THE STRUCTURE AND HYDRATION OF COMPOSITE MEMBRANES BASED ON POLYACRYLONITRILE

Galina A. TISHCHENKO[a], Miroslav BLEHA[b], Věra TYRÁČKOVÁ[b], Tatyana E. SUKHANOVA[a], Svetlana A. GULEVSKAYA[a], Kira A. KOSHCHEENKO[a] and Larisa K. SHATAEVA[a]

[a] *Institute of High-Molecular-Weight Compounds, Russian Academy of Sciences, St.Petersburg, Russia*

[b] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, The Czech Republic*

Received March 19, 1992
Accepted August 27, 1992

The morphology of polyacrylonitrile composite membranes containing microdispersions of ion exchange resins was investigated by gas adsorption, mercury porosimetry, and scanning and transmission electron microscopy. The relation between the structure, hydration and permeability of composite membranes at the transmembrane difference of pH and pNa was studied.

The preparation of composite ion exchange materials in the form of granules or membranes requires a good compatibility and adhesion of ion exchange resin dispersion with the polymeric binding agent[1 - 3], to ensure good mechanical properties of materials at high degrees of filling with dispersed particles. High hydration of the dispersion and of the binding agent, i.e. a single phase of the solvent which is the transport medium and ensures permeability of the structure, is of no lesser importance[1]. Electroneutral polymers, such as polyethylene, polypropylene, poly(vinyl chloride) and the like[3], are binding agents most frequently in use. However, these binding agents are hydrophobic and cannot ensure the existence of a continuous inner water phase in the membrane. Hence, such binding agent is a hindrance to the ionic flow[2,3].

In the preparation of biotechnological membranes and in the synthesis of biosorbents, a combination of high hydrophilicity and porosity of structure enhances permeability of the material to macromolecules of proteins and other physiologically active compounds. At the same time, the native (hydrated) state of the components is preserved[4].

The aim of this work consisted in an investigation of the relation between morphology, hydration and permeability of composite membranes containing polyacrylonitrile (PAN) as the binding agent.

EXPERIMENTAL

Composite membranes containing the carboxylic cation exchanger KMT (Institute of High-Molecular-Weight Compounds, St. Petersburg), the weakly basic anion exchanger AMBD (Institute of Macromolecular Chemistry, Prague), the strongly basic anion exchanger AV-17X8 (NPO Plastmassy, Russia) or the hemosorbent SKN (INO, Kiev, The Ukraine) as the dispersed phase were obtained by the wet procedure using PAN as the binding agent. Microdispersions of these sorbents with particles 3 – 6 μm in size were obtained by crushing standard sorbents in a ball mill and fractionating by sedimentation in water. The particle size and homogeneity of the dispersion were evaluated using a MBI-6 microscope (Lomo, St. Petersburg, Russia). The solution of PAN was obtained by dissolving the fibre Nitron in a 50% aqueous solution of recrystallized sodium thiocyanate at 80 °C to the final concentration 9 wt.%. The suspension of the sorbents, equilibrated with a 50% solution of NaSCN in an amount between 25% and 70% related to the weight of the composition was introduced into the solution of PAN so as to make its final concentration in the mixture not lower than 7 wt.%. The mixture was cast on glass supports from a nozzle with a slit width 100 μm and placed in water. The membranes were fixed on the support, washed from NaSCN and thermally treated[5] at the T_g of PAN (90 °C) for 1 min. The membrane thickness was measured with a micrometer.

For scanning electron microscopy the membranes were dried by lyophilization or dehydrated by using successive solvents (critical point method), then fractured in liquid nitrogen, after which a gold layer 10 nm thick was vacuum-deposited on the samples in the cell of a sputtering device (Balzers). The morphology of membrane surfaces and of the fracture was observed in a scanning electron microscope JSM-35 JEOL at 25 kV.

For transmission electron microscopy the samples were fixed in a 20% solution of osmic acid with 0.1 M cacodylate buffer, dehydrated in aqueous ethanol of increasing concentration and embedded in epoxy resin according to the Spurr method[6]. During the dehydration the material was additionally contrasted by using uranyl acetate. Ultrathin sections obtained with a Reichert microtome were contrasted with uranyl and lead acetates. The sections were investigated in a JEM-100B JEOL electron microscope. In all cases the morphology of composite membranes was investigated using membranes prepared without adding a dispersion of the sorbent (neutral PAN membranes) as the controls. The specific surface area of the pores was determined by the gas adsorption method using a Quantasorb (Quantachrome Corp., U.S.A.) apparatus. The total pore volume was measured by the mercury porosimetric method in a Porosimeter 225 (Carlo Erba Strumentazione, Italy), but only for membranes with the specific surface area above 1 m^2/g. The amount of water in the pores (moisture content) was determined by drying at 120 °C to constant weight. The exchange capacity of the membranes with respect to univalent sodium or chloride ions was obtained by potentiometric titration[7]. The carboxylic membranes were modified using Fe^{3+} ions by the equilibrium sorption method from 0.033 M $FeCl_3$ at pH 2.6. The content of Fe^{3+} ions in the membrane was determined spectrophotometrically at 254 nm after washing the membrane with 0.1 M HCl.

Permeability of the membranes with respect to the hydrogen (sodium) ion was investigated in a two-compartment cell, compartment volume 50 cm^3, separated by a membrane with the window diameter 2 cm. The compartments were filled with 0.1 M HCl (feed) and 0.1 M NaCl (receiver), or with 1 M NaCl and water, respectively. The rate of change in pH (pNa) in the receiving compartment was recorded continuously by means of glass electrodes. Each time the cation and anion exchange membranes were used, respectively, in their H^+ and Cl^- forms. Permeability P of the membranes to hydrogen (sodium) ions, Q (mg-equiv), within time t was calculated from experimental data using[8] the known equation (*1*):

$$Q = \frac{P c_0}{l} \left(t - \frac{l^2}{6D} \right), \qquad (1)$$

where P is the permeability coefficient (cm^2/s), c_0 is the starting concentration of the diffusant (mg-equiv/cm^3), l is the membrane thickness (cm), and D is the effective diffusion coefficient (cm^2/s).

RESULTS AND DISCUSSION

The formation of membranes by employing the "wet" procedure favours the formation of structures possessing the largest specific surface area and porosity. The composite membranes thus obtained contain a considerable amount of water. Heating of the membranes at T_g removes the excess of stress in the porous matrix of the polymer obtained under nonequilibrium conditions, causing a considerable contraction of the membranes and standardization of their properties. With an increase in the dispersion content from 25% to 70% the volume contraction of composite membranes decreases from 10 – 15% to 3 – 4%, respectively. The presence of a microdispersion of hydrophilic crosslinked sorbents reduces volume effects in the heat treatment of the composites compared with neutral PAN membranes, the contraction of which reaches 40%. The specific pore surface area of the composites and the moisture content do not vary with varying degree of filling with the dispersion. At the same time, porosity of the composite membranes remains sufficiently high, exceeding that of PAN membranes, probably due to the effect of the hydrophilic disperse phase on the formation of structure of the polymeric binding agent during coprecipitation. A comparison between integral porosity characteristics and pore size distribution (Fig. 1, Table I) makes possible an analysis of the role played by the disperse phase in the formation of structure of the composite membranes. As can be seen in Fig. 1, the PAN–KMT membranes are characterized by at least three porosity levels (with respect to the pore radius): 5 to 10 nm, 10 to 20 nm, 20 to 40 nm and more. It should be pointed out that, while the fraction of

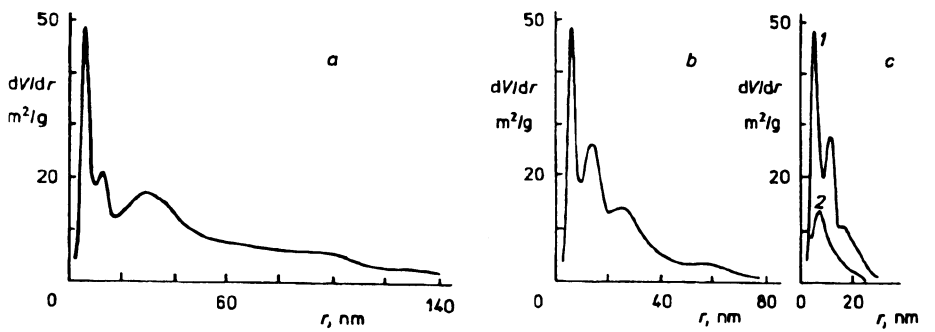

FIG. 1

Pore distribution in the PAN–KMT composite membranes depending on the ion exchanger content (wt.%): *a* 25; *b* 50; *c* *1* 75, *2* 100

the specific surface area of the PAN–KMT membrane pertaining to the pores of the first and second level is approximately the same, independent of the degree of filling with the dispersion, the contribution of the largest pores (third level) to the specific surface area decreases from 60% to 15% with increasing content of the dispersion.

In addition to the integral porosity characteristics, the composite morphology was also studied in all stages of the preparation and modification of the membranes by the SEM and TEM methods. It can be seen in Fig. 2 that prior to the heat treatment neutral PAN membranes (Fig.2*a*) and PAN–KMT membranes have slit-shaped macropores oriented to the surfaces. The specific surface area of pores of such membranes is small, not exceeding 1 – 2 m^2/g. After the heat treatment the macropores in the PAN membranes virtually disappear (Fig. 2*b*), but remain to a considerable extent in the composite PAN–KMT membranes (Fig. 2*c*) the membrane structure becomes "spongy" with a sufficiently uniform pore distribution. Investigation of the PAN–KMT membranes using large magnifications shows the morphological similarity between filled and unfilled membranes. It seems that the ion exchange resin and the polymeric binding agent have close electron density values and cannot be distinguished by SEM. Only contrasting of the ion exchange resin dispersion by sorption of Fe^{3+} ions makes visible the distribution of KMT particles throughout the membrane (Fig. 2*d*). It can be seen that the selective sorption of iron ions accompanied by a partial dehydration and thickening of the polymeric matrix with dispersed particles leads to their separation into a separate phase which is stained during fracturing of the membrane. Particles of the ion exchange resin are not aggregated and are uniformly distributed in the binding agent which, similarly to the neutral membranes, has a spongy structure.

All membranes obtained by employing the procedure just described have an asymmetrical structure. The air-facing membrane surface has a thin layer with packed

TABLE I
Characteristics of composite ion exchanger–polyacrylonitrile membranes

Ion exchanger (content[a], wt.%)	Capacity mg-equiv/g[a]	Water content g H_2O/g[a]	Surface area m^2/g	Pore volume cm^3/g
KMT (0)	–	3.8	73.4	0.18
KMT (25)	2.30	6.9	134.4	1.72
KMT (50)	4.54	6.2	110.8	0.77
KMT (67)	6.70	5.6	78.7	0.37
AV-17X8 (25)	0.80	6.0	125.4	1.20
AV-17X8 (50)	1.70	5.3	74.2	1.12

[a] Dry membrane.

structure (Fig. 3*a*), while the surface adhering to the glass support has a developed pore system (Fig. 3*b*), the same as the remaining volume of the membrane (Fig. 3*c*).

Transmission microscopy allows us to observe not only the distribution of disperse ion exchange resin particles in the binding agent due to the different contrasting density of these phases, but also the extent of their penetration at higher resolution values. TEM of the PAN–KMT membranes shows that the coprecipitation of PAN and of the KMT dispersion (dark network in Fig. 4) from aqueous sodium thiocyanate into water leads to a partial penetration of PAN chains into KMT pores. As a result, both the ion exchange resin and the binding polymer form a common structure, the micropores of which contain a continuous aqueous phase.

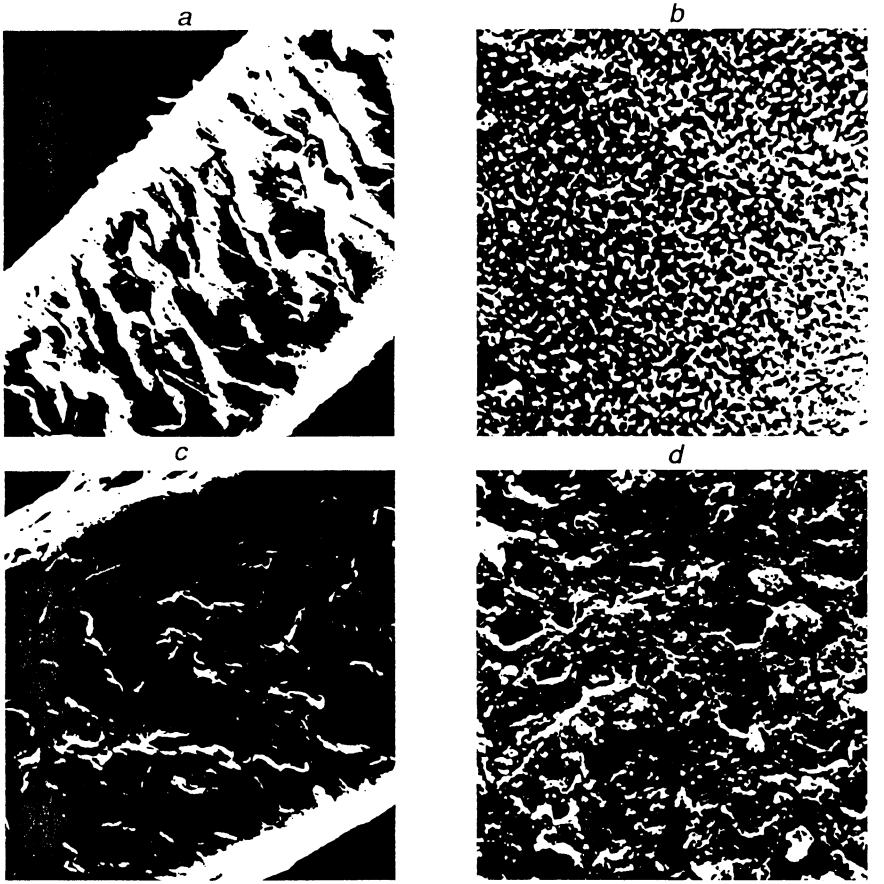

FIG. 2

Electron micrographs of composite membranes fractures: *a* PAN (. 500); *b* PAN heat-treated (× 5 000); *c* PAN–KMT (50 wt.%) in the H^+ form heat-treated (× 500); *d* PAN–KMT (50 wt.%) in the Fe^{3+} form heat-treated (× 625)

Transport characteristics of the composite membranes were examined with respect to hydrogen and sodium ions, i.e. at the transmembrane gradient of pH and pNa, and also with respect to some physiologically active compounds (riboflavin monophosphate, vitamin B_{12}, haemoglobin) at the transmembrane concentration gradient in 0.1 M NaCl. Table II shows that the permeability of all investigated membranes to low-molecular-weight electrolytes is very high, but decreases considerably for a high-molecular-weight penetrant. At the same time, the permeability coefficient for hydrogen ions of the PAN–KMT membranes is higher by almost an order of magnitude than with the composite membranes obtained using cellulose as the binding agent, although the moisture content of these materials is comparable (P = 13 . 10^{-10} m^2/s and 9 . 10^{-11} m^2/s, respectively)[4].

It should be pointed out that, if the composite membranes based on PAN with disperse particles of various sorbents are obtained by precipitating the composite from

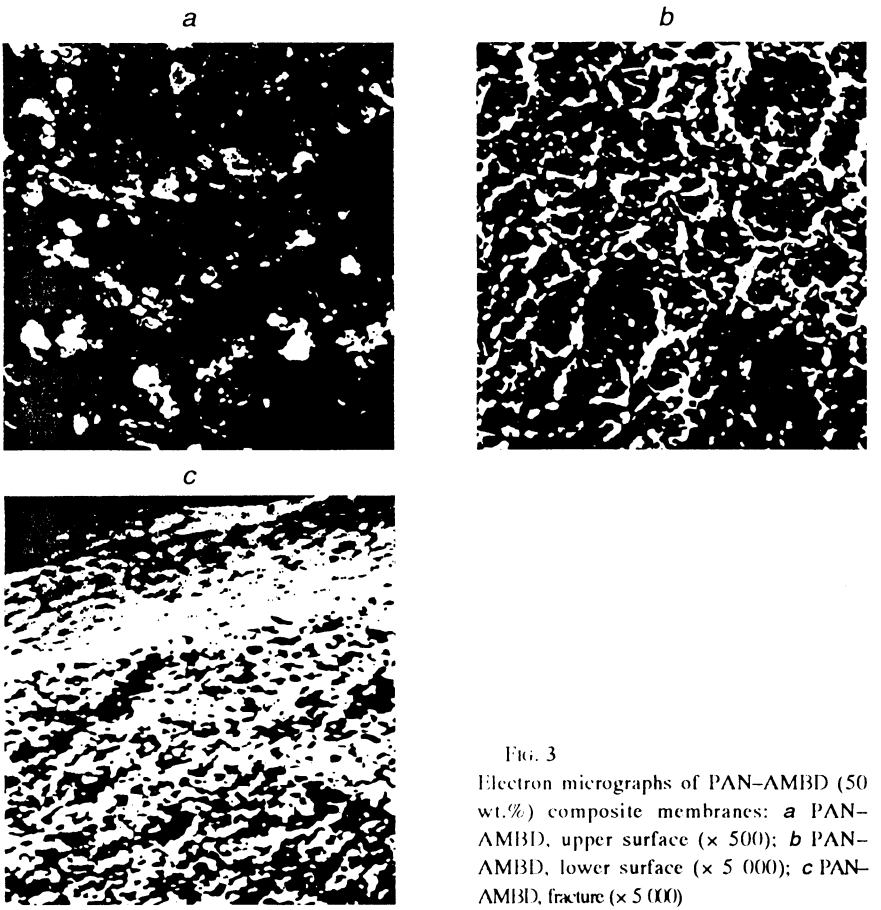

FIG. 3
Electron micrographs of PAN–AMBD (50 wt.%) composite membranes: *a* PAN–AMBD, upper surface (× 500); *b* PAN–AMBD, lower surface (× 5 000); *c* PAN–AMBD, fracture (× 5 000)

an aqueous salt solution, their basic morphological characteristics such as porosity, specific surface area, and moisture content depend predominantly not on the nature of the dispersion, but on its amount. This allows us to employ PAN as a universal binding agent.

CONCLUSIONS

The application of polyacrylonitrile as a polymeric binding agent for microdisperse ion exchangers makes possible the preparation of highly porous and hydrophilic polymer structures possessing a continuous inner water phase in the composite. The uniformity of structure and transport parameters in the composite membranes having the same degree of filling with miscellaneous ion exchangers suggests the use of polyacrylonitrile as the universal binding agent for heterogeneous ion exchange membranes.

TABLE II
Permeability ($P \cdot 10^{-10}$ m^2/s) of composite ion exchanger–polyacrylonitrile membranes to various species. RFM riboflavin monophosphate, B_{12} vitamin B_{12}, Hgb haemoglobin

Ion exchanger (content, wt.%)	H^+	Na^+	RFM	B_{12}	Hgb
KMT (0)	13.6	5.5	–	–	–
KMT (25)	14.2	5.9	–	–	–
KMT (50)	13.6	5.7	1.0	0.8	0.03
KMT (67)	12.1	5.5	–	–	–
AMBD (25)	14.3	6.0	1.7	0.6	0.03
AMBD (50)	13.8	5.8	–	–	–
SKN (25)	14.0	5.9	–	–	–
SKN (50)	13.0	5.6	0.6	0.5	0.07

FIG. 4
Transmission electron micrograph of the PAN–KMT (50 wt.%) membrane: distribution of KMT particles in the PAN matrix (× 15,000)

REFERENCES

1. Samsonov G. V., Melenevskii A. T.: *Sorbtsionnye i khromatograficheskie metody fiziko-khimicheskoi biotekhnologii.* Nauka, Leningrad 1986.
2. Timashev S. F.: *Fizicheskaya khimiya membrannych protsessov.* Khimiya, Moskva 1988.
3. Smirnova N. M., Laskorin B. N.: *Ionoobmennye membrany i ikh primenenie.* Khimiya, Moskva 1961.
4. Tishchenko G. A., Shataeva L. K., Blcha M., Vacík J., Papukova K. P., Samsonov G. V., Kálal J.: Vysokomol. Soedin., A *31*, 469 (1989).
5. Nachinkin O. I., Dyakonova E. B., Ruban I. G.: *Volokno-plenochnye polimernye svyazivayushchie agenty i produkty izgotovlyaemye iz nikh.* Khimiya, Leningrad 1980.
6. Spurr A. R.: J. Ultrastruct. Res. *26*, 3 1969.
7. Polanskii N. G., Gorbunov G. V., Polanskaya N. L.: *Metody issledovaniya ionoobmennykh materialov,* p. 159. Khimiya, Moskva 1976.
8. Crank J.: *The Mathematics of Diffusion,* 2nd ed., p. 51. Clarendon Press, Oxford 1975.

Translated by L. Kopecká.