·3	−6·6	−24·0
11	85	−3·7	−12·5	−19·0	−42·0
12	90			−30·2	−53·7
13	90			−34·6	−47·0

TABLE IV

Oriented concentration potentials (E_c^0, mV) on the cellulose acetate membrane 14 and on an asymmetrical UF membrane of a polymer aromatic sulfone as a function of KCl molality and membrane orientation

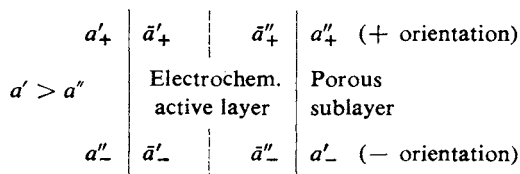| Membrane	0·1/0·01 (+)	0·01/0·1 (−)	0·1/0·001 (+)	0·001/0·1 (−)
14	−11·2	−11·1	−52·5	−53·3
Polymer sulfone	−	−	−8·3	−14·8
			−7·6[a]	−13·6[a]

[a] After a UF experiment.

mental results. Demisch[15] comes to an analogous conclusion by means of different considerations. Moreover, due to the difference in the mobilities of K^+ and Na^+, potentials in KCl and NaCl solutions would have to differ by an order of magnitude, which, however, is not confirmed by the experiment. Let us now consider the difference of the Donnan potentials. The concentration of negative fixed charges related to the volume of the pore liquid (fixed charge molality, X) in similar cellulose acetate membranes with low surface porosity amounts[15] to about 0·025 mol/l. If we estimate the value of E_c according to the TMS theory[16], we obtain -23 mV for 0·1 and 0·01M KCl in contact with the membrane. This value is comparable with the measured values (at least in the negative orientation), and also the sign corresponds to the experiment. As to the streaming potential, it results from a deformation of the electric double layer on the surface of transport paths by the osmotic stream of solvent from the less concentrated solution to the more concentrated one. The mobile part of the double layer transports a negative excess charge in cellulose acetate membranes at these relatively high salt concentrations. Consequently, a negative space charge accumulates on the side of the more concentrated solution and the streaming potential is added to the Donnan potential difference but can hardly be dominant as the following estimation shows:

According to Schmid[12],

$$E_{st} = -FXR_a q \, , \tag{1}$$

where F is the Faraday charge, X is the fixed charge molality, R_a is the areal resistance and q is the flux. Of course, this equation has been derived for a membrane between identical solutions; in our case we consider the osmotic pressure as the driving force for the flux q instead of mechanical pressure and, therefore, solutions cannot be identical. If we substitute 0·025 mol/l for X, 15 l/h m² for q in the negative orientation of the membrane, 3 l/h m² for q in the positive one[4], and 50 ohm cm² (refs[4,5]) for the area resistance R_a, we obtain $E_{st}^- = -5$ mV and $E_{st}^+ = -1$ mV, respectively, as a rough approximation.

Let us now try to explain the origin of E_c^0. First, we must take into account the gradient of the porosity or polymer density in the membrane. Let the skin (the active layer) of the membrane consist only of two parts, the outer having a lower porosity and a higher fixed charge molality than the inner one adjacent to the porous sublayer (Scheme 1). Therefore, in the positive orientation of the membrane, a dif-

a'_+	$\bar{a}'_+$	$\bar{a}''_+$	a''_+	(+ orientation)
$a' > a''$	Electrochem. active layer		Porous sublayer	
a''_-	$\bar{a}'_-$	$\bar{a}''_-$	a'_-	(− orientation)

SCHEME 1

ference of the Donnan potentials, E_{Don}^+, arises:

$$E_{Don}^+ = -\frac{RT}{zF}\left(\ln\frac{a'_+}{\bar{a}'_+} + \ln\frac{\bar{a}''_+}{a''_+}\right), \qquad (2)$$

where $\bar{a}'_+ > \bar{a}''_+$ are the activities of ions in the outer and inner part of the active layer, respectively, $a'_+ > a''_+$ are the respective activities of the adjacent solutions. The difference of the Donnan potentials in the negative orientation is expressed by the relation

$$E_{Don}^- = -\frac{RT}{zF}\left(\ln\frac{a'_-}{\bar{a}''_-} + \ln\frac{\bar{a}'_-}{a''_-}\right). \qquad (3)$$

As the fixed charge molality in the membrane is lower compared with that of the more concentrated solution and, therefore, $a'_+ \approx \bar{a}'_+; a'_- \approx \bar{a}''_-$, potentials arising on boundaries where solution a' is present are negligible (first terms in Eqs (2) and (3)). For second terms, we have $\bar{a}'_- > \bar{a}''_+$. Assuming that there is no remarkable difference between a''_+ and a''_- as the porous sublayer is electrochemically inactive, the value of E_{Don}^- must be greater than that of E_{Don}^+. Thus, the observed orientation dependence is explained only by means of the Donnan potentials in a gradient of fixed charge molality, which is obtained by a gradient in active layer porosity.

According to this explanation, the orientation dependence of E_c should vanish, if the activity a' is sufficiently lower than the effective fixed charge molality in the active layer, i.e., if $a'_+ < \bar{a}'_+; a'_- < \bar{a}''_-$, so that the first terms in both equations cannot be neglected. Indeed, the results in Table VI show that with $a' \approx 0.01$ the orientation dependence significantly diminishes and with $a' \approx 0.001$ only a 0.5 mV difference between the $(+)$ and $(-)$ orientation remains. Moreover, as to the ultrafiltration membrane, where a higher porosity and lower fixed charge molality in the skin $(\bar{a}'; \bar{a}'')$ is to be expected, the orientation dependence diminishes more slowly with decreasing activity a'. Thus, the results in Table V confirm the theory.

On RO membranes also an asymmetry of osmotic fluxes, J_s, is observed (Nos 4 and 5 in Table VI). As a consequence of J_s, the more concentrated solution in close vicinity to the membrane is diluted and E_c is suppressed. The dilution effect of the osmotic flux on E_c^0 is higher in the $(+)$ orientation and is added to the effect of the asymmetry of the fixed charge molality in the membrane. The streaming potential is another consequence of the osmotic flux. As has already been explained, a negative charge accumulates on the side of the more concentrated solution. Because the osmotic flux is higher in the positive orientation than in the negative one, the streaming potential compensates the dilution effect of J_s. The hydrolyzed RO membrane (No 6 in Table VI), is similar to the UF membrane (No 7 in Table VI) in that it

shows no orientation dependence of the osmotic flux, and the occurrence of E_s^0 cannot consist in this phenomenon.

CONCLUSIONS

1. Concentration potentials caused by a weak negative charge appear on reverse osmosis as well as on ultrafiltration and partly hydrolyzed reverse osmosis membranes of cellulose acetate. These potentials are higher with (annealed) reverse osmosis

Table V

Orientation dependence of concentration potentials (E_c^0, mV) on cellulose acetate membranes (CAM) vanishing with decreasing molality of KCl solutions

CAM	$10^{-1}/10^{-2}$ (+)	$10^{-2}/10^{-1}$ (−)	$10^{-2}/10^{-3}$ (+)	$10^{-3}/10^{-2}$ (−)	$10^{-3}/10^{-4}$ (+)	$10^{-4}/10^{-3}$ (−)
4	−3·4	−11·5	−43·4	−45·4	−48·4	−48·8
8	−2·2	−4·9	−22·1	−28·1	−42·2	−43·2

TABLE VI

Oriented osmotic fluxes of differently annealed and hydrolyzed membranes. Symbols: c_A the content of acetyl groups (in wt.%), T_a the annealing temperature (°C), J_w the water flux (in $1/h\ m^2$), J_s the salt flux (in $kg/h\ m^2$); (+) and (−) are orientations of the membrane

Membrane	c_A	T_a	J_w (+)	J_s (+)	J_w (−)	J_s (−)
7	39·1	20	11·0	1·308	10·7	1·243
			11·5	1·411	12·6	1·280
10	39·1	75	14·2	1·012	13·6	0·938
			12·1	1·012	14·5	0·977
11	39·1	85	23·8	0·512	19·3	0·434
			23·6	0·565	20·9	0·448
4	39·1	90	42·9	0·067	20·3	0·049
			42·1	0·065	20·1	0·052
5	36·4	90	43·3	0·045	16·3	0·020
			45·8	0·035	16·0	0·020
6	18·3	90	8·6	2·250	7·8	2·330
			7·6	2·210	6·6	2·280

membranes and decrease with increasing dimensions of transport paths in the active layer of unannealed ultrafiltration membranes and of hydrolytically aged reverse osmosis membranes. In this manner, variations in the concentration potential characterize variations in the morphology of the active layer.

2. The orientation dependence (asymmetry) of the concentration potential can be observed both on reverse osmosis and on more porous hydrolyzed or unannealed ultrafiltration weakly charged asymmetrical membranes with a pronounced gradient of fixed charge molality (porosity, density) in their active layer, provided that the following condition is fulfilled: The activity of the more concentrated solution in contact with the membrane is comparable with or higher than the fixed charge molality in the active layer, whereas the activity of the less concentrated solution is significantly lower than the fixed charge molality. In such a case, only the Donnan potential at the boundary between the active layer and the less concentrated solution is decisive for the membrane potential.

3. The orientation dependent (asymmetrical) concentration potential is higher in the negative orientation (the more concentrated solution. adjacent to the sublayer of the membrane).

4. The origin of the orientation dependence (asymmetry) of the concentration potential can be explained by means of an analysis of the Donnan potentials in a gradient of fixed charge molality in the active layer.

5. In accordance with the analysis, the orientation dependence of the concentration potential vanishes, if the activity of the more concentrated solution in contact with the membrane decreases sufficiently under the effective fixed charge molality in the active layer and/or if a membrane is used containing a thin, homogeneous active layer free from the fixed charge molality gradient.

6. Osmotic fluxes through an annealed reverse osmosis membrane are significantly higher in the positive orientation than in the negative one, but this asymmetry does not contribute to the orientation dependence of the concentration potential, because the asymmetrical dilution effect of the osmotic flux is compensated by the streaming potential caused by this flux.

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