

RELATIONSHIP BETWEEN ELECTRIC CONDUCTIVITY AND THE DEGREE OF CROSSLINKING, EXTENT OF HYDROLYSIS, SWELLING AND CONCENTRATION POTENTIALS*

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Received July 17th, 1975

Relationships between the electric conductivity of membranes, prepared by the polymerization of acrylonitrile in an aqueous $ZnCl_2$ solution followed by hydrolysis in the HCl vapours, on the one hand, and the degree of crosslinking, extent of hydrolysis, swelling and the concentration potentials (expressed as slopes of the membrane functions and permselectivity) on the other have been examined. The degree of crosslinking and the concentration of the carboxylic and amide groups after hydrolysis affect the conductivity through swelling. The dependences of the concentration potentials on the conductivity of membranes and the discrepancy between the dependences of the measured and calculated conductivities on the degree of crosslinking indicate that the conclusive effect on changes in conductivity of the membranes under investigation should be assigned to changes in ion mobility in the porous gel structure.

In an earlier paper¹ we described the preparation of acid hydrophilic membranes by the polymerization of acrylonitrile in an aqueous $ZnCl_2$ solution followed by the hydrolysis of the polymer in the HCl vapours; the degree of crosslinking of the substance depended on the monomer concentration in the initial polymerization mixture². It was shown that permselectivity and the slopes of the membrane functions determined from the concentration potentials were directly dependent on the degree of crosslinking of the gel.

This paper reports on the electric conductivity of membranes made of gels based on polyacrylonitrile and described earlier¹, on their relation to the degree of crosslinking and the extent of hydrolysis of the initial polyacrylonitrile, swelling, and the concentration membrane potentials; the question of the most important factor influencing the electric conductivity of gels is also examined.

THEORETICAL

The electrical conductivity of a charged gel is in principle determined by the concentration of charge carriers and by their mobility. The concentration of charge carriers in

* Part II. in the series Electrochemical Properties of Hydrophilic Weak-Acid Membranes from Hydrolyzed Polyacrylonitrile II; Part I: *Eur. Polym. J.* 10, 905 (1974).

the pore liquid follows (for constant properties of the electrolyte) from the number of dissociated groups and from the swelling of the gel; through the Donnan equilibria it is related to the fixed charge density which in turn is a function of chemical composition and swelling. The mobility of charge carriers — free ions — is under the same external conditions (ion type, electric field) a function of permeability, and thus of the steric order of the swollen gel, and of the fixed charge density; the fixed charge hampers the movement of the counterions by electrostatic forces and by an increase in intrinsic friction on the walls of the pores. Swelling, which affects both the concentration of charge carriers and their mobility, is controlled by the chemical composition and crosslinking of the gel; the steric order of the swollen gel also depends on the same factors, and moreover on the history of the gel. Consequently, the concentration of charge carriers and their mobility are determined by the same parameters, but acting in the opposite sense: The increasing degree of crosslinking on the one hand raises the concentration of charge carriers through a decrease in swelling, while reducing at the same time the permeability of the gel by narrowing the pores. The increasing extent of hydrolysis increases the number of dissociable groups, but at the same time reduces the concentration of charge carriers owing to an increase in swelling, which in turn increases the permeability of the gel by widening the pores.

The connection between the specific electric conductivity of the liquid in the pores, L_i , with the concentration of charge carriers in the internal and external electrolyte and with ion mobility was expressed by Schmid³ for a 1-1 electrolyte and a cation-active membrane by

$$L_i = F(u_+ + u_-) \left(C^2 + \left(\frac{\bar{X}}{2} \right)^2 \right)^{1/2} + (u_+ - u_-) \frac{\bar{X}}{2}, \quad (1)$$

where u_+ and u_- are mobilities of the cation and anion respectively, C is concentration of the external solution, X is concentration of the fixed charge, and F is the Faraday constant. Eq. (1), which has been derived from the Donnan equilibrium similarly to the important terms of the equation for the concentration potential in Teorell–Meyer–Sievers theory of fixed charges⁴, shows that the attaining of the Donnan equilibrium in the membranes examined here should be reflected in the existence of a functional relationship between the concentration potential and the electric conductivity of the membrane. Since according to Eq. (1) and to the TMS theory both conductivity and the concentration membrane potential increase with increasing concentration of fixed charges (dissociated groups), the concentration potential should increase with increasing conductivity. Since the concentration potential can increase only up to the theoretical value, one may expect that the plot of the dependence will have the form of an exponential or a similar curve tending to saturation.

Besides the electrolytic current, a convection flow of charge carriers is also operative in the porous gel in the electric field, as a result of the electroosmotic motion of the medium. The latter is carried along mainly by counterions which predominate in a charged gel over coions. Therefore it can be expected that the role played by convection conductivity in gels will increase with increasing charge density (high concentration of counterions), especially in contact with dilute electrolytes (large difference between the concentrations of the counter- and coions). A large participation of convection conductivity can be expected in gels having a low flow resistance. The increasing degree of swelling would have opposite effect on convection conductivity; namely, the decrease in swelling and the increase in the density of the fixed charge would lead to an increase in convection conductivity, while at the same time the flow resistance would also increase because of the narrowing of the pores. Which of the two above effect prevails, will decide about the potential use of the membrane.

EXPERIMENTAL

The preparation of gels, their chemical composition and measurements, as well as expressions used for the concentration potentials have been reported in detail earlier¹. The membranes were obtained from gels differing in the degree of crosslinking (characterized by the volume fraction of the monomer in the initial mixture). Each of the basic polymers was hydrolyzed for 2, 3 and 6 days in the vapours of 28% HCl. Zinc chloride was removed by washing in a 1% aqueous solution of NaHCO₃; the residues (if any) were removed during conditioning of the membrane (alternately 1% HCl, washing and 1% KHCO₃). The test to detect Zn²⁺ with Montequi agent in the gel and in the washing waters was also negative. The effect of the degree of covalent crosslinking on the electric conductivity of membranes was followed on gels having approximately the same extent of hydrolysis of the nitrile groups.

All measurements were carried out on membranes after long-term equilibration in a KCl solution having a molality of 0.1 mol/kg at pH 7. The membrane thicknesses were determined with an accuracy of 0.01 mm. The electric conductivity was measured at 25°C in 0.1 molal KCl, in conic cells described earlier¹. The platinum electrodes had areas of 1 cm²; the area of membranes exposed to measurement was 0.11 cm². A KONDU 3 conductoscope (Laboratorní přístroje, Prague), fed with a 5000 Hz current, was used as the measuring device. The standard deviation of the average from two resistance measurements of the membranes was 1.0 Ω cm.

RESULTS AND DISCUSSION

In hydrolyzed polyacrylonitrile there are two types of crosslinking — covalent, which takes place in polymerization, and physical, based on the dipole-dipole interaction between the sequences of nitrile groups untouched by hydrolysis. In the interpretation of results of this study we considered only the degree of the covalent crosslinking characterized by the volume fraction of acrylonitrile in the original polymerization mixture (v_0). The experimentally determined specific electric conductivity, (L_s), decreases with increasing crosslinking (Table I), and the respective dependence

on v_0 for an approximately identical extent of hydrolysis of the nitrile groups can be approximated by

$$L_s = 0.162 \exp(-8.12 v_0) \quad (\Omega^{-1} \text{ cm}^{-1}) \quad (2)$$

with a correlation coefficient of 0.98. The exponential form of (2) suggests that the strongest effect on conductivity is exhibited by the crosslinking at low v_0 (obviously, not lower than 0.4, or the product remains soluble). With increasing v_0 the conductivity decreases still slower and converges to zero, but the charge density increases¹. Therefore a decrease in conductivity with increasing v_0 means that the decrease in ion mobility due to an increase in the degree of crosslinking and narrowing of the pores is more important than an increase in charge density and the convection conductivities connected therewith. The reason is clear bearing in mind the low contents of the adsorbed electrolyte (Table I).

The electric conductivity of membranes made of hydrolyzed polyacrylonitrile increases with proceeding hydrolysis at each initial degree of crosslinking (Table I). With respect to the negligible fraction of convection conductivity, such increase in conductivity can be regarded either as a result of an increase in swelling and in ion mobility, or as a result of an increase in the number of dissociated groups and thus in the number of charge carriers in gel. The latter effect does not appear: higher charge densities were found with samples 6, 8, 9, and 10 (ref.¹), while the conductivities of just these gels are the lowest. On the contrary, the increase in conductivity with swelling is pronounced (Fig. 1). The second power of the correlation coefficient ($r_{xy} = 0.975$) of this dependence shows that the variability of conductivity is in 95% determined by the same effects as the volume swelling.

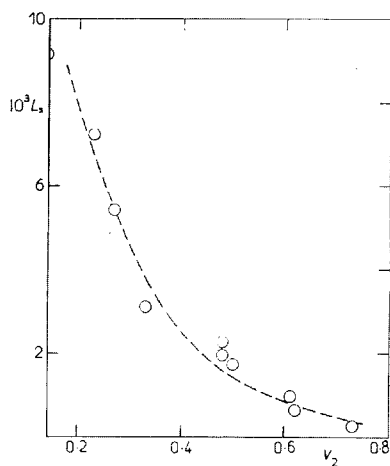


FIG. 1

Dependence of Specific Electric Conductivity L_s ($\text{ohm}^{-1} \text{ cm}^{-1}$) of Membranes on Volume Swelling v_2 ($\text{ml}_{\text{dry}}/\text{ml}_{\text{swollen}}$)

The swelling of the membrane is simultaneously affected by the degree of cross-linking and the extent of hydrolysis of the nitrile groups of the original polyacrylonitrile. Hydrolysis gives rise to amide and carboxylic groups, and hydration of these hydrophilic groups leads to an increase in swelling. The latter also increases with a decrease in the degree of physical crosslinking. If the increase in the content of hydrophilic groups due to hydrolysis from the least hydrolyzed gel to the most hydrolyzed one with the same degree of crosslinking is related to the lowest content of hydrophilic groups (d_1), and if the increase in swelling pertaining to the same gels is similarly related to the swelling of the least hydrolyzed gel having the same degree of crosslinking (d_2), the relative change in swelling can be defined as an increase in the volume of the swollen gel per the unit increase in the content of hydrophilic groups (d_2/d_1). The relative change in swelling markedly increases with the increasing degree of crosslinking; at a low degree of crosslinking (v_0 0.419 and 0.472), the swelling increases relatively faster than the content of hydrophilic groups ($d_2/d_1 > 1$), while at higher degrees of crosslinking it is the other way round ($d_2/d_1 < 1$). Similar conclusions can also be drawn if the relative change in swelling is calculated separately for the respective contents of the amide and carboxylic groups.

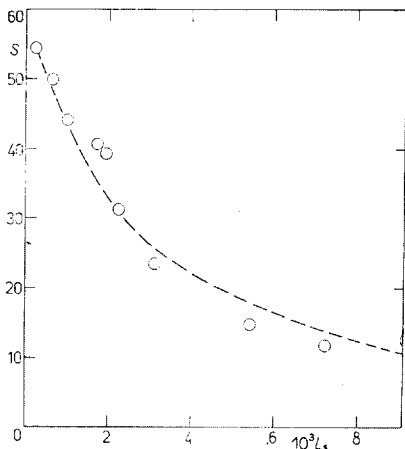


FIG. 2

Dependence of the Slopes S of Membrane Functions (mV per activity decade) on Specific Electric Conductivities L_s ($\text{ohm}^{-1} \text{cm}^{-1}$) of Variously Crosslinked and Hydrolyzed Membranes of PAN

Membranes in contact with solution of KCl 0.2 to 0.001M on one side and with 0.1M-KCl on the other side.

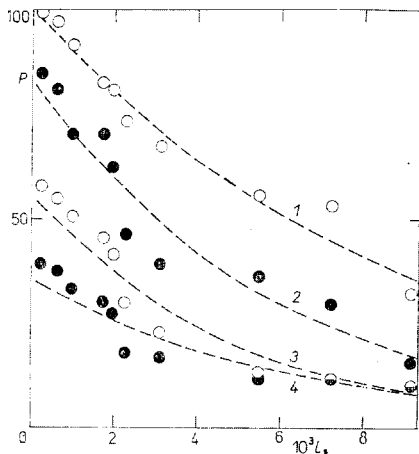


FIG. 3

Dependences of Permselectivities P (%) on Specific Electric Conductivity L_s ($\text{ohm}^{-1} \text{cm}^{-1}$) of Variously Crosslinked and Hydrolyzed Membranes of PAN

Molalities of KCl solutions: 1 0.1 and 0.05, 2 0.2 and 0.1, 3 0.5 and 0.25, 4 1.0 and 0.5.

In paper¹ the concentration potentials were characterized by the slope of the membrane functions of all gels (concentration range of solutions in contact with the membrane was on the one side 0.2–0.001 mol/kg, on the other 1.0 mol/kg in KCl), and by permselectivities calculated from the series of the concentration potentials of membranes between KCl solutions having molalities 0.1–0.05, 0.2–0.1, 0.5–0.25, 1.0–0.5 mol/kg. These characteristics of the concentration potentials were used also in this work. Fig. 2 shows the dependence of the slopes of the membrane functions on the specific electric conductivity (an exponential curve with a correlation coefficient of 0.97 can be plotted through the experimental points). The dependences of permselectivities on conductivity also have an exponential character (Fig. 3): the correlation coefficients (r_{xy}) decrease in the series of pairs of molalities (in accord with the order of curves): 0.97, 0.96, 0.93. The dependence of permselectivity on the electric conductivity fits best in the concentration range in which also the conductivity of membranes was measured, *i.e.* about 0.1 mol/kg KCl. It should be pointed out in this connection that the content of carboxylic groups in hydrolyzed polyacrylonitrile is comparatively low, amounting to 0.2–0.5 mequiv./g.

TABLE I

Characteristics of Membranes Made of Hydrolyzed Polyacrylonitrile and Their Specific Electric Conductivities (L_s) in a 0.1 Molal KCl Solution

v_0 Volume fraction of acrylonitrile in starting polymerization mixture, \bar{c}_+ , \bar{c}_- molarities of counter- and coions in membrane respectively.

Membrane	v_0	Hydrolysis days	\bar{c}_+	\bar{c}_-	$10^3 L_s, \Omega^{-1} \text{ cm}^{-1}$	
					exper.	calc. ^a
1 ^b	0.419	2	0.128	0.078	5.42	15.1
2	0.419	3	0.155	0.065	9.17	16.1
3	0.472	2	0.177	0.057	2.25	17.1
4 ^b	0.472	3	0.184	0.054	3.11	17.5
5	0.472	6	0.285	0.035	7.23	23.5
6	0.577	2	0.241	0.041	0.99	20.8
7 ^b	0.577	3	0.216	0.046	1.95	19.3
8	0.577	6	0.452	0.162	1.72	25.9
9	0.664	3	0.200	0.050	0.24	18.4
10 ^b	0.664	6	0.303	0.033	0.64	24.7

^a According to Eq. (1); values used for mobilities of cation and anion respectively were⁵ $2.6 \cdot 10^{-4}$ and $7.6 \cdot 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$. ^b Membranes with approximately the same extent of hydrolysis ($78 \pm 2.5\%$) of originally present nitrile groups in polymer.

The results summarized in Table I and II and in Fig. 1 indicate that the conductivity of gels is more affected by the structure (characterized by swelling and by the degree of crosslinking) than by the chemical composition. In spite of such predominance of the effect of the physical structure, a functional connection between the concentration potentials and conductivity has also been proved in the cases investigated in this work (Figs 2, 3), but the membrane concentration potential decreases with increasing electric conductivity, at variance with the theoretical assumptions. This means that the relationship between conductivity and the concentration potential cannot be a result of the mere establishment of the Donnan equilibrium controlled by the chemical composition, but that it is governed by some other mechanism. This is also why important discrepancies have been discovered between the experimentally determined specific conductivity values of membranes on the one hand and the values calculated from Eq. (1) derived from the Donnan equilibrium on the other (Table I): In gels with an approximately the same extent of hydrolysis (membranes 1, 4, 7, 10) the experimental values decrease with the degree of crosslinking while the calculated values increase. Moreover, the calculated values are always higher.

In spite of their considerable swelling, the hydrophilic gels from hydrolyzed polyacrylonitrile are a hindrance to ion mobility, which is the more important the higher the network density. If the electrolyte concentration in the pores of such gel is controlled by the Donnan equilibrium, departures in the electrochemical behaviour of the gel membranes from theory should be explained by the hindering of free ions due to the form conditions in the porous structure of the gel (density, size and shape

TABLE II

Effect of the Degree of Crosslinking and of the Extent of Hydrolysis of Polyacrylonitrile on Gel Swelling

v_0 Volume fraction of polyacrylonitrile in the starting polymerization mixture; content of constitutional units (mass.%): a and A of acrylic acid in the least or most hydrolyzed gel respectively, b and B of acrylamide in the least and most hydrolyzed gel respectively; d_1 difference of the total content of hydrophilic groups between the most and least hydrolyzed gel in per cent of the lowest content of hydrophilic groups^a, d_2 difference in volume swelling between the least and most hydrolyzed gel of the respective degree of crosslinking in per cent of the starting volume swelling^b.

v_0	a	b	A	B	d_1	d_2	d_2/d_1
0.419	2.1	79.2	3.2	87.1	11.1	92.8	8.36
0.472	1.8	63.2	3.9	86.1	38.5	108.7	2.82
0.577	1.9	56.1	3.0	80.0	43.1	27.1	0.63
0.664	1.4	53.6	3.4	74.6	41.8	17.7	0.42

$$^a d_1 = [(A + B) - (a + b)] \cdot 100 / (a + b); \quad ^b d_2 = [v_2(\max) - v_2(\min)] \cdot 100 / v_2(\min).$$

of the pores). The experimental data of specific electric conductivity and the quantities derived from the concentration potentials can therefore be used as supplementary integral characteristics and help to describe more adequately the porous network structure of hydrophilic gels with low charge density.

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Translated by L. Kopecká.