

## Specific Resistances of Hydrophilic Membranes Containing Ionogenic Groups

J. VACÍK and J. KOPEČEK, *Institute of Macromolecular Chemistry,  
Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia*

### Synopsis

This paper deals with an investigation of the dependence of specific resistances on pH for hydrophilic membranes containing ionogenic groups. Membranes based on poly(2-hydroxyethyl methacrylate) crosslinked with ethylene dimethacrylate were investigated. This basic structure was modified by copolymerization with ionogenic comonomers, i.e., methacrylic acid and/or diethylaminoethyl methacrylate. It is shown that the dependence of the specific resistance on pH passes through a maximum for cation-active membranes at  $\text{pH} \sim 3.5$ , for anion-active membranes at  $\text{pH} \sim 10$ , and for ampholytic membranes at  $\text{pH} \sim 6$ . The effect of the content of ionogenic groups, network density, and the degree of neutralization of membranes on the above dependence is discussed. In the final part of the paper the results are compared with more hydrophilic systems based on poly(2-hydroxyethyl acrylate) and it is shown that maxima in the dependence of specific resistances on pH can be suppressed by increasing the hydrophilicity of polymers.

### INTRODUCTION

Some time ago we investigated the properties of hydrophilic membranes containing ionogenic groups. We found that the introduction of weakly acidic and/or weakly basic groups into a hydrophilic polymer based on poly(2-hydroxyethyl methacrylate) strongly affects the diffusivity of inorganic salts through the polymer.<sup>1</sup> We also showed that the copolymerization of hydrophilic and hydrophobic monomers with a markedly different hydrophilicity supports the formation of heterogeneities in a three-dimensional network, which in turn influences the transport properties of these systems.<sup>2</sup> We also studied the effect of the content of ionogenic groups and network density of such membranes on concentration potentials.<sup>3</sup> In this paper we investigate membrane resistances of membranes based on (2-hydroxyethyl methacrylate)(HEMA) crosslinked with ethylene dimethacrylate (EDMA) which were modified by introducing weakly acidic and/or weakly basic groups. Methacrylic acid (MAA) and diethylaminoethyl methacrylate (DEAEMA), respectively, were used as carriers of weakly acidic and weakly basic groups. For all groups of membranes investigated—neutral (copolymers of HEMA–EDMA), acidic (copolymers of HEMA–EDMA–MAA), basic (copolymers of HEMA–EDMA–DEAEMA), and ampholytic (copolymers of HEMA–EDMA–MAA–DEAEMA)—we studied the dependence of the specific resistance of membranes on the content of ionogenic groups in the copolymer, on network den-

sity, pH, and temperature. In order to verify our starting assumptions used in the interpretation of the dependences measured, we also investigated membranes based on (2-hydroxyethyl acrylate) and those in which the acidic component was represented by acrylic acid, i.e., membranes having a similar structure but without substitution on the  $\alpha$ -carbon atom of the acrylic unit.

## EXPERIMENTAL

### Materials

(2-Hydroxyethyl methacrylate) was prepared by alkaline re-esterification of methyl methacrylate with ethyleneglycol. Diester (EDMA) was removed from the reaction mixture which was diluted with water, by several extractions with hexane; monoester (HEMA) was then extracted with ether. Purity was checked by the saponification number and gas chromatography. (bp  $79^{\circ}\text{C}/4$  torr;  $n_D^{20} = 1.4525$ .)

(2-Hydroxyethyl acrylate)(HEA), a product of Dow Chemical Corp., was used. Diester was removed from the raw product in a manner similar to HEMA extraction. This was followed by distillation *in vacuo* (three times). (bp  $52^{\circ}\text{C}/0.3$  torr;  $n_D^{20} = 1.4503$ .)

Ethylene dimethacrylate, a Chemapol product, was freed from hydroquinone with 5% NaOH. Upon drying with annealed  $\text{Na}_2\text{SO}_4$  it was distilled *in vacuo* three times. Purity was checked by gas chromatography and infrared spectrometry (absence of the  $-\text{OH}$  groups). (bp  $84^{\circ}\text{C}/1$  torr;  $n_D^{20} = 1.4549$ .)

Methacrylic acid, a Fluka product, was recrystallized from ethanol and rectified; its purity was checked by gas chromatography. (bp  $59^{\circ}\text{C}/10$  torr;  $n_D^{20} = 1.4314$ ; mp  $15.5^{\circ}\text{C}$ .)

Acrylic acid (AA), a Fluka product, was recrystallized from ethanol and rectified. (bp  $48.5^{\circ}\text{C}/15$  torr;  $n_D^{20} = 1.4224$ ; mp  $12.3^{\circ}\text{C}$ .)

2-Diethylaminoethyl methacrylate was prepared by alkaline re-esterification of methyl methacrylate with 2-(diethylamino) ethanol. The raw product was rectified. Purity was checked by gas chromatography. (bp  $80^{\circ}\text{C}/10$  torr;  $n_D^{20} = 1.4435$ .)

[2,2'-Azobis(methyl isobutyrate)] was obtained by saponification of (2,2'-azobisisobutyronitrile) with hydrogen chloride in a methanol solution. The precipitated iminoether hydrochloride was hydrolyzed with water at  $35^{\circ}\text{C}$ . The raw product was recrystallized five times from petroleum ether (mp  $30^{\circ}\text{C}$ ).

### Preparation of Membranes

The membranes were prepared by polymerization between two plane-parallel plates, one quartz and the other Teflon. The polymerization was carried out at  $25^{\circ}\text{C}$  for 16 hr with an ultraviolet high-pressure mercury discharge lamp (Osram HQE40L); [2,2'-azobis(methyl isobutyrate)] was the initiator. Upon completion of polymerization the membranes were conditioned in distilled water for two weeks. Before the experiment the membranes were conditioned several days in respective solutions. The compositions of the membranes are given in Tables I and II.

TABLE I  
Composition of Membranes Based on Poly(2-hydroxyethyl Methacrylate)<sup>a</sup>

Membrane no.	(2-Hydroxyethyl methacrylate), mole-%	DEAEMA, mole-%	MAA, mole-%	EDMA, mole-%
47	95.36	—	2.64	2.00
50	82.75	—	15.25	2.00
51	78.07	—	19.93	2.00
52	68.05	—	29.95	2.00
71	68.40	—	31.15	0.45
72	65.95	—	31.05	3.00
73	62.80	—	31.20	6.00
74	99.96	—	—	0.04
75	98.00	—	—	2.00
54	95.11	2.89	—	2.00
57	82.25	15.75	—	2.00
58	78.53	19.47	—	2.00
59	94.80	1.60	1.60	2.00
60	92.94	2.52	2.54	2.00
62	82.80	7.61	7.54	2.00
63	77.09	10.32	10.53	2.00

<sup>a</sup> Polymerized in presence of 20 vol-% butanol. [2,2'-Azobis(methyl isobutyrate)] =  $1.7 \times 10^{-2}$  mole/l. Thickness of membranes, ~0.1 mm. The other details are given in the "Experimental" section.

TABLE II  
Composition of Membranes Based on Poly(2-hydroxyethyl Acrylate)<sup>a</sup>

Membrane no.	(2-Hydroxyethyl acrylate), mole-%	MAA, mole-%	AA, mole-%	EDMA, mole-%
76	97.73	0.60	—	1.67
84	78.59	19.74	—	1.67
78	68.05	30.28	—	1.67
85	69.48	30.10	—	0.42
86	68.49	30.10	—	1.41
87	66.45	30.10	—	3.45
89	70.04	—	29.55	0.41
90	69.31	—	29.55	1.14
91	98.22	—	—	1.78

<sup>a</sup> For details of membrane preparation, see Table I and "Experimental" section.

## Procedures

### *Determination of Specific Resistance of Membranes*

The specific resistance of the membranes was determined in a cell<sup>4</sup> shown in Figure 1. The flow system guaranteed perfect stirring near the membrane surface. If not otherwise stated, all measurements were performed at 25°C in buffered 0.1N NaCl solutions. The specific resistance was calculated from

$$\rho_M = (R_t - R_s) A/D \quad (1)$$

where  $\rho_M$  is the specific resistance of the membrane ( $\Omega \times \text{cm}$ ),  $R_t$  is the resis-

tance of the solution plus the membrane ( $\Omega$ ),  $R_s$  is the resistance of the solution ( $\Omega$ ),  $A$  is the measured area of the membrane ( $\text{cm}^2$ ), and  $D$  is the thickness of the membrane (cm).

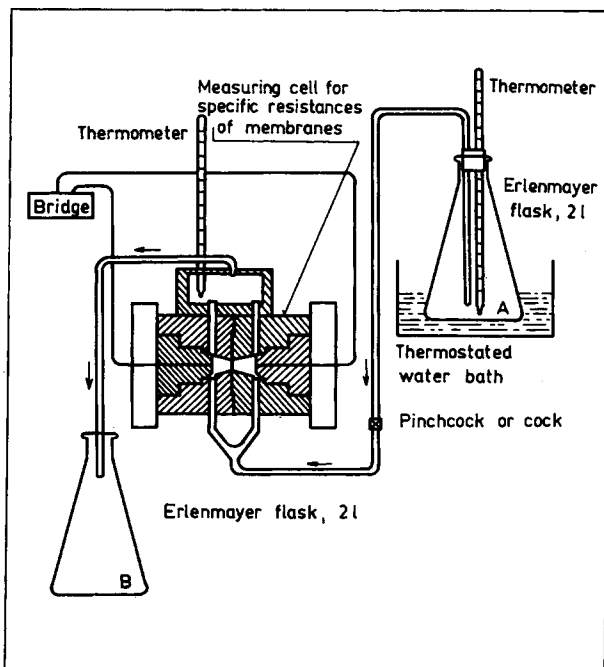


Fig. 1. Apparatus for measuring specific resistances of membranes.

Composition of the solution: 0.2474-g  $\text{H}_3\text{BO}_3$ ; 0.4655-g  $\text{H}_3\text{PO}_4$  (85%); 0.240-g  $\text{CH}_3\text{COOH}$  (glacial);  $\times$  ml 0.2N NaOH; 11.688-g NaCl; completed with  $\text{H}_2\text{O}$  to 2.000 ml.

#### *Determination of Titration Curves of Polymers under Investigation*

Titration curves were determined for selected polymers having a composition corresponding to the membranes under investigation. All titrations were carried out with a pH-meter (Philips PR9403) by using a hand-operated doser (Metrohm E457) allowing dosage with an accuracy of 0.0001 ml. All titrations were performed in a nitrogen atmosphere in the presence of 0.1N  $\text{NaNO}_3$ . The degree of neutralization was calculated from the condition of electroneutrality:

$$\alpha = (C_a + C_{\text{H}^+} - C_{\text{OH}^-})/C_M \quad (2)$$

where  $C_a$  is the concentration of sodium ions after addition of NaOH,  $C_{\text{H}^+}$  is the concentration of hydrogen ions,  $C_{\text{OH}^-}$  is the concentration of hydroxyl ions, and  $C_M$  is the total concentration of ionogenic groups in the titrated polymer.  $C_{\text{H}^+}$  and  $C_{\text{OH}^-}$  were calculated from the measured value of pH. Correction for the activity coefficients was neglected.

*Determination of the Degree of Equilibrium Swelling*

The degree of equilibrium swelling was determined by a procedure described earlier.<sup>1</sup>  $v_2$  is the volume fraction of the polymer in a gel swollen to equilibrium.

**RESULTS AND DISCUSSION**

It should be pointed out at the beginning that the majority of the figures contain dependences of specific resistances for cation-active, anion-active, and ampholytic membranes of a respective composition so that the reader may easily compare the dependences of all types of membranes. To make the discussion more understandable, the individual types of membranes must be discussed separately.

**Cation-Active Membranes**

The dependence of the specific resistance on the content of ionogenic groups for cation-active membranes (copolymer HEMA-EDMA-MAA) is

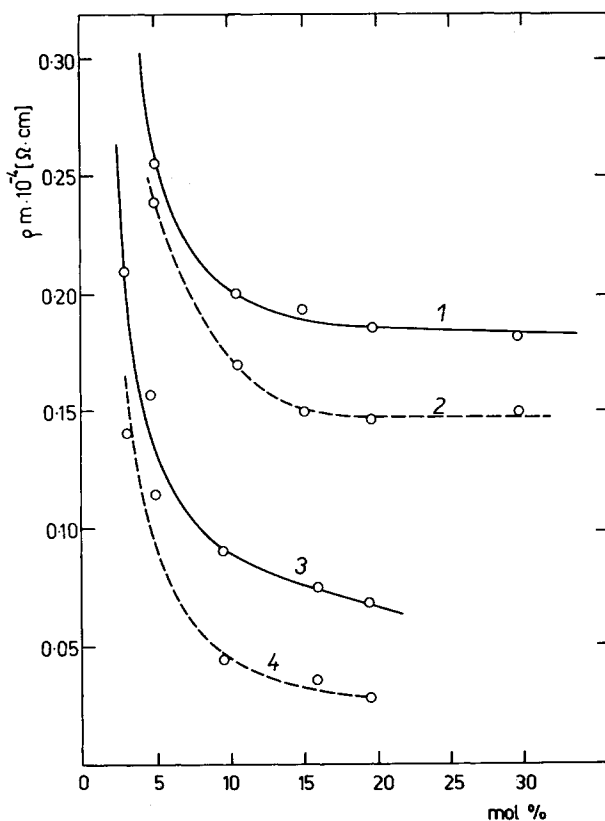


Fig. 2. Dependence of specific resistances of membranes ( $\Omega \times \text{cm}$ ) on the content of ionogenic components (mole-%). Copolymer (2-hydroxyethyl methacrylate)-2.0-mole-% EDMA-MAA: 1 = measured in 0.05M NaCl; 2 = measured in 0.1M NaCl. Copolymer (2-hydroxyethyl methacrylate)-2.0-mole-% EDMA-DEAMA: 3 = measured in 0.05M NaCl; 4 = measured in 0.1M NaCl.

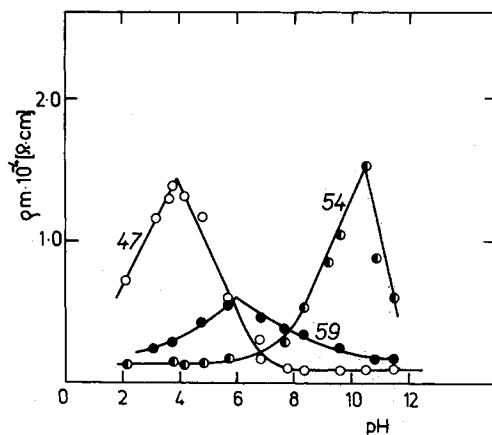


Fig. 3. Copolymers of (2-hydroxyethyl methacrylate) and EDMA with monomers containing ionogenic groups. Dependence of specific resistance of membranes on pH. Compositions of membranes 47, 54 and 59 given in Table I.

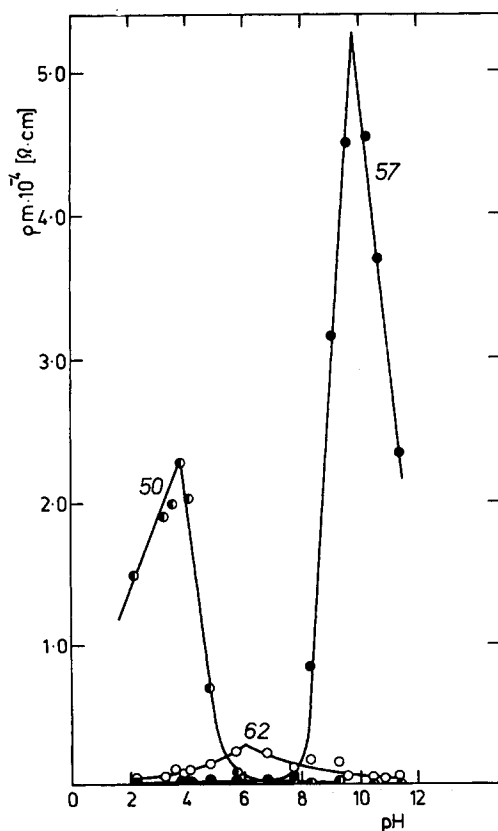


Fig. 4. Copolymers of (2-hydroxyethyl methacrylate) and EDMA with monomers containing ionogenic groups. Dependence of specific resistance of membranes on pH. Compositions of membranes 50, 62, and 57 given in Table I.

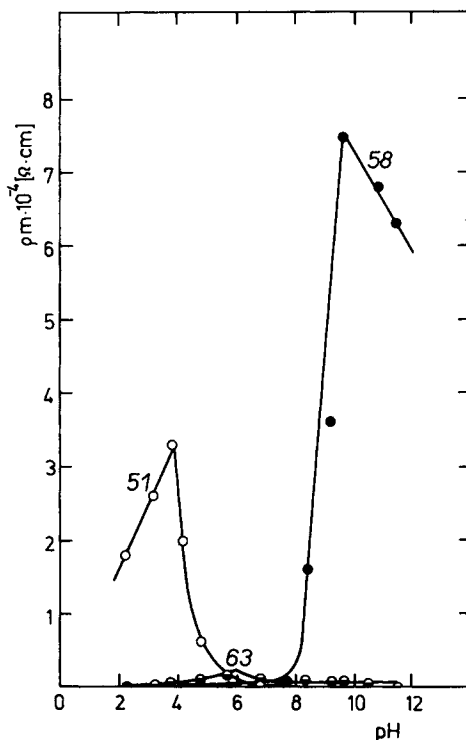


Fig. 5. Copolymers of (2-hydroxyethyl methacrylate) and EDMA with monomers containing ionogenic groups. Dependence of specific resistance of membranes on pH. Compositions of membranes 51, 58 and 63 given in Table I.

shown in Figure 2. (This dependence was measured in unbuffered solutions.) With increasing concentration of the ionogenic component, the specific resistance decreases. This effect is most marked at a lower content of the ionogenic component. The dependence is in agreement with the permeation coefficients of the same membranes.<sup>1</sup> A further increase in the content of the —COOH groups in the copolymer has little effect on the specific resistance. Similar conclusions were also obtained when the permselectivity of membranes was measured as a function of the content of ionogenic groups.<sup>3</sup>

We also studied the dependence of the specific resistance on pH. The experimental results for cation-active membranes (crosslinked with EDMA) with increasing content of MAA (for compositions of membranes, see Table I) are given in Figures 3–5. The results clearly demonstrate that in the region pH 1.5–3.5 the specific resistance increases and passes through a maximum at pH 3.5–4. After this, the specific resistance steeply decreases and, starting from pH 6–7 and more, remains at a constant low value.

The interpretation of the curves in the region pH > 3.5, i.e., beyond the maximum, is obvious. Here we have a change in the degree of ionization of the membrane with a change of pH (see Fig. 6). In the region pH > 7 the specific resistance is virtually constant and low because of a considerable ionization of fixed charges. In the pH region of 7 to 3.5, the ionization of MAA gradually decreases; this has as a consequence also a deswelling of the polymer matrix. At the same time the electrolyte concentration in the membrane

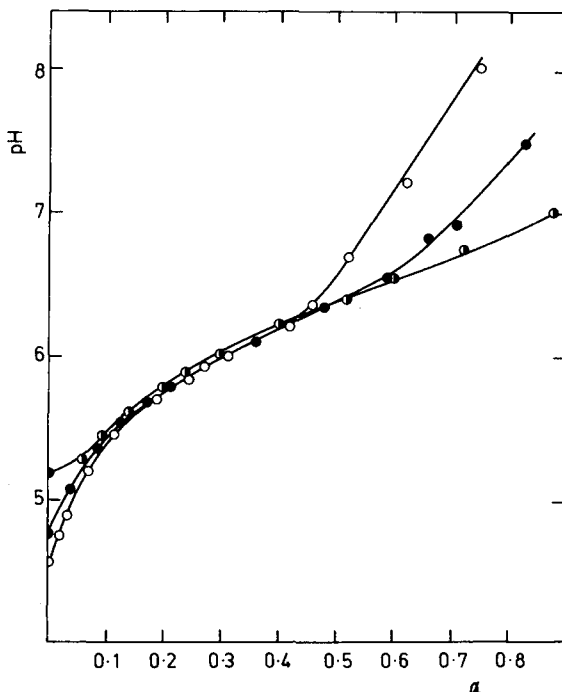


Fig. 6. Copolymers of (2-hydroxyethyl methacrylate)-2.0-mole-% EDMA-MAA. Dependence of the degree of neutralization ( $\alpha$ ) on pH of the ambient medium for copolymers having different content of MAA:  $\circ$  = copolymer 47;  $\bullet$  = copolymer 50;  $\circ$  = copolymer 52. Compositions of membranes given in Table I.

phase decreases and the specific resistance steeply increases. The changes in  $\rho_M$  in this region are more pronounced, the higher the concentration of MAA in the polymer (Figs. 3-5). The change in the degree of ionization of the membrane leads to a change in the equilibrium degree of swelling (Fig. 7). Figure 7 supplements the swelling data of the polymers studied which have been published in Table II of reference 1. It is evident that for basic membranes the dependence of the volume fraction of the polymer in the equilibrium swollen state ( $v_2$ ) on pH is essentially linear in the range of pH studied. Basic membranes (Fig. 7, membrane 54) deswell with increasing pH. Acidic membranes (Fig. 7, membrane 50) slightly change their degree of swelling in the region of low pH values. By increasing the neutralization degree, the degree of swelling is sharply increased (the value  $v_2$  decreases). The behavior of ampholytic membranes (Fig. 7, membrane 62) is a combination of the properties of acidic and basic membranes.

Besides the change in the equilibrium degree of swelling, one must also admit the effect of the change in the ratio of free and bonded water in the polymer in favor of bonded water;<sup>5</sup> this has as a consequence a limitation of the transport of salts through the membrane, and thus its resistance is increased. It is necessary to take into account also the possibility of preferential sorption of acidic components of the buffer solution in the region of low values of pH.

The decrease in  $\rho_M$  in the region of very low pH (see Figs. 3-5) can be interpreted by an increased effect of the concentration of protons on the trans-



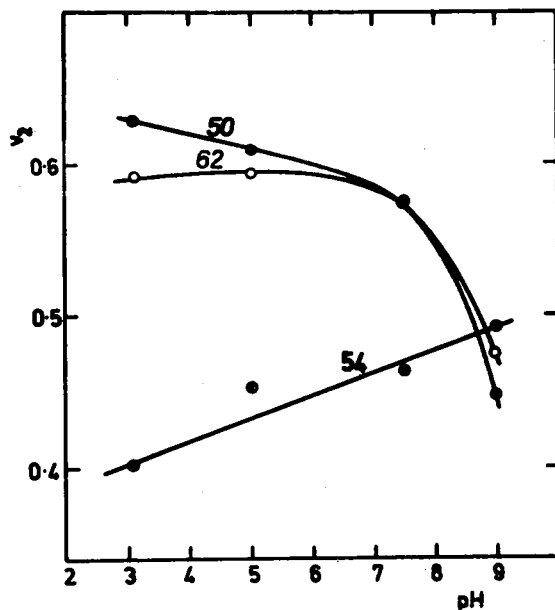


Fig. 7. Dependence of the change in the equilibrium degree of swelling ( $v_2$ ) on pH. Compositions of polymers 50, 54, and 62 given in Table I.

port of electric current in this region of pH. The increase in the concentration of  $H^+$  is also reflected in a decrease in the resistance of solution (0.1M NaCl + buffer solution) in this region of pH. The properties of membranes investigated in this region of pH will be strongly affected by the increased concentration of hydrogen protons, because they contain a large amount of hydroxyl groups and are therefore able to form hydrogen bonds. The decrease in the specific resistance of membranes in this region is also assisted by the faster transport of hydrogen protons. (Compared with  $Na^+$ ,  $H^+$  is approximately seven times more mobile.)

The literature offers only few data for the specific resistances of membranes in these regions of pH. Kertész and co-workers<sup>6-8</sup> studied cation-active membranes containing strongly acidic groups, the matrix of which was hydrophobic. They also observed maxima in the  $\rho_M$  versus pH dependence. The decrease in ionization connected with the decrease in hydration leads also to changes in resistances. (Changes are considerably higher, even up to five orders of magnitude compared with the membranes investigated in this work, obviously because of the hydrophobic matrix.) The maxima on curves in low pH regions were suppressed by measuring in solutions having the same ohmic value.

We also measured the dependence of  $\rho_M$  on pH in iso-ohmic solutions with  $R = 200 \Omega$ . The copolymers of HEMA-EDMA-MAA (See Table I) have the same  $\rho_M$  versus pH dependence as in measurements in solutions of different resistance.

It may be deduced from the results given above that the interpretation of maxima by affirming that  $\rho_M$  follows the course of resistance of the solution depending on pH is insufficient. To verify this assumption we studied the behavior of membranes with different network densities and different hy-

drophilicities (see below). The results of these measurements confirm our assumption that a mere increase in the hydrophilicity of the polymeric backbone is sufficient for suppressing maxima on the  $\rho_M$  versus pH dependence. The maxima of these dependences can also be considerably reduced by using a better solvent (swelling agent) of the polymer (ethanol-water).

### Dependence of the Specific Resistance of Cation-Active Membranes on Network Density

Figure 8 shows that the resistance of the membrane strongly increases with increasing network density. The total character of the curve remains unchanged; the maxima are more pronounced. To stress this phenomenon, we chose for measurements of the above dependence, membranes with 30 mole-% of MAA in the initial polymerization mixture and three different network densities (membranes 71, 72, 73—for compositions, see Table I). The increased network density contributes to a decrease in the hydrophilicity of the membrane and also to a decrease in the free volume in the membrane.<sup>1</sup> The decrease in the salt concentration inside the membrane then markedly raises its resistance. It can be seen from the values given in Figure 6 that in the region pH = 3.5 the resistance of the cation-active membrane containing 30 mole-% MAA increases three to four times compared with a neutral mem-

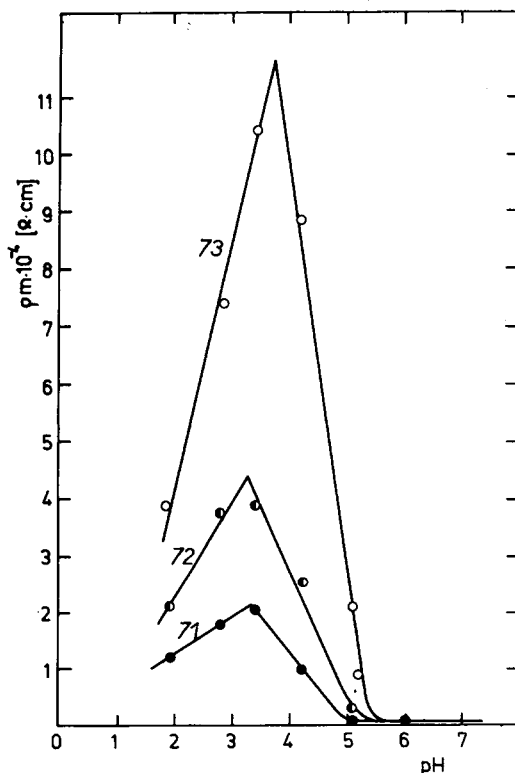


Fig. 8. Copolymers of (2-hydroxyethyl methacrylate), EDMA, and MAA with different network densities. Dependence of specific resistance of membranes on pH. Compositions of membranes 71, 72, and 73 given in Table I.

brane, while an increase in the concentration of the crosslinking agent from circa 2 mole-% to 6 mole-% leads to an increase in the membrane resistance by one order of magnitude.

### Specific Resistance of Cation-Active Membranes Based on Poly(2-Hydroxyethyl Acrylate)

The dependence of the specific resistance on pH for membranes based on poly(2-hydroxyethyl acrylate) is different from that for membranes based on poly(2-hydroxyethyl methacrylate). The HEA-AA copolymers do not virtually exhibit any maxima in the  $\rho_M$  versus pH dependence. Unpronounced maxima are found for the HEA-MAA copolymers. A comparison of the above dependences for both types of copolymers as a function of network density is given in Figure 9. It is obvious that in both cases there is an increase in the membrane resistance with decreasing ionization of the ionogenic component, but in the case of acrylic acid the increase in resistance is not pronounced. It should be stressed, however, that also for the HEA-MAA copolymer the increase in resistance is much less pronounced than for the HEMA-MAA copolymer. An explanation of the phenomena observed

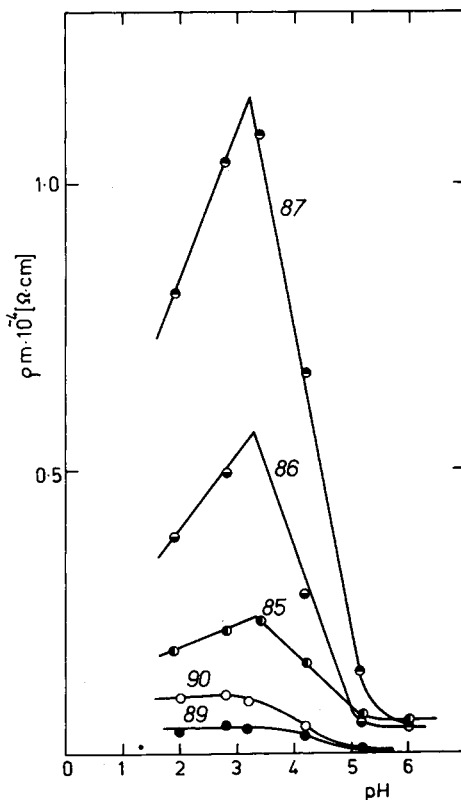


Fig. 9. Copolymers of (2-hydroxyethyl acrylate), EDMA, and AA (89, 90); and copolymers of (2-hydroxyethyl acrylate), EDMA, MAA (85, 86, 87) with different network densities. Dependence of specific resistance of membranes on pH. Compositions of membranes 85, 86, 87, 89, 90 given in Table II.

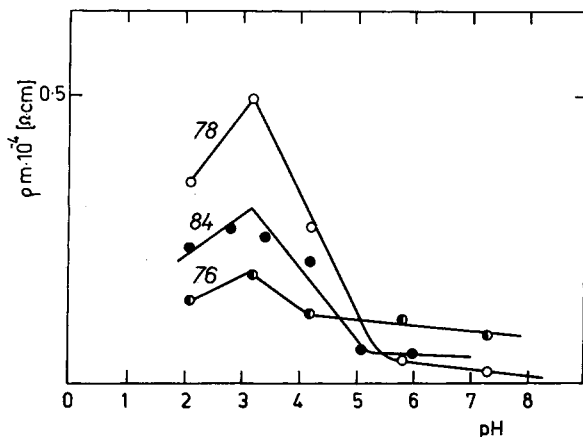


Fig. 10. Copolymers of (2-hydroxyethyl acrylate), EDMA, and MAA with different MAA content. Dependence of specific resistance of membranes on pH. Compositions of membranes 76, 78, and 84 given in Table II.

should be looked for in a different hydrophilicity of the systems under investigation. In the most hydrophilic polymer (copolymer HEA + AA) the lowest pH values do not reflect the effect of the increasing concentration of hydrogen ions, because the membrane contains a sufficient amount of water and, thus, also of electrolyte for the transport of electric current. If the  $\rho_M$  versus pH dependence for membranes 89 and 90 is replotted on a larger scale, for these membranes, too, an insignificant indication of maxima can be observed in the region  $\text{pH} \sim 3$ . A considerable effect of the concentration of the crosslinking agent, and thus also of network density on the membrane re-

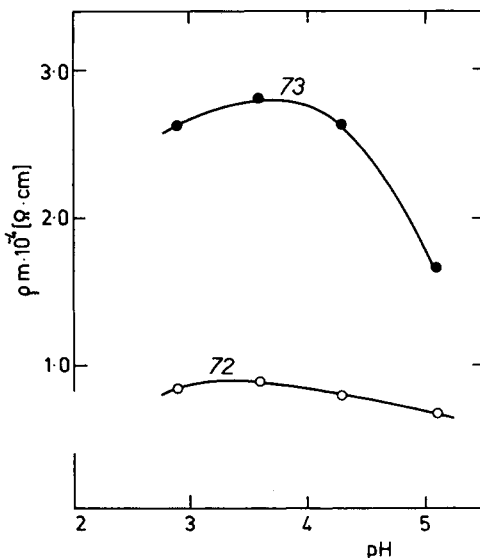


Fig. 11. Copolymers of (2-hydroxyethyl methacrylate), EDMA, and MAA. Dependence of specific resistance of membranes on pH (not corrected) in ethanol-water solutions (1:1). Compositions of membranes 72 and 73 given in Table I.

sistance, is caused by a decrease in the free volume in the membrane as discussed earlier.

The hydrophilicity of the polymer backbone can also be influenced by a change in the concentration of the ionogenic component in the membrane. In this case too, the transport of current by means of hydrogen ions in the low pH region will be rather pronounced. Figure 10 shows the  $\rho_M$  versus pH dependence for the HEA copolymer with increasing MAA concentration (for membrane composition, see Table II). The decisive role of the hydrophilicity of the polymer backbone, and thus of the degree of equilibrium swelling and of salt permeability, in the  $\rho_M$  versus pH function is borne out by the results summarized in Figure 11. This function was measured in an ethanol-water (1:1) solvent for two different concentrations of the crosslinking agent and for the membranes consisting of the HEMA-MAA-EDMA copolymer (compositions given in Table I). Because of the higher swelling of the membrane in this mixed solvent, the maxima on the curve are suppressed. The system behaves more or less as membranes based on poly(2-hydroxyethyl acrylate).

It may be summarized, therefore, that the degree of hydrophilicity of the polymeric backbone and the free-water fraction in the membrane derived therefrom<sup>5,9</sup> plays a decisive role in the shape of the  $\rho_M$  versus pH dependence in the low pH region.

### Anion-Active Membranes

The dependence of the specific resistance for anion-active membranes (copolymers of HEMA-EDMA-DEAEMA) on the concentration of ionogenic groups in the membrane for two electrolyte concentrations is given in Figure 2. The curves fit in with the results obtained both by measurements with the cation-active membranes and by measurements of the permselectivities of the membranes. In the low-concentration region of ionogenic groups the effect of the DEAEMA content is more pronounced than for the cation-active membranes (Fig. 2). This is obviously because the dependences were measured in unbuffered solutions. The deviations observed in the investigation of the dependence of specific resistance on pH (see below) were not so pronounced.

Figures 3 through 5 show dependences of  $\rho_M$  on pH. It can clearly be seen therefrom that the dependences obtained for the anion-active membranes also pass through a maximum. Starting from low pH values up to pH  $\sim 7$ , the specific resistance is low and constant; for pH  $> 7$ ,  $\rho_M$  increases up to a maximum that lies approximately at pH = 10. This phenomenon is caused by a decrease in ionization and a deswelling of the polymer matrix connected with it. At a pH higher than 10 the specific resistance steeply decreases. The figures clearly demonstrate that the maxima are higher than for the cation-active membranes of a corresponding composition.

The reason for the above finding consists in a higher hydrophobicity of the basic component compared with the acidic component;<sup>1</sup> and this leads to a larger deswelling of anion-active membranes with a change in pH (Fig. 7). Several factors contribute to the decrease in the resistance of the anion-active membranes at high pH: (1) the deswelling (already mentioned) of the poly-

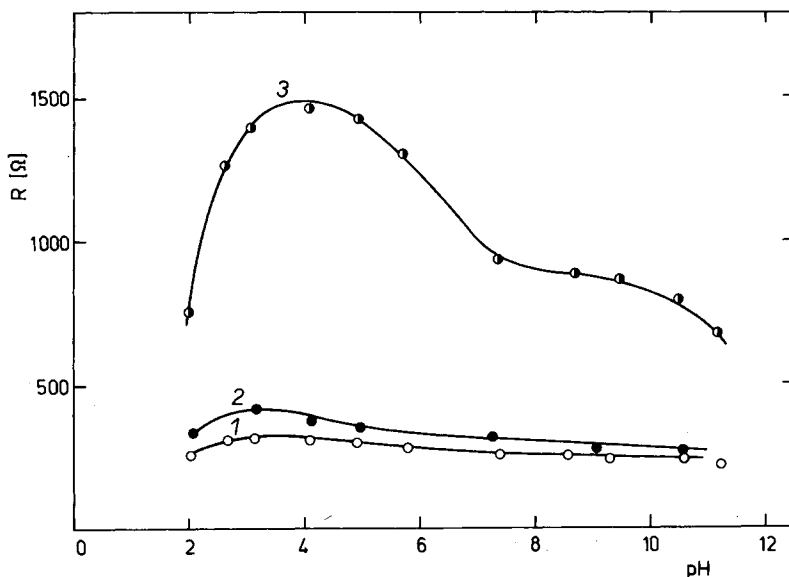


Fig. 12. Dependence of resistances of neutral polymers and solution on pH: 1 = solution (composition given in "Experimental"); 2 = copolymer of (2-hydroxyethyl acrylate)-EDMA (membrane 91—composition given in Table II); 3 = copolymer of (2-hydroxyethyl methacrylate)-EDMA (membrane 75—composition given in Table I).

mer matrix, then (2) the increased participation of the  $\text{OH}^-$  ions in the passage of current through the membrane at the pH used in the investigation, and also (3) the possibility of ionization of alcoholic groups of the basic poly(2-hydroxyethyl methacrylate) skeleton (Fig. 12). This figure shows that the resistance of the neutral membrane decreases at high pH without having passed through a maximum in the alkaline region. Such a course indicates the phenomenon discussed above. As to the increased contribution of the  $\text{OH}^-$  ions to the membrane conductivity at  $\text{pH} > 10$ : it may be interpreted similarly to the effect of the  $\text{H}^+$  ions in the low pH region on the decrease in the resistance of the cation-active membranes.

### Ampholytic Membranes

As has been said in the Introduction to this paper, the specific resistances of the ampholytic membranes had also been studied (copolymers of HEMA-EDMA-MAA-DEAEMA). Figures 3 through 5 show the  $\rho_M$  versus pH dependence for the ampholytic membranes with various contents of ionogenic groups [(MAA) = (DEAEMA): for compositions of membranes, see Table I]. One can see that the dependence passes through a maximum at  $\text{pH} = 6.1$ , which is the isoelectric-point value<sup>10</sup> determined by Jacobson. Thus, the results confirm the structure of the internal salt in these copolymers as discussed above.

The height of the maxima decreases with increasing content of the ionogenic component. This phenomenon, too, confirms the existence of the internal salt. On both sides of the maximum the specific resistance of the membranes decreases. This phenomenon can be interpreted by an increase in the content of mobile counterions in the membrane on both sides of the

isoelectric point. This is in accord with the dependence of the permeability of these membranes on pH discussed earlier.<sup>1</sup> The results demonstrate that the method for measuring the  $\rho_M$  versus pH dependence allows very exact determination of the position of the isoelectric point for crosslinked polyelectrolytes.

### Neutral Membranes

For comparison with membranes containing ionogenic groups we also measured resistances of neutral membranes, based both on HEMA (Figs. 12 and 13) and on HEA (Fig. 13). The results show that not only hydrophilicity of the polymer matrix (see curves 2 and 3, Fig. 12) but also the free volume in the membrane (Fig. 13) plays a decisive role in the specific resistance in the membrane. The specific resistance also passes through a maximum at low pH in the case of the neutral membranes based on HEMA (Fig. 13), but this maximum is much lower than for the cation-active membranes. In the region of high pH the dissociation of the alcoholic group of the basic monomer obviously predominates and this causes a monotonic decrease in the specific resistance, with increasing pH. For lower network densities (membrane 74, Fig. 13) these dependences exhibit a much less pronounced course because of the larger free volume in the membrane.<sup>1,5,9</sup>

Figure 12 also shows the effect of the equilibrium effect of swelling on the  $R$  (resistance,  $\Omega$ ) versus pH function. Although in the copolymer based on HEA and strongly swollen with water, the course of the above function prac-

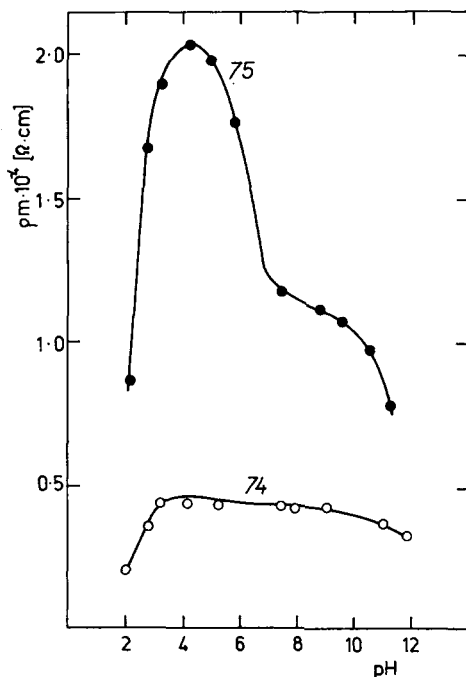


Fig. 13. Copolymers of (2-hydroxyethyl methacrylate) and EDMA with different network densities. Dependence of specific resistance of membranes on pH. Compositions of membranes 74 and 75 given in Table I.

tically does not differ at all from that in the solution, in the case of the low-swollen copolymer based on HEMA (curve 3, Fig. 12), at low pH the transport of the current via more mobile hydrogen protons becomes operative.

## CONCLUSIONS

The cation-active, anion-active, ampholytic, and neutral membranes based on (2-hydroxyethyl methacrylate) and (2-hydroxyethyl acrylate) were characterized by the dependences of specific resistances on pH, on the content of ionogenic groups in the copolymer, on network density, and on temperature.

It was shown that the dependence of  $\rho_M$  of the cation-active membranes on pH passes through a maximum in the region  $\text{pH} \sim 3.5$ . This phenomenon was interpreted by a change in the degree of ionization of the membrane with pH; by a change in the degree of equilibrium swelling; and, consequently, by a change in the free-to-bonded water ratio in the polymer. The decrease in the region of low pH was explained by an increased role played by protons in the transport of electric current in this region of pH.

The increase in density of the three-dimensional network has as a consequence an increase in  $\rho_M$  within the whole range of network densities investigated here. On the other hand, the effect of the concentration of the ionogenic component becomes pronounced only in the region of low concentrations of the ionogenic comonomer.

The dependence of  $\rho_M$  on pH for the anion-active membranes is similar to the maximum in the region  $\text{pH} \sim 10$  and can be interpreted similarly to the behavior of the cation-active membranes.

The ampholytic membranes have a maximum in the  $\rho_M$  versus pH dependence in the isoelectric point ( $\text{pH} \sim 6$ ). This phenomenon can be interpreted by an increase in the content of mobile counterions on both sides of the isoelectric point. The method of measuring the dependence of  $\rho_M$  on pH allows determination of the isoelectric point of crosslinked polyelectrolytes.

By comparing the above dependences with the membranes based on poly(2-hydroxyethyl acrylate) it was demonstrated that for strongly hydrophilic systems with a sufficient amount of free water in the polymer, the maxima in the  $\rho_M$  versus pH dependences can be suppressed.

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