

Properties of Cation Exchange Membranes Obtained in the Presence of Diluents

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Synopsis

The effect of inert diluents on the properties of cation exchange membranes had been studied. The membranes were prepared by modification of high-molecular polyethylene ($\bar{M}_n = 1.19 \times 10^6$) with styrene and divinylbenzene in the presence of toluene or heptane and following sulphonation. In the monomer mixture the diluent content was in the range of 5–30 wt. % and divinylbenzene was 3 or 7 wt %. The results obtained indicate that the properties of thus obtained membranes depend on the kind and amount of the diluent. It was found that the membranes, obtained in the presence of toluene, have much better transport properties than the membranes obtained in the presence of heptane at the same concentration in the monomer mixture. The best diffusion coefficient for sodium chloride was found for the membranes, obtained in the presence of 5 or 10 wt % toluene.

INTRODUCTION

The properties of ion-exchange materials may be modified by carrying out the polymerization of the monomer in the presence of an inert diluent. The studies of Millar et al.^{1–3} show that when styrene and divinylbenzene are copolymerized in the presence of a diluent, the resulting structure differs from that produced in the absence of a diluent. The cation exchangers obtained from such copolymers show considerable change in the mechanical properties, exchange kinetics, and the equilibrium. These characteristics are mostly determined by the nature and amount of the diluent and the crosslinking agent in the monomer mixture.

The effect of the kind and amount of the diluent on the properties of ion exchange membranes have been discussed in several studies.^{4–7} The experimental results show that, by carrying out copolymerization of styrene and divinylbenzene in the presence of defined amounts of diluents, it is possible to prepare weak base anion exchange membranes having better transport properties than these exhibited by the membrane prepared in the absence of diluents.^{6,7}

Results for the influence of the kind and amount of the inert diluent on the properties of cation exchange membrane with sulfonic groups are presented in this paper. The investigations cover toluene and heptane in the range of 5–30 wt % at varying divinylbenzene content in the monomer mixture.

A knowledge of the changes in the properties of membranes is of interest from the practical point of view.

EXPERIMENTAL

Membrane Preparation

The membranes used in the present investigation were obtained by copolymerization of styrene and divinylbenzene (DVB) monomers within a film of high-molecular polyethylene ($\bar{M}_n = 1.19 \times 10^6$ and $d = 937 \text{ kg/m}^3$), followed by sulfonation.⁸

The copolymerization was carried out for 2 h at 358 K and for 4 h at 368 K. The inert diluent content in the monomer mixture ranged from 5 to 30 wt %. The divinylbenzene content in the monomer mixture was 3 or 7 wt %. The poly(styrene-co-divinylbenzene) copolymer in the polyethylene/poly(styrene-co-DVB) system was 22 wt %.

The cation exchange membranes were prepared by sulfonation of polyethylene/poly(styrene-co-DVB) systems with a 15 wt % ClSO_3H solution in 1,2-dichloroethane for 5 h at 318 K and then hydrolyzed with a 20 wt % NaOH solution. The membranes in the sodium form were thus obtained.

Methods Used

The ion exchange capacity and the water content of the membranes were determined by the standard procedure.⁹

The electrical resistance was measured in 0.1M NaCl by the procedure reported earlier.¹⁰ The measurement was made at 298 K.

The transport numbers were determined from the concentration potential measured in the cell, using silver-silver chloride electrodes in the system 0.02–0.10M sodium chloride. The measurements were made at 298 K and a stirring rate of 300–500 rpm. Prior to making measurements, the membranes were soaked in the more dilute solution at 298 K for two days.

The diffusion coefficient of sodium chloride was determined from transport measurements at 298 K when the membrane was separating 0.1M NaCl solution from bi-distilled water. The method was described in our previous paper.¹¹

The tensile strength and elongation at break were determined for the membranes in a swollen state and in Na form at 298 K. The elongation rate used was 50 mm/min. The length of the examined part of the sample was 22 mm, its width was 0.4 mm, and its thickness from 0.20 to 0.25 mm.

The toluene regain was calculated from the variation of the weight of the sample before and after swelling in toluene. The equilibrium was reached after 48 h.

RESULTS AND DISCUSSION

The effect of inert diluents in the monomer mixture on the properties of polyethylene/poly(styrene-co-divinylbenzene) sodium sulfonate membranes obtained has been studied. The results obtained for the membrane properties depending on the nature and the amount of the diluent at 3 and 7 wt % DVB content in the monomer mixture are presented in Tables I and II.

It was found that, in the case when the divinylbenzene content was kept constant, the water content of the membranes (Table I) decreases with an

TABLE I
 Characteristics of Membranes Prepared at Different Diluent
 and Divinylbenzene Content in the Monomer Mixture^a

Diluent content (wt %)	Ion-exchange capacity (meq/g)		Water content (g/g)		Volume fraction of water (cm ³ /cm ³)		Tortuosity factor	
	A	B	A	B	A	B	A	B
	Toluene							
5	1.98	1.79	0.288	0.215	0.242	0.196	5.84	7.46
10	1.61	1.77	0.251	0.225	0.213	0.180	6.85	8.24
20	1.67	1.57	0.223	0.218	0.191	0.188	7.69	7.85
30	1.62	1.35	0.225	0.216	0.175	0.181	8.53	8.19
	Heptane							
5	1.75	1.99	0.241	0.223	0.179	0.193	8.30	7.62
10	1.85	1.83	0.265	0.214	0.203	0.162	7.67	9.30
20	1.55	1.62	0.200	0.214	0.155	0.188	9.79	7.85
30	1.69	1.46	0.212	0.178	0.169	0.132	8.88	11.76
	Absence of a diluent							
	2.01	1.77	0.266	0.190	0.203	0.158	7.67	9.59

^aA = data for membrane prepared from monomer mixture containing 3 wt % DVB; B = data for membranes prepared from monomer mixture containing 7 wt % DVB.

increase in the amount of toluene or heptane in the polymerization mixture. For mixtures containing 20 or 30 wt % toluene or heptane, its values were according to Millar's observation for cation exchangers. The membranes obtained from copolymers, synthesized in the presence of toluene have water content higher than that of membranes prepared from copolymers in the presence of heptane or in the absence of a diluent in the monomer mixture. The ion-exchange capacity of membranes essentially does not change when

TABLE II
 Transport Number, Electrical Resistance, and Diffusion
 Coefficients of Membranes for NaCl at 298 K^a

Diluent content (wt %)	Transport number (\bar{i}_{Na^+})		Diffusion coefficient (10 ⁶ cm ² /s)		Specific resistance (10 ² Ω m)	
	A	B	A	B	A	B
	Toluene					
5	0.861	0.789	2.70	1.70	1.99	4.35
10	0.927	0.810	2.31	1.52	2.68	4.81
20	0.945	0.882	1.93	1.32	3.00	5.37
30	0.942	0.875	1.52	1.49	5.51	4.78
	Heptane					
5	0.875	0.870	1.41	1.46	2.64	5.64
10	0.912	0.817	1.75	1.50	2.21	6.07
20	0.932	0.884	1.50	1.42	2.67	7.22
30	0.869	0.957	1.63	1.70	8.32	6.56
	Absence of a diluent					
	0.970	0.935	1.23	1.75	2.32	3.00

^aA, B: Symbols A and B as in Table I.

varying the type and amount of the diluent. These phenomena were accompanied by an increase on the tortuosity factor value (calculated from the volume fraction of water,¹¹ Table I) and an increase in the electrical resistance of the membranes with the dilution of the monomer mixture (Table II).

The electrical resistance of membranes, obtained from a system prepared in the presence of 30 wt % toluene or heptane, increased 2.5 or 3.5 times, respectively, as compared to that of a membrane obtained in the absence of a diluent at the same DVB content in the monomer mixture. At the highest dilution ratios used (30 wt %) the electrical resistance of the membrane obtained from polyethylene/poly(styrene-co-DVB) system prepared in the presence of toluene was lower than that of a membrane obtained from system prepared in the presence of heptane. The transport number of the membranes change with ambiguity when varying the type and amount of the diluent (Table II).

By diffusion coefficient values free diffusion of electrolytes through the membrane is judged. In the studies that were carried out, those values were determined using the kinetic relations, shown in Figure 1. The diffusion coefficients were calculated from slope of the linear part of the curves, where the steady flow had already been attained. The results obtained are presented in Table II. It can be seen from the data in the table that the diffusion coefficients of sodium chloride for the membranes obtained from copolymers synthesized in the presence of toluene (from 5 to 20 wt %) are higher than those obtained for membranes prepared from copolymers synthesized in the presence of heptane and absence of a diluent. Maximum values of diffusion coefficient were obtained at 5 and 10 wt % toluene, respectively— 2.7×10^{-6} cm²/s and 2.31×10^{-6} cm²/s. The values cited are 50–70% higher than those for the membrane prepared in the absence of a diluent. At a higher degree of dilution of the monomer mixture with these diluents, the diffusion coefficient values decrease. Analogous results are also obtained for the membrane properties at 7 wt % DVB. Their values are lower in comparison with those at 3 wt % DVB, due to the higher degree of crosslinking and heterogeneity of the material.

The analysis of the results for properties of the membranes shows that the relationships established are mostly due to the structural inhomogeneity of the

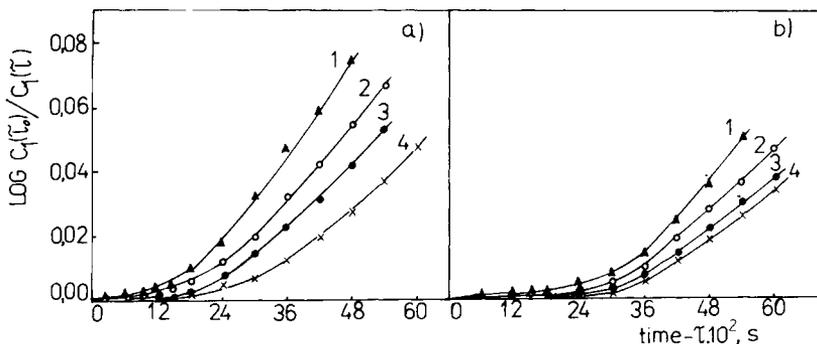


Fig. 1. $\text{Log } C_1(\tau_0)/C_1(\tau)$ vs. time for sodium chloride transport across the membranes at different toluene (a) and heptane (b) content in the monomer mixture: (1) 5 wt %; (2) 10 wt %; (3) 20 wt %; (4) 30 wt %. The DVB content is 3 wt %.

TABLE III
Some Properties of Polyethylene/Poly(styrene-co-Divinylbenzene) Systems Prepared at Different Toluene and Heptane Content in the Monomer Mixture^a

Type	Toluene regain (g/g)	Tensile strength (MPa)	Elongation at break (%)
HMPE	0.097 ^b	40.1	404
PE/poly(St-co-DVB)	0.610 ^c	43.9	305
PE/poly(St-co-DVB) prepared in the presence of 5 wt % toluene	0.541 ^c	35.6	270
PE/poly(St-co-DVB) prepared in the presence of 30 wt % toluene	0.586 ^c	35.2	180
PE/poly(St-co-DVB) prepared in the presence of 5 wt % heptane	0.536 ^c	32.7	180
PE/poly(St-co-DVB) prepared in the presence of 30 wt % heptane	0.559 ^c	37.6	230

^aThe divinylbenzene content is 3 wt %.

^bCalculated for 1 g amorphous phase in HMPE (crystallinity = 53.5%).

^cCalculated regarding poly(St-co-DVB) copolymer content in the system.

material. The good properties of the membranes obtained from polyethylene/poly(styrene-co-DVB) system, prepared in the presence of toluene, may be explained by the better contact between polyelectrolyte regions in the membranes and their structure.

According to Millar et al.,^{1,2} when styrene and divinylbenzene copolymerize in the presence of a solvating diluent toluene, the copolymer is formed in the swollen state. The nuclei are less entangled than those existing in the presence of a nonsolvating diluent, where a phase separation occurs and the tendency of the growing chains to entangle inside the virtually unswollen nuclei increases. The large number of chain entanglements and the uneven degree of crosslinking of poly(styrene-co-DVB) copolymer in the polyethylene, obtained in the presence of heptane, result in the lower toluene regain of polyethylene/poly(styrene-co-DVB) system (Table III) and lower water content of membranes derived from it (Table I).

Poly(styrene-co-DVB) copolymer in which the sulfonate groups are mainly entangled during the sulfonation is formed in the amorphous phase of polyethylene and this is indicated by five times higher toluene regain value in comparison with that of unmodified high-molecular polyethylene (HMPE), calculated regarding the amorphous phase of polyethylene (Table III).

The differences in the structure of copolymers caused by varying the polymerization conditions also affects the mechanical properties of polyethylene/poly(styrene-co-DVB) system (Table III).

The tensile strength and the elongation at break were measured to characterize the mechanical properties. The polyethylene/poly(styrene-co-DVB) system, prepared in the presence of 5 wt % toluene, has 19% lower tensile strength than polyethylene/poly(styrene-co-DVB), prepared in the absence of

a diluent, while 5 wt % heptane causes the tensile strength to decrease by 25%. The elongation at break changes from 305 (in the absence of a diluent) to 270% at 5 wt % toluene and 180% at the same content of heptane, respectively.

The studies of the porosity of the material that are carried out (by the Mercury intrusion method) show that membranes from PE/poly(styrene-co-DVB) systems, prepared in the presence of 5 and 30 wt % toluene have volume porosity (V) and average pore size (R) respectively as follows: $V = 0.0376 \text{ cm}^3/\text{g}$; $R = 0.06 \text{ }\mu\text{m}$ and $V = 0.0452 \text{ cm}^3/\text{g}$; $R = 0.0055$ and $0.0125 \text{ }\mu\text{m}$. Membranes prepared in the presence of heptane have $V = 0.2042 \text{ cm}^3/\text{g}$; $R = 0.125$ and $0.5 \text{ }\mu\text{m}$ (at 5 wt % of heptane) and $V = 0.2507 \text{ cm}^3/\text{g}$ and a wide pore size distribution (from 0.0083 to 0.0830 μm) at 30 wt % heptane.

References

1. J. R. Millar, D. G. Smith, W. E. Marr, and T. R. Kressman, *J. Chem. Soc.*, **218**, 2779 (1963).
2. J. R. Millar, D. G. Smith, W. E. Marr, and T. R. Kressman, *J. Chem. Soc.*, **1964**, 2740.
3. J. R. Millar, D. G. Smith, W. E. Marr, and T. R. Kressman, *J. Chem. Soc.*, **1965**, 304.
4. A. S. Tevlina and S. F. Sadova, *Zh. Prikl. Khim.*, **38**, 1643 (1965).
5. K. Dusek, *Polymer Networks. Structure and Mechanical Properties*, A. J. Chempff and A. S. Newman, Eds., Plenum, New York, 1971, p. 245.
6. G. Posniak and W. Trochimczuk, *Agnew Makromol. Chem.*, **92**, 155 (1980).
7. G. Posniak and W. Trochimczuk, *Agnew Makromol. Chem.*, **104**, 1 (1982).
8. A. Dimov and I. Alexandrova, *Desalination*, **46**, 361 (1983).
9. D. M. Wallace, *Ind. Eng. Chem. Process Des. Dev.*, **6**, 423 (1967).
10. A. Dimov and I. Alexandrova, *J. Chem. Soc., Faraday Trans. I.*, **83**, 284 (1987).
11. A. Dimov and I. Alexandrova, *Synthetic Polymeric Membranes*, B. Sedlacek and J. Kohovec, Eds., de Gruyter, New York, 1987, p. 55.
12. S. Prager, *J. Chem. Phys.*, **33**, 122 (1960).

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