

# Dependence of the Electrotransport Properties of Polyarylene Sulfamide Membranes on Their Chemical Composition and Concentration of Equilibrium Electrolyte Solutions

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Received April 25, 1996

**Abstract**—The electrotransport characteristics of homogeneous polyamide membranes are studied as a function of the content of poly-*m*-phenyleneisophthalamide (Phenylone) in the polymer. The most significant changes in the transport properties are found to occur after the molar fraction of Phenylone in the samples is increased from 0 to 30%. A further increase in the fraction of the inert binder in the membranes (40–60 mol %) makes no considerable impact on the electrotransport characteristics. The concentration dependences of specific electroconductivity  $\kappa$ , diffusion permeability  $P$ , and electroosmotic permeability  $t_w$  of the membranes in aqueous sodium chloride solutions are obtained in a wide concentration range. The nature of the concentration dependences of  $P$  and  $\kappa$  is shown to undergo a change with the growing molar fraction of Phenylone. The results obtained are compared to similar dependences for homogeneous perfluorinated sulfocationite membranes with close values of exchange capacity and specific moisture content. According to the experimental data, electrochemical properties of homogeneous poly(arylene sulfamide) membranes can be finely adjusted by the changing structure of transport channels in the polymer.

## INTRODUCTION

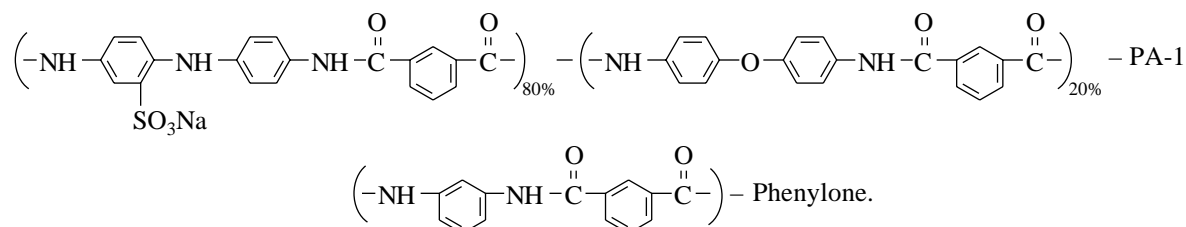
The efficiency of the electrochemical methods of water desalination and their ability to compete with other methods depend to a large extent on properties of the ionite membranes. The use of homogeneous membranes of the Kaspion type that are obtained from sulfonate-containing aromatic polyamides [1, 2] open fresh possibilities for electrodialytic separation of univalent and divalent cations. When synthesizing these films, one can easily vary the structure and configuration of macromolecular chains, and, correspondingly, their hydrophilicity and other structural parameters [3]. In so doing, electroconductivity of the samples varies by 1 to 2 orders of magnitude. It was found that membranes of this type have a specific microstructure that can be viewed as a system of transport channels. The latter is characterized by formation of hydrogen bonds between the carbonyl and amide groups in which hydrated water takes part. In this case the material can be made charge-selective, which ensures higher efficiency of separation, in particular, of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions [2]. To analyze in detail the trans-

port mechanism of ions and solvent in membranes of this type, one needs information about the influence exerted by the structure and composition of the polymer on the entire complex of electrotransport and macroscopic properties.

In this work, for a series of samples, we study the dependences of specific electroconductivity  $\kappa$ , diffusion permeability  $P$ , and electroosmotic permeability  $t_w$  on the concentration of equilibrium sodium chloride solutions. As shown in [5–7], the concentration dependences of the electrodiffusion properties inherent in ion-exchange membranes can be utilized to estimate their structural features in the framework of modeling concepts [5] and serve as a basis for a complete description of interrelated transport characteristics of ions and water [6].

## EXPERIMENTAL

We studied an aromatic polyamide with a sulfo group (PA-1), poly-*m*-phenyleneisophthalamide (Phenylone), and their mixtures:



Synthesis of the polymers is described in [8]. Membrane films were prepared from solutions containing a mixture of the two polymers (PA-1 and Phenylone) in dimethylformamide (DMF) by pouring the solutions on a polished glass surface and then drying in air at room temperature and in a vacuum at 100–110°C for 24 hours. The membranes thus obtained were transparent dark-green films 50 to 70  $\mu\text{m}$  in thickness.

The molar content  $\omega$  of Phenylone in the samples under study varied from 0 to 60%. The physicochemical characteristics of polyamide membranes containing different amounts of PA-1 (polymer 1) and Phenylone (polymer 2) are listed in the table. The notation in the table is as follows:  $\omega$  and  $\gamma$  denote molar and weight contents of Phenylone in the samples under study, respectively;  $E$  is an exchange capacity calculated per unit of dry weight on the basis of the above molecular formula of the copolymer and expressed in units of g-equiv/mg;  $W$  represents the total moisture content measured in 0.1 M NaCl;  $n_w$  is the specific moisture content of a sample (for 0.1 M NaCl), expressed in mole of  $\text{H}_2\text{O}$  per mole of the  $\text{SO}_3$  group; and  $\kappa_{\text{iso}}$  denotes the electroconductivity values in isoconducting points of equilibrium sodium chloride solutions, in  $\text{S cm}^{-1}$ .

As the homogeneous films were obtained in the  $\text{Na}^+$  form, they were not subjected to chemical conditioning, which is a procedure common for the preparation of ion-exchange membranes [9]. Instead, the films were immediately equilibrated with the sodium chloride solution under study for 24 hours.

In order to obtain the concentration dependences of the membrane electroconductivity, we employed the mercury-contact technique [10]. The sample resistances were determined with the aid of a VM-507 impedance meter at a frequency of about 200 kHz. The conductivity was calculated with the relationship

$$\kappa = \frac{l}{RS}, \quad (1)$$

where  $S$  is the membrane area in contact with mercury, expressed in units of  $\text{cm}^2$ ;  $l$  is the sample thickness, cm; and  $R$  denotes the real constituent of the impedance measured,  $\Omega$ . The measurement accuracy was  $\pm 3$ –5%.

The diffusion flux of the salt through a membrane was measured under the experimental conditions described in [11].

The integral coefficients of permeability  $P$  were calculated with the equation

$$P = \frac{lV}{Sc_2} \frac{dc}{d\tau}, \quad (2)$$

where  $l$  is the thickness of a membrane, cm;  $S$  is the working area of a sample,  $\text{cm}^2$ ;  $c_2$  denotes the concentration of a solution under study, g-equiv  $\text{l}^{-1}$ ; and  $\frac{dc}{d\tau}$  represents the rate of the concentration change in the compartment containing "pure" water.

The transport number for water  $t_w$  was determined by the volume technique in a cell with the polarizing reversible silver–silver chloride electrodes [12]:

$$t_w = \frac{\Delta V d F}{18 t I}, \quad (3)$$

where  $\Delta V$  is the liquid volume transported in capillaries, expressed in ml;  $I$  is the current, in mA;  $t$  denotes time intervals, expressed in s, at which the measurements were taken;  $S$  is the working area of a membrane,  $\text{cm}^2$ ;  $F$  is the Faraday number,  $\text{C mol}^{-1}$ ;  $d$  represents water density,  $\text{g ml}^{-1}$ ; and 18 is the weight of 1 mole of water, expressed in units of grams per mole of water.

When measuring transport numbers for water, we found that the values of  $t_w$  could not be reproduced at a polarizing current density of  $30 \text{ mA cm}^{-2}$ , and the sample in the cell underwent considerable deformation under the action of the electrical current, which disturbed the conditions of the experiment and calculations. We found that employing higher current densities ( $40$ – $45 \text{ mA cm}^{-2}$ ) allowed us to avoid the film deformation, shorten the electrolysis duration, and obtain reproducible values with a relative experimental error of no more than 7%.

All the measurements were carried out under isothermal conditions, at a temperature of 298 K.

## RESULTS AND DISCUSSION

As seen in the table, increasing the Phenylone content in the polymer leads to a decrease in the exchange capacity and moisture content. Figure 1 illustrates the dependences of electroconductivity  $\kappa$ , diffusion permeability  $P$ , and electroosmotic permeability  $t_w$  of membranes under study on the polymer composition, measured in 0.1 M NaCl. As seen, the most significant changes in the transport properties occur upon going from sample 1 to sample 3. These samples contain the least amount of the inert fragment. Increasing the Phenylone molar content (40–60%) in the membranes further makes no appreciable changes in the electrotransport characteristics. Figure 1c compares the electroconductivity data to similar dependences (curve 3) obtained in [13], where some heterogeneous cationite membranes of the MK-40 type containing different amounts of a KU-2 ion-exchange resin and polyethylene were studied comprehensively, and to  $\kappa$  for a number of polyamide membranes containing Phenylone (curve 2) [3]. As seen in Fig. 1c, all polymeric compositions display a similar decrease in the electroconducting properties with the growing content of the inert component. However, in the case of homogeneous poly(arylene sulfamide) compositions containing Phenylone (curve 1) the change in  $\kappa$  is not that dramatic. An increase in the Phenylone content from 0 to 60 mol % is found to result in a sixfold decrease in  $\kappa$  and a 2–2.5-fold decrease in  $P$  and  $t_w$  (for 0.1 M NaCl).

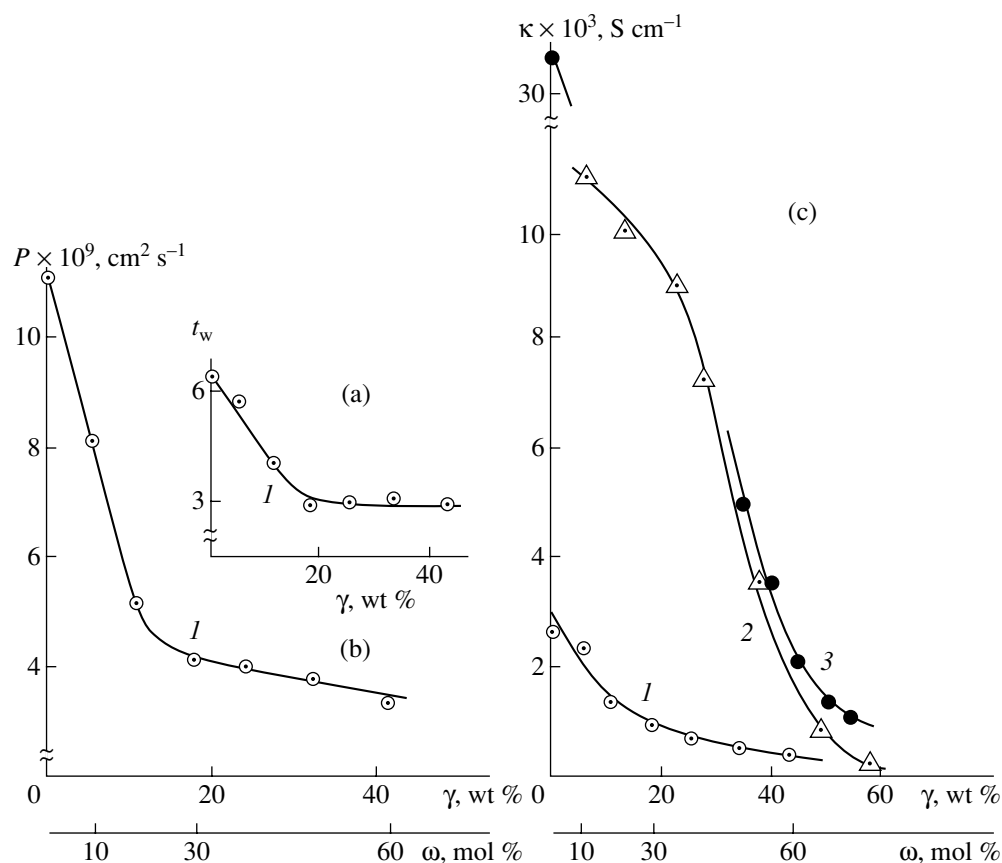
Physicochemical characteristics of the sulfocationite polyamide membranes containing different amounts of poly-*m*-phenyleneisophthalamide

Sample number	$\omega$ , mol %	$\gamma$ , wt %	$E$ , mg-equiv g <sup>-1</sup>	$W$ , % $\frac{\Delta m}{m}$	$n_w$ , $\frac{\text{mol H}_2\text{O}}{\text{mol SO}_3^-}$	$\kappa_{\text{iso}} \times 10^4$ , S cm <sup>-1</sup>
1	0	0	1.69	47.44	15.45	22.5
2	10	5	1.60	45.17	15.60	21.0
3	20	11	1.50	39.33	14.57	12.0
4	30	18	1.39	35.78	14.30	10.5
5	40	25	1.26	32.24	14.11	6.5
6	50	34	1.12	29.37	14.40	5.8
7	60	43	0.96	21.16	12.21	4.1

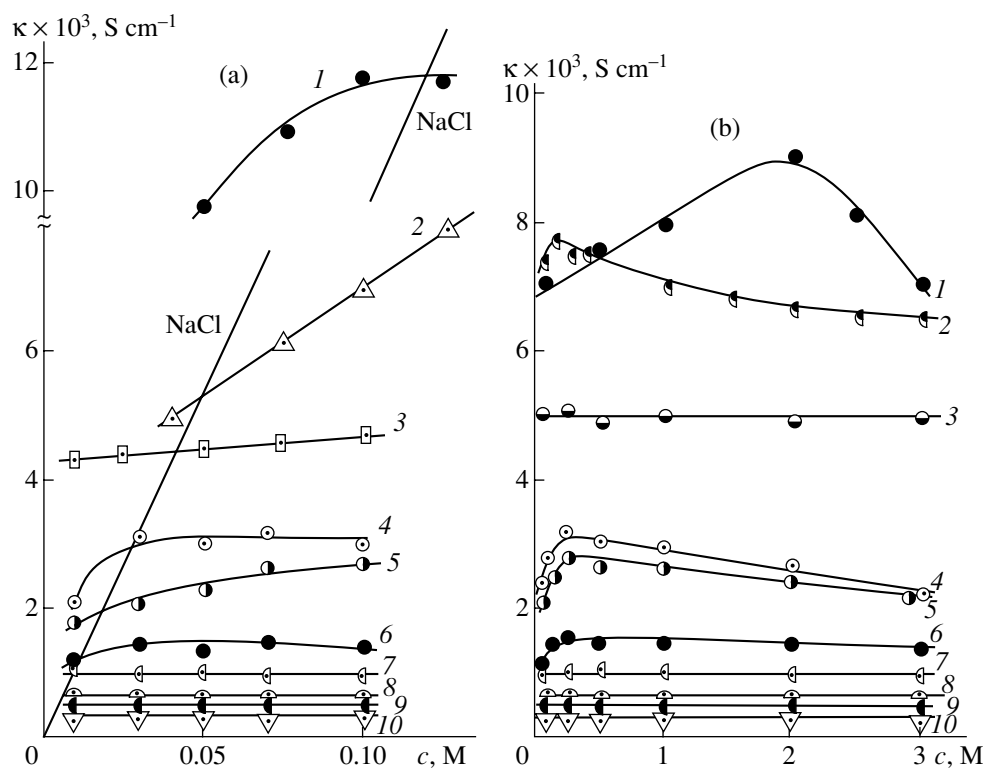
Structural investigations of different types of sulfocationite membranes based on poly(phenylene phthalamides) [14–16] showed that formation of the hydrogen bonds between the carbonyl and amide groups leads to emergence of a system of transport channels varying from 0.5 to 1.0 nm in size, depending on the composition of the polyamides. The structural changes in the matrix depend on the amount of the sulfo compo-

nent [16, 17]. With our samples, we can assume that, at  $\omega > 30$  mol %, macromolecules are packed so densely that a further decrease in the number of sulfo groups makes no difference.

The concentration dependences of the electroconductivity for polyamide films in equilibrium sodium chloride solutions and similar dependences for sulfocationite membranes MF-4SK with close values of the



**Fig. 1.** The effect of the polymer composition on (a) water transport number, (b) coefficient of diffusion permeability, and (c) electroconductivity; the dependences are obtained in 0.1 M NaCl solution for (1) polyamide membranes containing Phenylene, (2) polymers with different Phenylene content [3], and (3) MK-40 membrane containing different amounts of polyethylene [13].

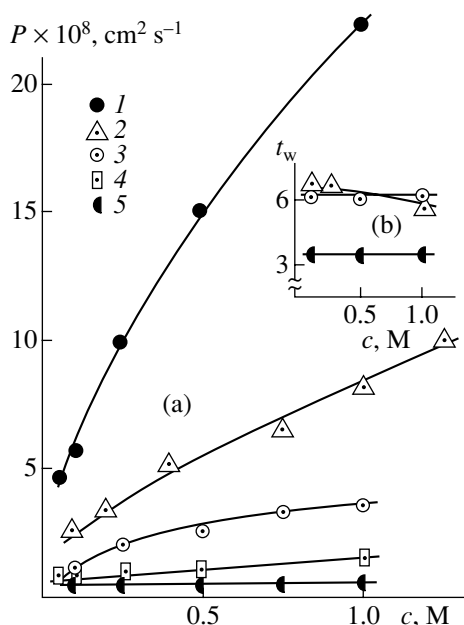


**Fig. 2.** (a) The concentration dependences of electroconductivity in dilute NaCl solutions for (1) MF-4SK at  $n_w = 11.1$  and  $E = 0.93$  [18], (2) MF-4SK at  $n_w = 11.9$  and  $E = 0.76$  [19], (3) MF-4SK at  $n_w = 5.1$  and  $E = 0.93$  [18], and (4–10) samples 1 to 7, respectively; and (b) similar dependences in a wide range of NaCl concentrations for (1) MEC-CDC, (2) MK-100, (3) MF-4SK-101 at  $n_w = 7.1$ , and (4–10) samples 1 to 7, respectively. The values of  $n_w$  and  $E$  are given in mol  $\text{H}_2\text{O}$  per mol  $\text{SO}_3$  and g-equiv  $\text{mg}^{-1}$ , respectively.

exchange capacity and moisture content are presented in Fig. 2. The electrochemical and structural properties of the MF-4SK membranes were discussed in [18, 19]. As seen in Fig. 2, the concentration dependences of the electroconductivity for the membranes based on polyphenylene phthalamides change their character upon going from sample 7 to sample 1 with the largest exchange capacity. The corresponding curves are more convex. The electroconductivity of samples 4 to 7 weakly depends on the concentration of an external solution. The electroconductivity of all samples of perfluorinated membranes grows with the growing solution concentration. In this case, the absolute values of the electroconductivities are 2 or 20 times those for polyarylene sulfamide films (Fig. 2a). The electroconductivity of membranes is compared with the electroconductivity of NaCl solutions in Fig. 2a. As is known, these plots allow one to find coordinates of the isoelectroconductivity points of membranes [7], which are presented in the table. The concentration dependences of the electroconductivity for a series of samples studied in a wide range of NaCl concentrations are presented in Fig. 2b. For comparison, this figure also contains the dependences for homogeneous commercial membranes of the MF-4SK-101 type ( $n_w = 7.1$ ) produced by ONPO Plastopolimer (St. Petersburg), the MEC-CDC membranes produced by Morgan (France),

and the MK-100 membranes (Cherkassy, Russia). The dependences were measured under analogous experimental conditions. A comparison with the commercial samples of homogeneous membranes (curves 1–3) shows that, on average, the electroconductivity of the series containing Phenylone is lower by a factor of 2 to 3 over the entire concentration range studied.

In order to study other transport characteristics, it was of interest to examine samples with different concentration dependences of the electroconductivity. To this aim, we investigated the concentration dependences of the diffusion permeability for samples 1 and 6 and compared the results obtained with the analogous data for perfluorinated membranes (Fig. 3). The diffusion permeability coefficients of the sample free of Phenylone increase with the increasing solution concentration, whereas those of the membrane with an equimolar composition remain unchanged. The results presented show that the values of  $P$  for the MF-4SK membranes with  $n_w = 11.1$  and  $11.9$  are 2–30 times those for the polyamide membranes (Fig. 3a), while the sample with  $n_w = 5.1$  has close values of the diffusion coefficients. The transport numbers for water  $t_w$  do not depend on the concentration of an equilibrium electrolyte solution in the concentration interval under study and have comparable values with those for the MF-4SK membrane with  $n_w = 11.9$  (Fig. 3b). The transport num-



**Fig. 3.** The concentration dependences of (a) integral coefficients of diffusion permeability and (b) transport numbers for water, obtained in equilibrium NaCl solutions for (1) MF-4SK at  $n_w = 11.1$  and  $E = 0.93$  [18], (2) MF-4SK at  $n_w = 11.9$  and  $E = 0.76$  [19], (3) sample 1 at  $\omega = 0\%$ , (4) MF-4SK at  $n_w = 5.08$  and  $E = 0.93$  [18], and (5) sample 6 at  $\omega = 50\%$ . The values of  $n_w$  and  $E$  are given in mol  $\text{H}_2\text{O}$  per mol  $\text{SO}_3$  and g-equiv  $\text{mg}^{-1}$ , respectively.

bers for water that we obtained for our membranes are consistent with the numbers of water molecules per polymer chain found by independent structural methods [4].

Comparing the changes observed in electrotransport properties of the polyarylene sulfamide membranes and the perfluorinated membranes, which are rigid-chain polymers, points to significant differences in the structure and the state of water in them. The conductivity of polyamide membranes containing poly-*m*-phenylenephthalamide at  $n_w < 14.0$  does not depend on the electrolyte concentration over the whole concentration range studied. The conductivity of the MF-4SK membrane becomes concentration-independent only at  $n_w < 10.0$  [19]. The perfluorinated membranes differ from membranes studied in this work in that a cluster-channel structure forms in the former upon swelling. In the cluster-channel structure, the water is localized largely within clusters and is almost absent near the hydrophobic fluorocarbon matrix. In polyamide membranes, a larger fraction of water is localized near cations of metals, while the rest of the water interacts with the amide groups, leading to formation of the hydrogen bonds [1]. This can explain the large specific moisture content of the samples of polyamide membranes whose electrodiffusion properties stop depending on the concentration of an equilibrium solution. A relatively small change (20%) in moisture content of the samples under

study brings about essential changes in electroconduction, diffusion, and electroosmotic properties. The absolute values of the aforementioned transport characteristics on average are 3 to 4 times lower than those for the perfluorinated membranes with similar values of the exchange capacity and specific moisture content. This is connected not only with the structure of the transport channels, but also with their effective size. The latter was estimated on the basis of the NMR spectroscopy data. The transport channels of perfluorinated membranes range from 2 to 4 nm in size, whereas those of polyamide membranes range from 0.5 to 1.0 nm [14, 16, 20].

## CONCLUSION

The study performed has revealed the nature of the concentration dependences of electrotransport properties for a series of polyamide membranes containing different amounts of poly-*m*-phenyleneisophthalamide. The dependences were measured in sodium chloride solutions and compared with analogous parameters of homogeneous perfluorinated sulfocationite membranes. The study shows that electrotransport behavior of ionite membranes can accurately be controlled by varying the make-up and morphology of the polymer composition.

## ACKNOWLEDGMENTS

The authors acknowledge N.A. Yanul' from the Karpov Research Institute of Physical Chemistry, for donating samples of membranes.

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