THE EFFECT OF pH AND TEMPERATURE ON THE ELECTRICAL CONDUCTIVITY OF MEMBRANES MADE OF METHACRYLIC ACID COPOLYMERS

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The specific resistance was measured of swollen homogeneous and heterogeneous ion-exchange membranes made of methacrylic acid copolymers with N-(2-hydroxypropyl)methacrylamide and of its copolymers with 2-hydroxyethyl methacrylate. In the case of copolymers of 2-hydroxyethyl methacrylate and methacrylic acid, an increase in the methacrylic acid content raises the specific resistance of the membrane if the carboxylic groups are not ionized. At the degree of neutralization 0·5 the dependence becomes a reverse one. In copolymers of N-(2-hydroxypropyl)methacrylamide with 50 and more per cent of methacrylic acid the specific resistance of the membrane increases with increasing content of methacrylic acid in the case of the nonionized form while remaining virtually unchanged in the ionized form. All the investigated copolymers of N-(2-hydroxypropyl)methacrylamide have a maximum on the curve describing the dependence of the specific resistance on pH. This pH coincides with pH at which the diffusion mobility of the charge carrier of Na^+ is highest. The dependence of the specific resistance on temperature can be described in terms of an empirical equation $\varrho_T = \varrho_0 e^{-bT}$.

Measurement of the electrical conductivity of ion-exchange materials with various degrees of neutralization of functional groups provides information on the mobility and transfer of counterions in the phase of the swollen ion-exchanger[1,2]. In an earlier study we measured the specific conductivity of hydrophilic ion-exchange membranes made of copolymers with various content of methacrylic acid and 2-hydroxyethyl methacrylate and determined the dependence of specific conductivity on pH (ref.[3]). By changing the hydrophilicity of the monomers, the solvent and other conditions of synthesis, the microstructure of the polymer can be varied to a large extent, and materials with various degrees of porosity can be prepared[4]. In this study, the specific resistance of swollen ion-exchange membranes made of copolymers

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of methacrylic acid (*I*) with N-(2-hydroxypropyl)methacrylamide (*II*) crosslinked with hexahydro-1,3,5-triacryloyltriazine (*III*) and of copolymers of *I* with 2-hydroxyethyl methacrylate (*IV*) crosslinked with ethylenedimethacrylate (*V*) having various degrees of neutralization of carboxylic groups has been measured and the results are compared with data provided by measurements of the diffusion permeability of these materials.

EXPERIMENTAL

Preparation of Membranes

To a mixture of monomers and solvent (20% by mass of the polymerization mixture), 2,2'-azobis(isobutyronitrile), 0·1% by mass per the overall mass of the monomers, was added as initiator, and the mixture was immediately placed in the mould. The mould was hermetized and thermostated to 60°C. The polymerization lasted 14 h. The membranes thus obtained, 0·108—0·115 cm thick, were freed from the residue of the monomers and low-molecular weight compounds by washing them with water several times, and gradually immersed into buffer solutions with varying pH in order to restrict stress in the membranes which may lead to their mechanical damage due to a sudden change in swelling. The equilibrium state of the membrane and solution was achieved within several weeks.

Characterization of Membranes

Measurements of the degree of neutralization of carboxylic groups, α, by potenticmetric titration has been described earlier[6]. Permeability of the membranes with respect to hydrogen and sodium ions was measured[7] in a transport vessel provided with a stirrer in each separate cell, 50 ml in volume. The pore size of heterogeneous membranes (minimal 10—30 nm) and the statistical distance between the crosslinks of homogeneous membranes (2—3 nm) were determined by employing a described procedure[3,4].

The electrical conductivity of the membranes was measured at a frequency 4 kHz by means of a TESLA-RCL bridge in a cell described earlier[3]. Membranes with various degrees of neutralization of carboxylic groups in equilibrium with solutions of 0·1M-NaCl and 0·01M-HCl or 0·01M phosphate or acetate buffers were measured, so that the total ionic strength of the solution was 0·11—0·12. Solutions flowing through the cell were thermostated, the temperature difference between the cell and thermostat not exceeding 1°C. The specific resistance of the membrane ϱ_M ($\Omega \times$ cm) was calculated using the equation[5]

$$\varrho_M = \frac{R_t - R_s}{d} \times A\,, \qquad (1)$$

where R_t is the resistance of the solution and membrane (Ω), R_s is the resistance of the solution (Ω), A is the measured membrane surface (cm^2), and d is the membrane thickness (cm).

RESULTS AND DISCUSSION

Measurements of specific resistance showed that the specific resistance of heterogeneous membranes made of copolymers of methacrylic acid with N-(2-hydroxypropyl)methacrylamide (Table I, samples 1 – 4) was lower than that of homogeneous membranes of the same type (samples 5 – 8) and much lower than that of homogeneous membranes made of copolymers of methacrylic acid and 2-hydroxyethyl methacrylate (samples 9 – 14). In copolymers of methacrylic acid with 2-hydroxyethyl methacrylate an increased content of methacrylic acid units raises the specific resistance of the membrane if the carboxylic groups are not ionized. However, at the degree of neutralization of carboxylic groups α 0·5 the dependence is reversed, in full agreement with the results published earlier[3]. This allows a conclusion to be drawn that with increased ionization the hydration of the copolymer increases (proportionately to the content of carboxylic groups) and the specific resistance of the membrane decreases.

Copolymers of N-(2-hydroxypropyl)methacrylamide are more hydrated than those of 2-hydroxyethylmethacrylate (Table I). The increased hydration by the matrix

TABLE I

Structure of membranes made of methacrylic acid copolymers (*I*); v_1 is the ratio of the volume of water in the copolymer to the total volume of the swollen copolymer, ϱ_M is the specific resistance (25°C), α is the degree of neutralization

Membrane No	Comonomers (mol.%)			Solvent	v_1	Structure	ϱ_M ($\Omega \times$ cm)	
	I	*II*	*IV*				$\alpha = 0$	$\alpha = 0·5$
Crosslinking component — *III* (4 mol/100 mol of comonomers)								
1	100	—	—	water	0·86	porous	246	84
2	90	10	—	water	0·84	porous	188	84
3	70	30	—	water	0·88	porous	96	84
4	50	50	—	water	0·90	porous	100	96
5	10	90	—	water	0·70	homogeneous	110	138
6	—	100	—	water	0·92	homogeneous	168	213
7	100	—	—	DMF	0·79	homogeneous	473	54
8	50	50	—	DMF	0·84	homogeneous	360	70
Crosslinking component — *V* (2 mol/100 mol of comonomers)								
9	30	—	70	butanol	0·37	homogeneous	16 400	150
10	20	—	80	butanol	0·37	homogeneous	20 100	75
11	15	—	85	butanol	0·38	homogeneous	20 400	150
12	5	—	95	butanol	0·41	homogeneous	15 900	676
13	2·6	—	97·4	butanol		homogeneous	13 400	1 800
14	—	—	100	butanol	0·42	homogeneous	11 400	10 000

based on N-(2-hydroxypropyl)methacrylamide counterbalances the effect of the concentration of carboxylic groups on the magnitude of specific resistance.

If the dependences of ϱ_M on the methacrylic acid content in the copolymer of N-(2-hydroxypropyl)methacrylamide at α 0 and α 0·5 are compared, it can be seen that at the methacrylic acid content 50% and more ϱ_M remains virtually unchanged for the ionized form and increases with increasing methacrylic acid content for the nonionized form (Fig. 1). This effect seems to be related not only to the steric effect of closely situated ionogenic groups on the mobility of the counterions, but also to the hindering effect of a system of intramolecular hydrogen bonds in the polyelectrolyte network on the mobility of the hydrated counterion. An increase in the electrical mobility of the polyelectrolyte which accompanies ionization of the carboxylic groups is usually connected with two factors, namely, with an increased swelling of the polyelectrolyte network[1,3] and with the increased concentration of charge carriers in the system which is analogous to the increase in the electrical conductivity of solutions with increased ionic strength[5].

All measured samples had a maximum on the curve representing the dependence of specific resistance on pH of the equilibrium solution, *i.e.* on the degree of neutralization of carboxylic groups (Fig. 2). The maximum is more pronounced for samples with a higher content of methacrylic acid in the copolymer. The pH value at which

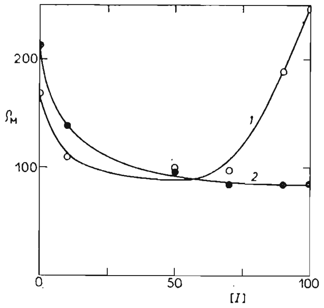

FIG. 1

Dependence of the specific resistance (Ω cm) of membranes made of copolymers of methacrylic acid and N-(2-hydroxypropyl)-methacrylamide on the content of methacrylic acid ([I] in %) 1 $\alpha = 0$, 2 $\alpha = 0·5$

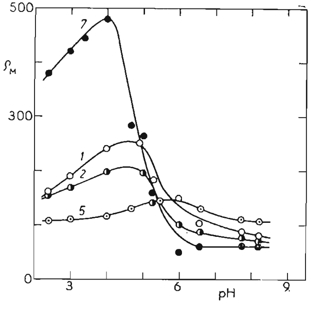

FIG. 2

Dependence of the specific resistance of membranes on pH of the equilibrium solution (curves for membranes of the same number, *cf.* Table I) the specific resistance of a homogeneous sample crosslinked with hexahydro-1,3,5-triacryloyltriazine reaches its maximum is higher by 1·5 pH units than that of a similar homogeneous sample crosslinked with ethylenedimethacrylate, the data on which have been reported earlier[3].

In the case of heterogeneous samples the extreme value of ϱ_M lies still higher, in the pH range 4·0—5·0. If one accepts a hypothesis forwarded earlier, that pH $_{max}$ characterizes the range of conformational transition in the poly(methacrylic acid) network, the observed dependence may be explained through a greater steric hindrance to the conformational transition in the poly(methacrylic acid) network crosslinked with hexahydro-1,3,5-triacryloyltriazine, compared with the poly(methacrylic acid) network crosslinked with ethylenedimethacrylate. Similarly, hindrance to the conformational transition is greater in the case of homogeneous networks than in that of heterogeneous (porous) ones. The cause of the extreme on the curve representing the dependence of ϱ_M on pH for the copolymer of N-(2-hydroxypropyl)methacrylamide not containing any ionogenic groups remains however unexplained.

Since the electrical conductivity of the membrane under investigation has an ionic character, it is affected by the same factors as those affecting the electrical conductivity of the solution. With increasing pH of the solution the concentration of ionized solid (immobile) ionogenic groups and the concentration of mobile sodium ions also increase, as the change in the volume of the crosslinked networks under investigation is rather small[4].

If we compare the dependence of the specific resistance and diffusion coefficients of charge carriers on pH of the equilibrium solution, we can see that the range of pH of the highest specific resistance coincides with that of the highest diffusion mobility of the charge carrier Na^+ (Table II). It seems that the interaction between the mobile counterion and fixed ionogenic groups which prevents the motion of the

TABLE II

Specific resistance ϱ_M of the membrane made of poly(methacrylic acid) (sample 1) and diffusion coefficients of counterions[15] D_i^+ for this membrane at various degrees of neutralization of carboxylic groups (α)

pH	α	ϱ_M	D_{Na^+}	D_{H^+}
			10^6 cm^2 s^{-1}	
2·0	0	110	—	4·9
4·0	0	230	1·7	9·8
5·2	0·25	170	1·1	—
6·7	0·50	100	0·9	—
8·0	0·85	90	0·8	7·8

counterion caused by diffusion does not affect essentially the motion of these ions brought about by an external electrostatic field. Hence, if α increases to 0·5, the diffusion coefficient of sodium ions decreases to half its original value, while the conductivity of the membrane increases. It is known that the mobilities of ions in electrolyte solutions calculated from the mass transfer and from conductivity data differ considerably from each other because of the electrophoretic and relaxation effects. Some other effects also appear in the crosslinked polyelectrolyte, due to the Donnan exclusion of the electrolyte from the polymeric phase and to the thermal oscillations of polymer chains.

Beyond the boundary of neutralization of carboxylic groups (in the pH range below 4·0, Fig. 2) the decrease in resistance may be explained by a partial absorption of the electrolyte due to a decrease in the Donnan effect, because the mobility of hydrogen ions exceeds that of sodium ions by at least one order of magnitude[8].

With increasing temperature the specific resistance of the membranes decreases, which may be explained by an increase in the degree of ionization of carboxylic groups in these membranes. On the other hand, however, the general dependence of ϱ_M on temperature also strongly depends on the morphology of the samples (*cf.* curves *1* and *7* in Fig. 3), on the character of the crosslinkig agent and on the hydrophilicity of the matrix (*cf.* curves 7 and 9). It seems that in this case one should consider the effect of temperature on the swelling of the polyelectrolyte network, on the chain mobility and on the properties of close surroundings of ionogenic groups.

It has been mentioned in our earlier paper that with increasing temperature in the range 5–70°C, only an insignificant change can be observed in the volume and swelling of heterogeneous copolymers of methacrylic acid and hexahydro-1,3,5-triacryloyltriazine[9]. It can be assumed that the dependence of ϱ_M on temperature is defined

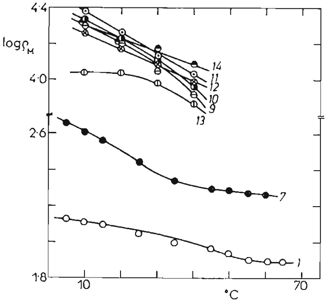

FIG. 3

Temperature dependences of the specific resistance of membranes at pH 4·00–4·15 in 0·1M-NaCl solution (curves for membranes of the same number, *cf.* Table I) by the same factors as the static dielectrical permeability of the swollen polyelectrolyte. In this case the observed dependence ϱ_M (T) is related to some properties of the structure of the crosslinked polyelectrolyte and is not connected with the mobilities of counterions. It has been reported in the literature that the temperature has an unusually weak influence on the mobility of sodium and hydrogen ions. A change in viscosity with temperature and diffusion of water may also be neglected, because for aqueous solutions $D\eta/T$ is constant in the temperature range used in the investigation[10,11].

It is known that the static dielectrical permeability, ε_T, of most liquids may be described by Abegg's empirical equation[12]

$$\varepsilon_T = \varepsilon_0 e^{-LT}, \qquad (2)$$

where ε_0 and L are empirical constants and T is temperature (K). These quantities may also be ascertained for the phase of the swollen crosslinked polyelectrolyte using data on thermodynamic compensation in a series of equilibria[13].

The observed dependence ϱ_M (T) may also be described in terms of an empirical equation

$$\varrho_T = \varrho_0 e^{-bT}, \qquad (3)$$

in which ϱ_0 and b are empirical constants, T is temperature (K). (The calculated ϱ_0 and b values of the copolymers under investigation are summarized in Table III).

TABLE III

Parameters of Eq. (*4*) for the temperature dependence of the specific resistance of membranes

Membrane No	I mol.%	b K^{-1}	$\varrho_0 \cdot 10^{-3}$ $\Omega \cdot$ cm
1	100	0·013	9·16
7	100	0·025	650
9	30	0·030	850
10	20	0·028	500
11	15	0·027	316
12	5	0·021	43·5
13	2·5	0·021	40·0
14	0	0·018	25·2
Solution	—	0·017	69·5

[a] 0·1M-NaCl solution with 0·01M buffer solution (pH 4·0).

Such an exponential form of the temperature dependences of the specific resistance and dielectric permeability may be explained from a simple physical standpoint: In the matrix of a crosslinked polyelectrolyte, the motion of counterions is prevented by their ion-ion interactions with ionogenic groups of the polymer which depend on the dielectrical permeability.

It has been suggested[14] that the ion exchanger should be regarded as a solid with purely ionic conductivity, where the charge and mass transfer depend on some defects in the regular structure of the polymeric matrix. This model can obviously be improved by introducing a temperature dependence of structural characteristics of the polymer. The empirical characteristics of carboxylic membranes obtained in this study may be employed in an analysis of the nonequilibrium and nonisothermal transfer processes of solvents and counterions through these materials.

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