

## ELECTROCHEMICAL BEHAVIOUR OF POLYELECTROLYTE COMPLEX MEMBRANES

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Oriented concentration potentials and DC resistances of Symplex polyelectrolyte membranes made of cellulose sulfate (CS) as a polyanion and of poly(dimethyldiallylammonium chloride) (PDMDAAC) or benzyl-[2-(dodecylcarbamoyl)ethyl]dimethylammonium chloride (Quartolan) as counter-cations were measured and correlated to dialysis permeability coefficients. Concentration potentials showed that the preparation method used leads to membranes with an excess of the charge of one component. Cationic symmetrical PDMDAAC/CS membranes, anionic asymmetrical Quartolan/CS membranes and anionic asymmetrical combination of both types have the fixed ion molarity 0.05, 0.005 and 0.001 mol per litre of imbibed liquid, respectively. Specific resistances are  $10^4 \Omega \text{ cm}$  in 0.005M- and 0.01M-KCl,  $10^3 \Omega \text{ cm}$  in 0.05M-KCl and even higher in combined membranes. Areal resistances are low due to small membrane thickness. A linear correlation between DC conductivity and permeability has been found. Thus, also Symplex polyelectrolyte membranes can be tested by electrochemical methods.

Symplex<sup>1,2</sup> polyelectrolyte membranes are a new class of polymer separation membranes. They are formed by a simultaneous interfacial reaction of a synthetic polycation and a cellulose-based polyanion. Their net charge makes them an appropriate object of electrochemical studies. Despite their porosity, the permeability of Symplex membranes is dependent on their polarity and thus on their (free) fixed ion molarity (FIM). This property of the membrane material can be characterized by the concentration potential. Moreover, the oriented concentration potential affords information of the symmetry or asymmetry of the membrane<sup>3</sup>. Electric resistance of the membrane being dependent on FIM, diffusion coefficient and hydraulic resistance, is an integral characteristic of general permeability of the membrane.

The article deals with DC electric resistances and oriented concentration potentials of two types of Symplex membranes made from a cellulose-based polyanion and synthetic counter-ions, as well as of their combination. Permeabilities of the membranes in dialysis are also evaluated.

## EXPERIMENTAL

**Materials.** Sodium cellulose sulfate (Na-CS) was prepared by homogeneous sulfation with nitrosyl hydrogen sulfate<sup>4</sup> of cellulose dissolved in a dinitrogen oxide–dimethylformamide solution. Linear poly(dimethyldiallylammonium chloride) (PMDAAC) was made by radical cyclopolymerization. Quartolan (benzyl-[2-(dodecylcarbamoyl)ethyl]dimethylammonium chloride) was a commercial tenside (Hydrierwerk Rodleben).

**Membrane preparation.** An Na-CS layer was spread on a separable support and the respective cation was cast on it. The composed membrane was prepared by combining two simple membranes (Quartolan/CS on PMDAAC/CS).

**Electrochemical measurements.** A universal cell made from organic glass and consisting of two independently thermostatted compartments (Fig. 1) was used. For concentration potential measurements a membrane disc (18 mm in diameter) without support was inserted between them, the compartments being filled with one of the following KCl solution pairs of the concentrations  $0.01 \parallel 0.005$ ;  $0.02 \parallel 0.01$  or  $0.1 \parallel 0.05$  mol l<sup>-1</sup>. After equilibration, the cell was filled with the same fresh pretempered (25 °C) pair of KCl solutions, calomel electrodes in protective electrolyte bridges were inserted in their orifices, magnetic stirring was switched on, temperature was checked, temperature sensors were pulled out and the value of the potential was read on a Meratronik (Poland) digital voltmeter. A second value of the potential was read after commuting calomel electrodes, the mean value of both readings used. Diffusion potential was neglected because of the small concentration difference and owing to the fact that KCl is an equitransferent electrolyte. Two independent measurements were carried out. The concentration potential obtained with the more concentrated KCl solution in contact with the cationic layer was designated as (+). After commuting the KCl solutions the (-) value was determined.

Membrane resistances were measured in the same cell using Pt electrodes immersed in the KCl solutions. Pt electrodes were fed with constant stabilized direct current from an electronically controlled source<sup>5</sup> using current densities of 0.25, 2.55 and 5.10 A m<sup>-2</sup>. The value was calculated from the voltage drop on a built-in standard resistance. The potential drop on the membrane was measured by means of the calomel electrodes; the resistance was calculated using Ohm's law. The membrane resistance was determi-

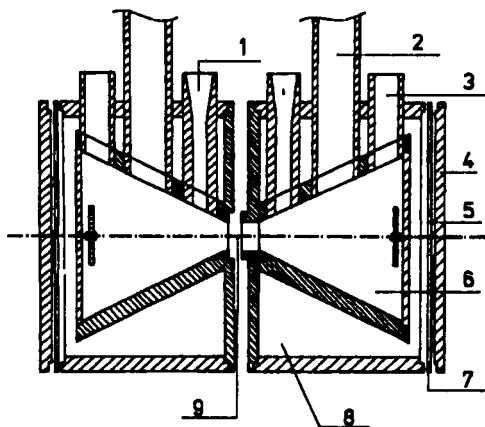


FIG. 1

Schematic cross-section of the universal two-compartment cell for electrochemical characterization of membranes: 1 for SCE, 2 for Pt electrode, 3 for thermometer, 4 outer lid, 5 magnetic stirrer, 6 KCl solution, 7 packing, 8 thermostating liquid, 9 for membrane

ned as a difference between resistances measured with and without the membrane in the cell. All measurements were carried out at 25.0 °C.

*Dialysis.* Dialysis experiments were carried out in a similar cell. One compartment was filled with KCl solution, the other one with distilled water. Solution concentrations were determined by refractometry and permeability coefficients were calculated according to ref.<sup>6</sup>.

## RESULTS AND DISCUSSION

The dependence of concentration potentials on the concentration of dilute KCl solution may be caused by screening the fixed charges by ions present in solution at relatively high concentrations. This is accompanied, in the case of Symplex membranes, by swelling of the polymer matrix and – at concentrations above 1 mol l<sup>-1</sup> – by dissolution of the membrane. Therefore, the concentration potentials at concentrations where their values tend to zero or where the sign of these values seems to change (Table I) should be interpreted as potentials of microporous, noncharged mixing barriers. Consequently, the effective FIMs are expected to be  $\leq 0.05$  mol l<sup>-1</sup> for PDMDAAC/CS  $\leq 0.005$  mol l<sup>-1</sup> for Quartolan/CS and  $\leq 0.01$  mol l<sup>-1</sup> for combined membranes.

The PDMDAAC/CS membrane bears a positive net charge. Concentration potential is independent on the orientation of the cationic layer towards KCl solutions; therefore, these membranes made of two polyions are assumed to be homogeneous. Contrarily, for Quartolan/CS membranes an excess of negative charge and orientation dependence of concentration potentials are observed. This effect may be interpreted as the result of a composition gradient in the cross-section of these membranes made of polyions and mobile organic ions.

As expected, anisotropy is observed with the combined membrane due to its special chemical composition along its cross-section. The FIM represents a “median value” between those of its components.

TABLE I  
Oriented concentration potentials (mV) of Symplex membranes in KCl solutions of given concentrations (mol l<sup>-1</sup>)

Membrane	0.01    0.005		0.2    0.01		0.1    0.05	
	+	-	+	-	+	-
PDMDAAC / CS	+11.8	+10.5	+9.2	+8.9	+3.6	+2.8
Quartolan / CS	-5.9	-9.8	+0.7	-3.7	+1.8	+0.3
Combined membrane	-5.7	-10.2	-3.7	-8.7	+1.0	-1.1

As far the resistance is concerned (Table II), a more (PDMDAAC/CS, combined membrane) or less (Quartolan/CS) pronounced dependence of electrolytic resistance on current density is observed. This can be explained by higher electrolyte input brought into the membrane at higher current densities and causing swelling as discussed above. Consequently, only the results obtained at the lowest current density can be compared.

At lower concentrations, the resistance of the combined membrane exceeds the sum of resistances of its components, very probably due to an incomplete contact between the two membranes, whereas at the highest concentration the resistance of the combined membrane nearly equals to the resistance of the Quartolan membrane. This behaviour corresponds in principle with the swelling properties discussed above.

It is worth mentioning that the areal resistances of Symplex membranes are comparable with those of ion-exchange membranes, but only owing to their extremely low thickness (0.0015 cm). The difference in specific resistances, however, makes at least two orders.

TABLE II  
Areal and specific resistances ( $\Omega \text{ cm}^2$  and  $\Omega \text{ cm}$ , respectively) of Symplex membranes in KCl solutions

Current density $\text{A m}^{-2}$	0.005M-KCl		0.01M-KCl		0.05M-KCl	
	$R_A^M$	$R_S^M \cdot 10^{-3}$	$R_A^M$	$R_S^M \cdot 10^{-3}$	$R_A^M$	$R_S^M \cdot 10^{-3}$
PDMDAAC / CS						
0.25	11	7	11	7	1	0.7
2.55	15	10	3	2	1	0.7
5.10	15	10	2	1	0	0
Quartolan / CS						
0.25	20	13	24	16	3.9	2.6
2.55	17	11	19	13	3.1	2.1
5.10	18	12	17	12	3.1	2.1
Combined membrane						
0.25	203	81	81	32	6.3	2.5
2.55	178	71	76	30	3.1	1.5
5.10	144	58	81	32	3.1	1.2

The trend in permeability values (Table III) is in general agreement with trends in resistances. The permeability coefficients  $P$  in 0.01M-KCl can be correlated to DC areal conductivities  $L_A$  in the same solution at  $5.1 \text{ A m}^{-2}$  by the linear equation

$$P \cdot 10^4 = 8.618 L_A + 1.755$$

with a correlation coefficient  $r = 0.980$ . Therefore, it can be expected that electrochemical methods will be useful also for characterising transport properties of Symplex membranes.

TABLE III  
Dialysis permeability of Symplex membranes for KCl<sup>a</sup>

Membrane	Permeability coefficient $\cdot 10^4, \text{ cm s}^{-1}$	
	0.01M-KCl	0.05M-KCl
PDMDAAC / CS	6.1	11.2
Quartolan / CS	1.69	4.49
	2.46	5.04
Combined membrane	2.20	9.00

<sup>a</sup> Cationic layer adjacent to the KCl solution.

## CONCLUSION

Oriented concentration potentials prove Symplex polyelectrolyte membranes to be internally symmetrical or asymmetrical in dependence on the type of the counteranion used. The (free) fixed ion molarity of Symplex membranes can be evaluated from oriented concentration potentials and is approximately 0.05, 0.005 and 0.01 mol per litre of imbibed liquid for PDMDAAC/CS, Quartolan/CS and combined membranes, respectively. The specific resistance of Symplex membranes is by two orders higher than that of ion-exchange membranes but, owing to their extremely low thickness, comparable or lower areal resistances than those of ion exchange membranes were found. Conditions can be found under which areal conductivities are linearly correlated to permeability coefficients in dialysis.

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