

Transport Properties of Asymmetric Polyamide Membranes

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Synopsis

Transport properties of asymmetric copolyamide membranes made by interfacial polycondensation were studied. The directional flow preference observed in diffusion experiments with ionic permeants can be explained by the swelling behavior of the membrane. As a consequence of the weak acidic and weak basic endgroups, the ion exchange characteristics of the membrane are a function of the pH value in the ambient solution and can be changed from cation to anion exchange properties. Like a bipolar double membrane, it is composed of an cationite and an anionite region. The current-voltage characteristics were found to be asymmetric.

INTRODUCTION

Transport theory and processes which take place in polymer membranes are of both practical and theoretical interest. In recent years, much work has been done to develop synthetic membranes with desired properties which can be effectively utilized in separation processes or as protective coatings in a variety of industrial and biomedical devices.

A case of particular interest is the preparation of membranes possessing a gradient of composition, i.e., asymmetric membranes.^{1,2} For example, most biologic membranes are highly asymmetric. It is believed that the special transport properties of these membranes can be attributed, at least in part, to their asymmetry. The more general methods in membrane formation consist of special processing of ready-made polymers in order to give the material a more or less well-defined physical microstructure. Thus, asymmetric membranes possessing a gradient of composition cannot be prepared by these procedures. Membrane asymmetry can be achieved by some chemical aftertreatments like radiation-induced graft copolymerization of monomer sorbed in a gradient within a polymer film^{1,2} or polymerization of previously built-up multilayer films.^{3,4}

A new way to prepare asymmetric polymer membranes is the simultaneous synthesis of polymer material and the membrane itself by interfacial polycondensation. Here, two reactive multifunctional components are dissolved in two mutually immiscible solvents. Polycondensation takes place at the interface where the membrane is formed in a diffusion-controlled reaction.^{5,6} Membrane morphology and properties are determined by the special mechanism of membrane formation and can be varied to some extent by choosing the right reaction conditions. In this paper, we want to report investigations of the transport

TABLE I
Conditions of Preparation and Some Properties of the Used Membranes

Membrane layer	Concentration of monomers ^a	Reaction time, sec
Nylon 610	$c_{HD} = 0.3$ mole/l. $c_{SC} = 0.1$ mole/l.	150
Crosslinked Copolyamide	$c_{HD} = 0.3$ mole/l. $c_{SC} = 0.1$ mole/l. $c_{BTTC} = 0.01$ mole/l.	1650
Membrane thickness		$x = 50 \pm 4 \mu$
Water content		$W = 90\%$ (w/w)
Content of benzenetricarboxylic acid units in crosslinked layer		$x_{BTA} = 36$ mole %

^a c_{HD} : Concentration of 1,6-diaminohexane in water; c_{SC} : concentration of sebacic acid chloride in benzene; c_{BTTC} : concentration of 1,3,5-benzenetricarboxylic acid chloride in benzene.

properties of asymmetric copolyamide membranes prepared by interfacial polycondensation.

EXPERIMENTAL

Membranes were prepared by interfacial polycondensation as described elsewhere.^{7,8} Conditions of preparation and some membrane properties are summarized in Table I.

Diffusion experiments and determination of membrane potentials were performed in a H-shaped diffusion cell. The membrane was clamped in the crossmember of the stirred cell and separated a solution of 0.1 to 0.2 mole/l. from distilled water. The temperature was maintained at 30°C. The exposed

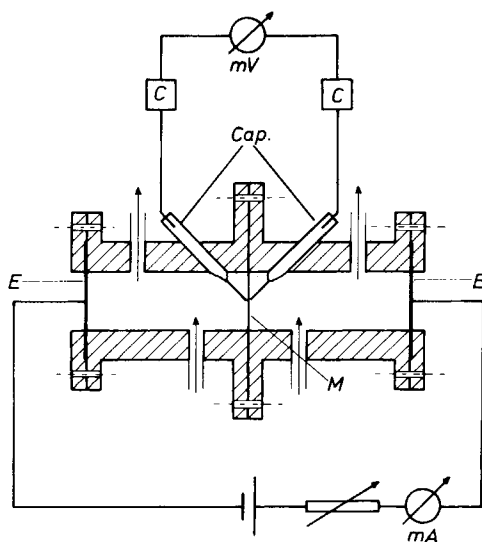
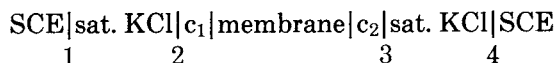


Fig. 1. Schematic representation of used cell and measuring circuit for the determination of stationary current-voltage characteristics: M, membrane; E, Ag/AgCl electrodes; Cap., Luggin capillaries; C, Calomel electrodes.

membrane area was 12.6 cm². The rate of electrolyte diffusion was followed by means of a conductivity cell in the distilled water chamber. Concentration measurements of glucose and alcohols were carried out by colorimetric methods.^{9,10}

The cell circuit for determination of membrane potentials is represented by



where SCE is the saturated Calomel electrode and junctions 1–4 were effected by platinum diaphragms. Potentials were measured with a Knick volt-meter with an accuracy of ± 0.3 mV.

Measurements of the area resistance were made in a simple acrylic cell with fixed platinum electrodes. The exposed area was 0.785 cm². A Wayne Kerr conductivity bridge at 1592 cycles per second was used. The buffers were prepared according to the data of Conway¹¹ and were made up to 0.10 and 0.20 ionic strength solutions by addition of the appropriate amount of sodium chloride. Stationary current–voltage characteristics were measured in an acrylic cell with a circuit schematically represented in Figure 1 using two fixed Ag/AgCl electrodes. The current was measured with an ammeter. The difference of electric potential across the membrane was determined by means of two Luggin capillaries with two saturated Calomel electrodes. The ohmic resistance of the two thin liquid layers between capillaries and membrane surface was determined by measuring the current–voltage characteristics without the membrane with unchanged distance of the capillaries.

RESULTS AND DISCUSSION

Membrane Morphology

A detailed discussion of the experimental procedures for the preparation and the investigation of membrane morphology has been presented elsewhere.^{7,8,16} We will only review the more relevant aspects here briefly.

Stable polyamide membranes consisting of two layers with controlled structure can be produced by preparation of a supporting layer of crosslinked copolyamide on a thin layer of nylon 610. This is easily achieved by exchange of the organic phase during the reaction. Both layers have different structures and functions. The thin layer shows a smooth surface without holes. Here, the polymer chains are mainly oriented perpendicular to the membrane surface in the direction of membrane growth. The order of chain packing decreases with increasing membrane thickness. The surface of the crosslinked layer is rough and rugged and contains large holes. Figure 2 shows scanning electron micrographs of the two surfaces.

The undried water-swollen membranes contain about 90% water which saturates the hydrogen bonds of the amide groups and separates the chains. The mean distance between two chains separated by hydrate water as calculated from the water content is 12 to 13 Å.

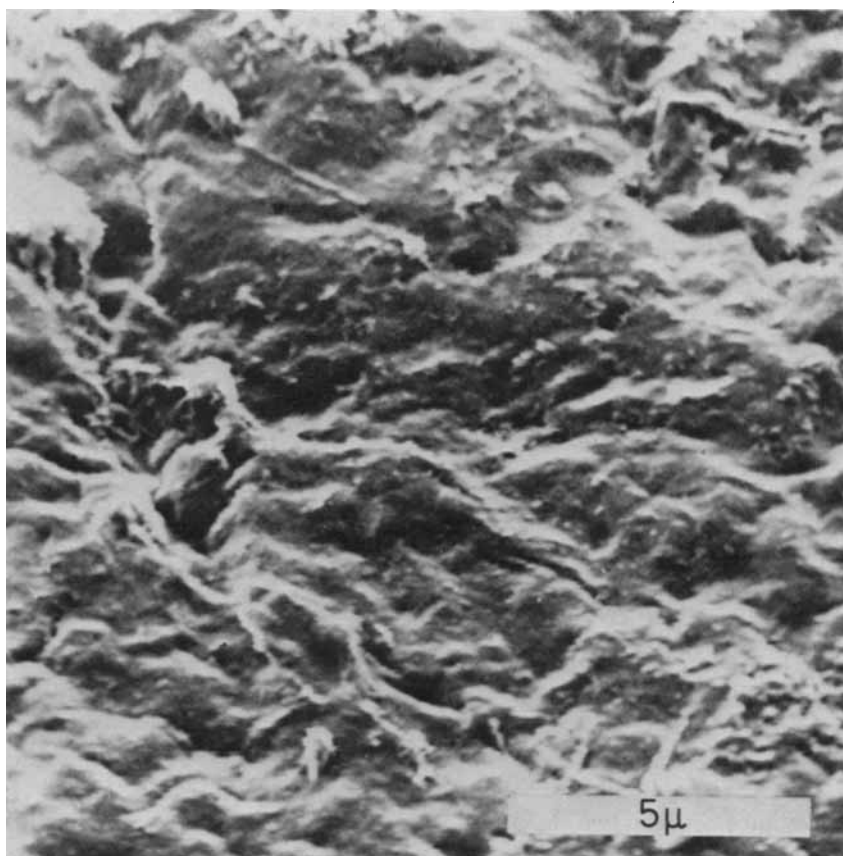
The crosslinked supporting layer behaves like a moderately crosslinked polyelectrolyte gel, i.e., both equilibrium water content and membrane dimen-

sions are markedly influenced by the salt concentration in the outer aqueous phase.¹² The shrinkage in salt solutions and swelling in pure water are completely reversible; a membrane carrying an attached weight, if dipped alternately into salt solution and distilled water, will contract and expand, performing mechanical work. Similar simple mechanochemical systems have been described previously by Katchalsky.¹³

In addition to the gradient of inhomogeneity caused by the decrease of chain order with increasing thickness, the special mechanism of membrane formation by interfacial polycondensation gives rise to an asymmetric distribution of endgroups. The surface of the thin, dense layer which has been in contact with the water phase containing the diamine bears only amino endgroups. The opposite surface, adjacent to the organic phase during the reaction, will be rich in carboxylic acid endgroups. Between the two sides, the distribution of endgroups will change continuously from weak basic to weak acidic.

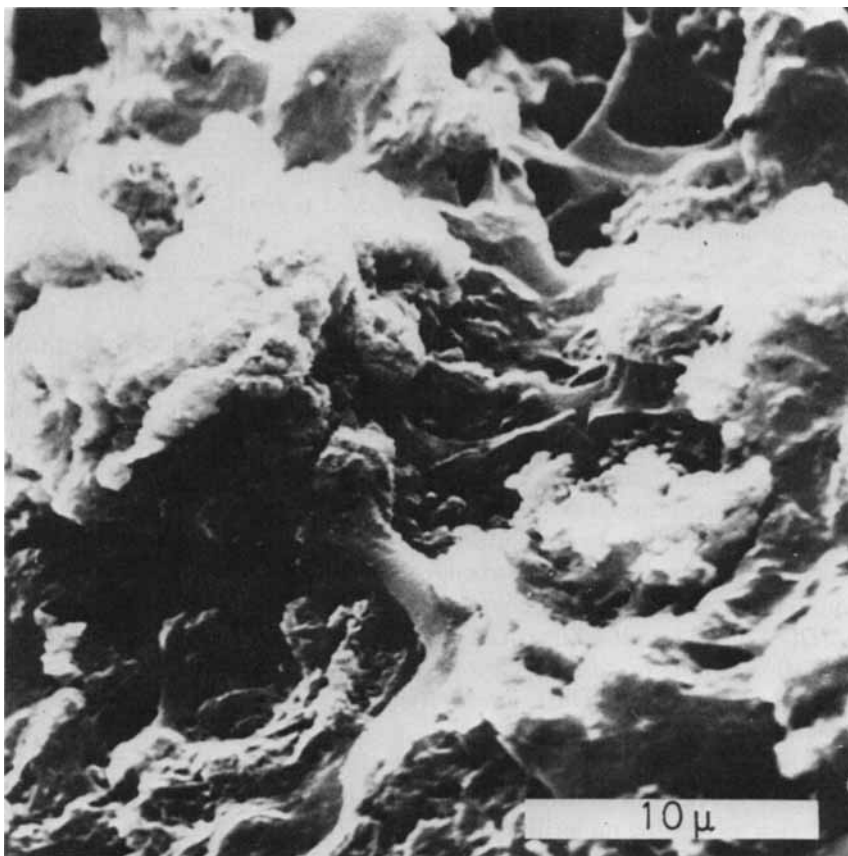
Diffusion Experiments

In order to investigate the transport behavior of the membrane, diffusion experiments have been carried out with a variety of ionic and nonionic permeants.



(a)

Fig. 2 (continued)



(b)

Fig. 2. Scanning electron micrographs of the two different membrane surfaces: (a) smooth surface of diffusion-controlling layer; (b) surface of crosslinked supporting layer.

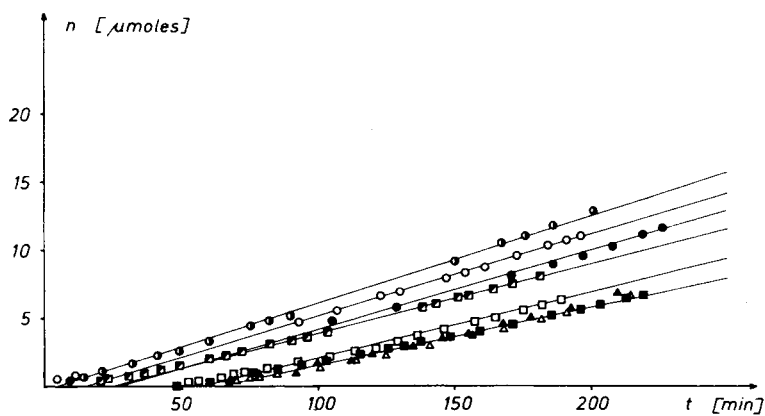


Fig. 3. Time-mass curves for the diffusion of sodium chloride through several membranes which were prepared under identical conditions in "plus" direction. Molar number n is standardized for each experiment on a concentration difference $\Delta c = 1.0$ mole/l.: (\bullet , \circ , \circ) membrane 1, three experiments; (\blacksquare , \square , \square) membrane 2, three experiments; (\blacktriangle , \triangle) membrane 3, two experiments.

TABLE II
Diffusion Coefficients and Preference Factors of Ionic Permeants

Permeant	pH Value of concentrated solution	D , cm ² /sec	$F = D(+)/D(-)$
Sodium chloride	6-7	$4.0 \pm 0.5 \times 10^{-10}$	1.5
Hexamethylenediamine	12	$8.0 \pm 0.5 \times 10^{-8}$	1.1
Hexamethylenediamine 2HCl	4-5	$2.8 \pm 0.7 \times 10^{-10}$	1.3

With electrolytes, a directional flow preference can be observed, i.e., the diffusion rate as calculated from the slope of a mass-time diagram is faster in the direction from the amino endgroup side to the carboxylic endgroup side ("plus direction") than in the opposite "minus" direction. Figure 3 represents the mass-time curves for a set of membranes. The curves are well reproducible. In all cases, the values of the obtained diffusion coefficients agree within 5% to 10% of each other. No relation has been found between the time diffusion lag (intercept between the extrapolation of the straight lines with the time axis) and the diffusion coefficient. Both diffusion coefficient D and preference factor $F = D(+)/D(-)$ differ for different permeants and the pH values of the concentrated salt solutions. The preference factor reaches a maximum value in the neutral region (NaCl diffusion). Diffusion coefficients and preference factors for ionic permeants are given in Table II.

No directional flow preference can be detected with nonionic permeants. For a homologous series of permeants, the diffusion coefficient decreases continuously with increasing molecular volume (Table III).

As already mentioned, the equilibrium water content of the membrane can be varied in a rather wide range simply by changing the salt concentration in the ambient aqueous phase. The dependence of permeability on the hydration level has been studied with methanol using membranes brought into equilibrium with sodium chloride solutions in the concentration range of 0 to 1.0M. The results are given in Table IV and represented in Figure 4. The relations given by Yasuda et al.¹⁴ for the dependence of permeability of water-swollen membranes on their hydration level (free-volume theory) do not apply in this case. However, the relative decrease of the diffusion coefficient $\Delta D/D_{c=0}$ can be correlated quite well with the loss of membrane volume $\Delta V/V_{c=0}$ due to shrinkage (Fig. 5).

A plausible explanation for the directional flow preference in electrolyte dif-

TABLE III
Diffusion Coefficients of Nonionic Permeants

Permeant	V , ml/mole	$D \times 10^8$, cm ² /sec
Water ^a	18.09	0.67 ± 0.04
Methanol	40.49	9.6 ± 0.6
Ethanol	58.37	5.3 ± 0.5
<i>n</i> -Propanol	74.81	3.5 ± 0.6
Isopropanol	76.32	1.5 ± 0.4
Glucose	110.2	0.025

^a Calculated from the kinetics of membrane shrinkage in sodium chloride solutions.^{7,8}

TABLE IV
Dependence of Diffusion Coefficient of Methanol on the Equilibrium Water Content of Membranes Shrunk in Sodium Chloride Solutions

c_{NaCl} , moles/l.	W , %	$D_c/D_{c=0}$	$\Delta D/D_{c=0}$, %	$\Delta V/V_{c=0}$, % ^a
0	91.6	1.00	0	0
0.2	87.8	0.62	38.2	31.4
0.4	85.0	0.58	42.2	44.4
0.6	82.7	0.55	44.8	52.9
0.8	83.4	0.54	45.9	49.6
1.0	81.2	0.39	60.9	57.8

^a Calculated from water content W .^{7,8}

fusion experiments can be given using the results mentioned above and the knowledge of membrane morphology: The rate of diffusion is determined by the distance of chains in the thin dense layer. The crosslinked supporting layer which is grafted on it regulates the membrane hydration level by its swelling properties. Expansion and shrinkage of the crosslinked layer will cause an equivalent variation of pore size in the diffusion determining layer. In the case of electrolyte diffusion in the "plus" direction, the crosslinked layer is separated from the salt solution by the dense layer. Here, the membrane does not shrink and a diffusion coefficient corresponding to a membrane in equilibrium with pure water will be measured.

In the opposite "minus" direction, the membrane shrinks and thus the diffusion coefficient decreases. The following experiment, which is schematically represented in Figure 6, illustrates this concept: In two parallel diffusion experiments, the diffusion of methanol through the membrane from pure water into 0.2M sodium chloride solution was investigated. Under otherwise identical conditions, the diffusion was faster when the salt was adjacent to the dense layer ("plus side") than in the opposite experiment. In the first case, the diffusion coefficient was identical with the value obtained with membranes in equilibrium with pure water. In the second case, it corresponded to the value determined in experiments with membranes shrunk in 0.2M sodium chloride solutions.

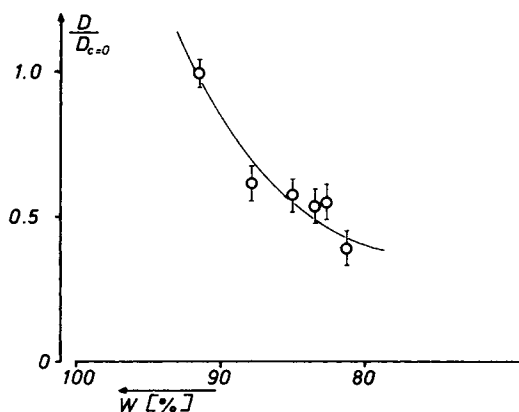


Fig. 4. Dependence of diffusion coefficient D of methanol on hydration level W of the membrane.

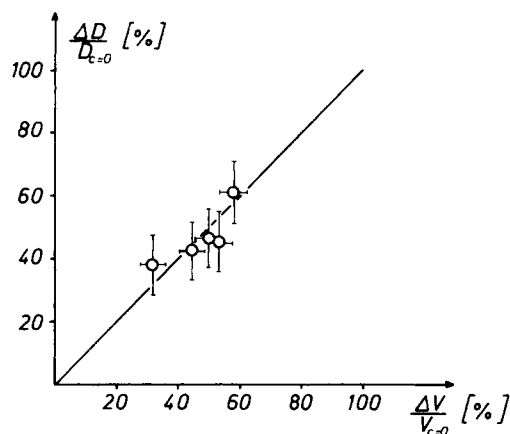


Fig. 5. Correlation between relative decrease of methanol diffusion coefficient $\Delta D/D_{c=0}$ and loss of membrane volume $\Delta V/V_{c=0}$ due to shrinkage in sodium chloride solutions.

Membrane Properties Connected with the Ion Exchange Characteristics of the Membrane

The polyamide membranes contain weak acidic and weak basic endgroups, as a consequence of which they exhibit ion exchange properties. Two factors determine the special characteristics of our membrane:

1. The polyampholyte material exhibits an isoelectric point, and both density and sign of the fixed charge can be changed by the pH value in the ambient solution.

2. The special mechanism of membrane formation by interfacial polycondensation gives rise to an asymmetric spatial distribution of endgroups, i.e., the surface of the dense diffusion-determining layer bears only amino endgroups; the opposite surface is rich in carboxylic acid endgroups. Between the surfaces, both density and sign of the fixed charge change in a continuous manner from anion exchange to cation exchange properties.^{7,8} Such a laminar combination

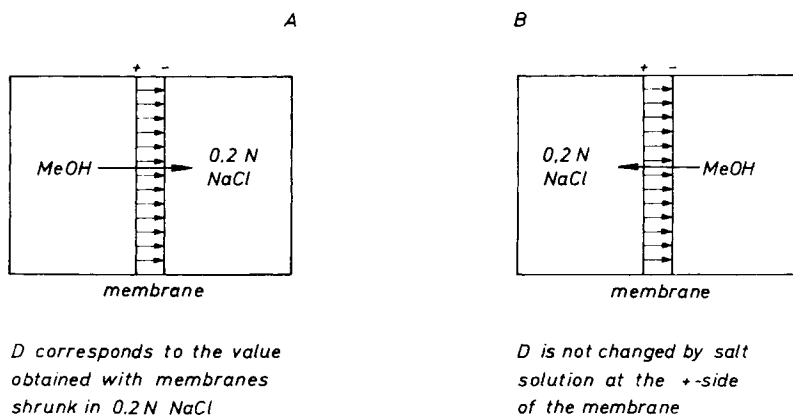


Fig. 6. Directional flow preference observed in experiments with methanol diffusing through the membrane into salt solutions.

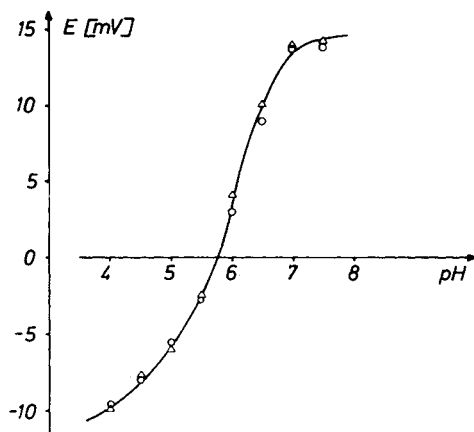


Fig. 7. Dependence of membrane potential E on pH value in the ambient solutions at a fixed concentration ratio of 2.0: (O) $c_+/c_- = 2.0$; (Δ) $c_+/c_- = 0.5$ (c_+ = salt concentration at the smooth surface; c_- = concentration at the opposite surface).

of cationite and anionite regions is called a “bipolar double membrane” and should exhibit rectifier properties when a current is passed through it.^{15,17}

The amphoteric character of the membrane is clearly demonstrated by the strong dependence of the membrane potential on the pH value of the outer solution (Fig. 7). At high pH values, the membrane bears a negative fixed charge and is, to varying degrees, cation selective. At low pH values, the charge is positive and the membrane behaves like an anion exchanger. At a pH of 6, there is no net charge within the membrane. Here, at its isoelectric point, the polyampholyte presumably exists partly in a zwitterionic form. By measuring the concentration potential in hydrochloric acid (0.2*N*–0.1*N*) and in sodium hydroxide (0.2*N*–0.1*N*), permselectivities in the acidic and basic regions of 0.9 and 0.8, respectively, were determined.

The pH value has also a marked effect on the area resistance of the membrane (Fig. 8). The area resistance was measured in 0.1*N* buffered sodium chloride

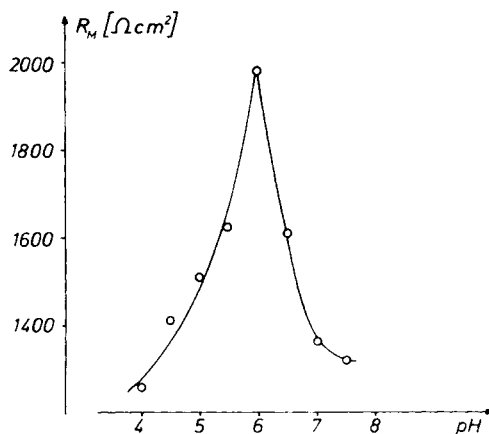


Fig. 8. Dependence of membrane area resistance R_M on pH value in 0.1*N* buffered sodium chloride solutions.

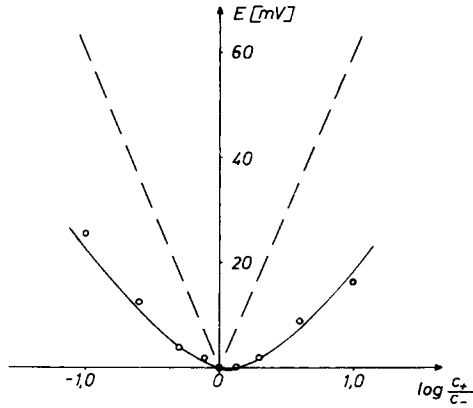


Fig. 9. Dependence of membrane potential on logarithm of concentration ratio $\log(c_+/c_-)$ (solid line). Broken lines: Nernst straight lines for cation exchange and anion exchange membranes.

solutions. At the isoelectric point, free charges carrying gegenions are at a minimum and the resistance rises to a sharp maximum. Figure 9 shows the dependence of the concentration potential in sodium chloride solutions on the concentration difference on both sides of the membrane. The typical parabolic

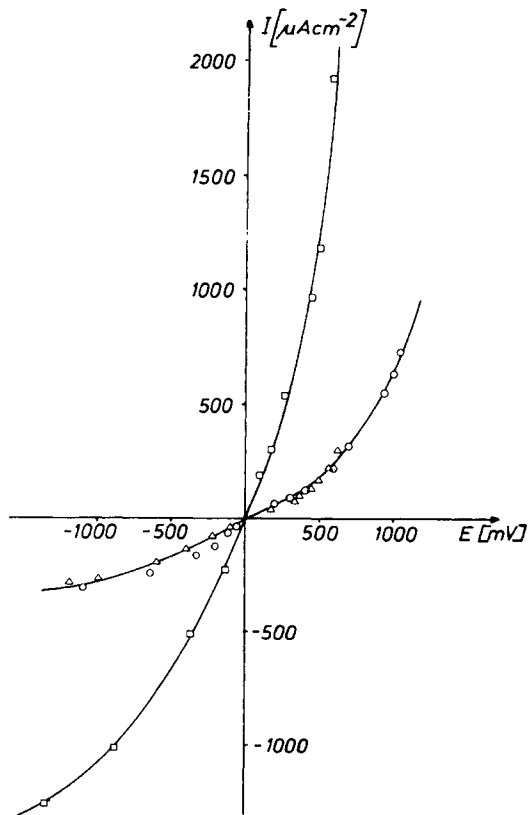


Fig. 10. Stationary current-voltage characteristics of membrane in sodium chloride solutions: (O, Δ) $c = 0.01$ mole/l.; (\square) $c = 0.1$ mole/l.

dependence of the concentration potential on the logarithm of the concentration ratio which has been derived for bipolar double membranes¹⁷ has been observed.

Being an ionic analogue to the semiconducting plane diode, a bipolar double membrane should exhibit nonlinear current-voltage characteristics.¹⁵ The stationary current-voltage characteristics measured in two different sodium chloride solutions are represented in Figure 10. Outside a rather wide linear range (about from -500 to +500 mV), the curves are asymmetric. No nonstationary current-voltage characteristics could be obtained. The transition from blocking to transmitting requires about 1 min. This somewhat low rectifying effect is due to two reasons. First, the concentration of fixed charges is quite low. Second, there is no step junction between the two phases but a rather continuous change from cationite to anionite region.

CONCLUSIONS

Asymmetric polymer membranes of controlled structure and gradient of inhomogeneity can be prepared by interfacial polycondensation. By choosing suitable reaction conditions, a variety of membranes with different properties can be fabricated which could be utilized in separation processes such as reverse osmosis, ion exchange, or dialysis.

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