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TUBULAR INTERPOLYMER ANION EXCHANGE MEMBRANES 2. WEAK BASE ANION EXCHANGE MEMBRANES AND THEIR TRANSPORT PROPERTIES

A series of tubular weak base anion exchange membranes with diethylamine groups has been obtained from polyethylene/poly(styrene-co-divinylbenzene) systems [PE/poly(St-co-DVB)] containing various amounts of DVB (from 1 to 6 wt.-% in the aromatic component of the polymeric material). The membranes had similar ion exchange capacities (ca. 1.6 mmol/g), but differed in the molar concentrations of ionic groups (from 4.5 to 7.6 mmol/cm³).

The transport properties of the membranes were characterized in the system: diluted HNO₃/membrane/concentrated NH₄OH. The membranes have been found suitable for dialytic removal of nitric acid from aqueous solutions. The best properties had the membrane obtained from the system containing 3 wt.-% of DVB. For this membrane, the flux, transport rate constant, and efficiency coefficient were 8.3×10^{-8} mol/cm²s, 24.7×10^{-4} s⁻¹, and 0.730, respectively.

1. INTRODUCTION

Low energy demand, for not being accompanied by any phase transitions, is the main advantage of the separation process involving membranes. Therefore these processes are competitive with the traditional methods of purification and separation.

The dialysis may serve as an example of membrane separation. The conventional dialysis, according to GRAHAM [1], is the process of selective diffusion of low molecular compounds through semipermeable membranes from a solution containing colloids and polymers to water.

The Donnan dialysis [2] is a specific dialytic process in which ionic selectivity and the Donnan potential [3] are utilized to induce an interdiffusion of counterions.

The difference between the two dialytic processes is shown schematically in fig. 1. In the conventional dialysis, ions diffuse across the membrane to water. In the

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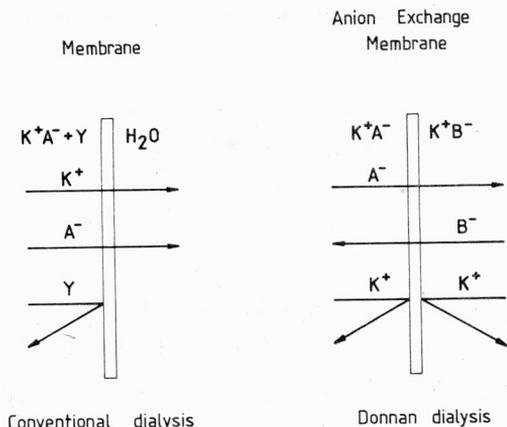


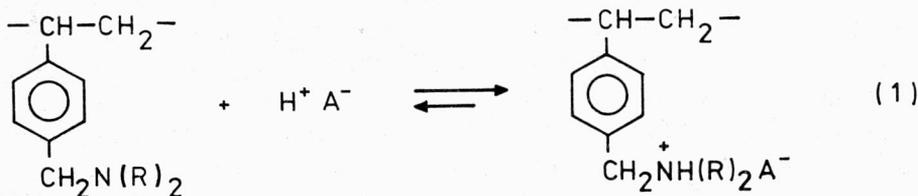
Fig. 1. Schematic diagram of conventional and Donnan dialyses

A^- , B^- — anions, K^+ — cation, Y — colloidal or polymeric material

Donnan dialysis, carried out using an anion exchange membrane, two counterions A^- and B^- diffuse through the membrane in opposite directions until an equilibrium is reached. The opposite fluxes of anions are coupled to ensure the electroneutrality since the coions are excluded from the membrane phase due to the Donnan effect [3].

The Donnan dialysis can conveniently be used in the wastewater treatment. This technique is essential both in purification of wastes and in recovery of valuable solution components. It can be applied to deacidification of rinse waters from nitrocellulose plants [4], separation and concentration of heavy metals from galvanic baths [2], [5]–[7], etc.

Weak base anion exchange membranes [8]–[11], used as diaphragms in the dialytic separation of acids, have some interesting properties. They reveal their ion exchange properties only in a protonized form, i.e., in solutions of $\text{pH} < 7$. The ion exchange groups (usually amine) bound protons with the free electron pairs at nitrogen atoms. The positively charged groups are then capable of linking electrostatically acid anions:



where R is hydrogen or alkyl group and A^- denotes an acid anion. In a solution of $\text{pH} > 7$, the groups deprotonize



The contribution of weak base groups to an ion exchange process in a neutral medium is negligibly small since the apparent equilibrium constant of the reaction [12], [13]:



is, depending on R, of 10^{-5} – 10^{-6} order.

The weak base membranes were applied as dialytic diaphragms to the separation of acids from the solutions used in hydrometallurgy [8], [14]. Such a process proceeds effectively since:

1. The coions (cations) are excluded from the membrane phase by the Donnan equilibrium [3].
2. Hydrogen ions have much higher mobility than other cations [8].
3. Due to ion-pairing, a specific sorption of strong acids by weak base ionic groups occurs [15], [16].

The ion exchange membranes obtained from interpenetrating polymer network (IPN) systems [17], such as polyethylene/poly(styrene-co-divinylbenzene) system [PE/poly(St-co-DVB)] [18] seem to be particularly predestined for the use in diffusion separation processes because of their high selectivity, good electrochemical properties and excellent mechanical and osmotic stability. The membranes of this type can be formed into any shape; they can be used in the form of sheets or tubes.

An application of tubular ion exchange membranes instead of traditional sheet-shaped ones has the following advantages:

1. The dynamics of diffusion and ion exchange processes is enhanced.
2. The effect of concentration polarization is diminished.
3. The size of equipment can be considerably reduced.

The aim of this work was to prepare weak base anion exchange membranes obtained from PE/poly(St-co-DVB) systems and to apply them to removal of nitric acid from aqueous solutions.

2. EXPERIMENTAL PROCEDURE

2.1. PREPARATION OF MEMBRANES

Tube-shaped samples of PE/poly(St-co-DVB) systems were obtained according to the procedure described elsewhere [18]. The crosslinking degree of the IPN system (weight percentage of DVB in the aromatic component of the polymer material) was 1,3,4, or 6. The tubes were chloromethylated with methyl-chloromethyl ether in the presence of SnCl_4 as catalyst [19] and aminated with diethylamine [9].

2.2. METHODS

The equilibrium swelling degree of the membranes was determined in 0.0005 M aqueous HCl solution [9] and the total ion exchange capacity was found according to Hecker's method [20]. The specific resistance of the membranes was measured in 0.2 M aqueous HCl solution in a cell similar to that described by GRYTE and GREGOR [21]. The tensile strength and elongation at break of the membranes swollen in 0.0005 M aqueous HCl solution were measured with a tensile testing machine ZT-40.

The transport experiments were carried out in a laboratory dialyser at room temperature. The measuring set is shown schematically in fig. 2. Diluted HNO_3 flew

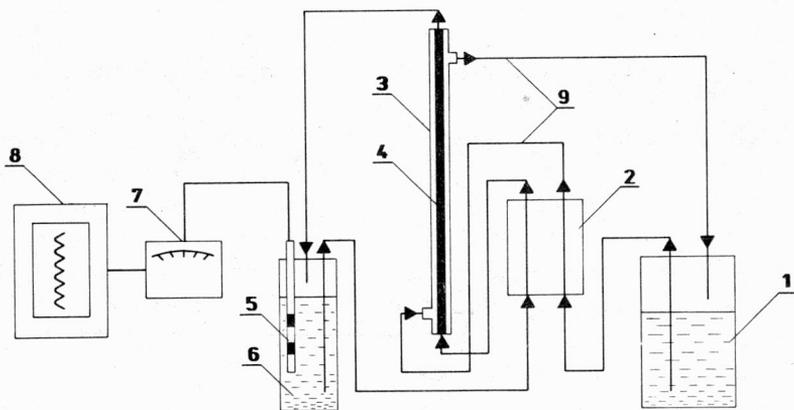


Fig. 2. Schematic diagram of a diffusion measuring set

1 - ammonium hydroxide solution, 2 - pump, 3 - jacket, 4 - ion exchange tube, 5 - electrode, 6 - nitric acid solution, 7 - conductometer, 8 - recorder, 9 - silicon tubes

inside the ion exchange tube (5 mm outer diameter, 0.3 mm wall thickness, 0.5 m long). The active surface of the membranes was 75 cm^2 . Concentrated NH_4OH was fed to the jacket surrounding the ion exchange tube. The solutions circulated concurrently with the same rate of $0.55 \text{ cm}^3/\text{s}$.

Prior to each measurement the membranes were conditioned for 0.5 h in the same measuring set and then fresh solutions were introduced to start a run. The concentration changes of HNO_3 solution were followed by recording the conductivity of the solution.

The experiments were carried out for two different concentration ratios of $\text{NH}_4\text{OH}:\text{HNO}_3$, namely 100:1 and 50:1. The concentration of NH_4OH was 5 mol/dm^3 . The volumes of diluted and concentrated solutions were measured before and after each run.

The dialysis was characterized by:

1. The efficiency coefficient EF

$$EF = (c_0 - c_t)/c_0 \quad (4)$$

where c_0 and c_t are initial and actual concentrations of nitric acid [g/dm^3], respectively, at time t .

2. The HNO_3 transport rate constant k [7]

$$k = F/V_r \ln \frac{F}{F - V_c S} \quad [\text{s}^{-1}] \quad (5)$$

where F is the recirculation rate of acid solution in the tubular membrane [cm^3/s], V_c and V_r are the total volume of recirculated acid and the volume of acid in the ion exchange tube, respectively, [cm^3], and S is the slope of the linear plot $\ln c_0/c_t$ vs. time [s^{-1}].

3. RESULTS AND DISCUSSION

The transport properties of ion exchange membranes depend primarily on their structure. In this work, the structure of membranes was modified by changing the crosslinking degree of the starting IPN systems.

The characteristics of resulting membranes are shown in tab. 1.

Table 1

Characteristics of weak base anion exchange membranes

Sample* A-a/b	Exchange capacity Z_c mmol/g dry membrane	Water content P_w g/g dry membrane	Molarity of ion groups** C_m mmol/cm ³	Specific resistance in 0.2 M HCl $\Omega \times \text{m}$	Tensile strength MPa	Elongation at break %
A-30/1	1.62	0.363	4.45	6.4	9.7	94
A-30/3	1.60	0.315	5.06	7.3	10.1	82
A-30/4	1.62	0.274	5.90	8.5	10.3	33
A-30/6	1.61	0.212	7.58	11.0	10.6	14

*Designation: a – weight fraction of monomers in the initial mixture; b – content of DVB isomers in the monomer mixture.

** The molarity of the ion exchange groups was calculated as $C_m(Z_c/P_w) \rho_w$ where ρ_w [g/cm^3] is density of water.

The effect of crosslinking degree upon the properties of the membranes can clearly be seen. The membranes have good mechanical stability. The tensile strengths are similar and the elongation at break reduces by the factor of 6 as the crosslinking degree increases.

The specific resistance of the membranes also increases with crosslinking degree by the factor of 2.

The molar concentration of ionic groups in the membranes increases by nearly 50% as the DVB content changes from 1 to 6 wt.-%. This is related to the equilibrium swelling of the membranes in water, since all the membranes have similar ion exchange capacities and contain ionic groups of the same kind.

The transport properties were measured in the model system:

concentrated NH_4OH /membrane/diluted HNO_3 .

The driving force of the NO_3^- ion transport is the Donnan potential [3]. In this system, hydroxy anions are transported to nitric acid where they react with hydrogen cations to weakly dissociated water molecules. Hence, the NO_3^- driving force induced by the OH^- concentration potential becomes very large. On the ammonium hydroxide side, ammonium nitrate is formed which can directly be used as fertilizer. A selective transport of nitric acid proceeds via formation of ion pairs between the weak base groups and acid molecules as shown in reaction (1). The hydrogen cations are transported along with NO_3^- anions since ammonium hydroxide, being weaker a base than the membrane polybase, does not affect the fully protonized form of the latter. The backward flow of NH_4OH has been found insignificant with respect to the effectiveness of the transport of acid. In a similar system where a strong base, NaOH , was used instead of NH_4OH , the effectiveness of deacidification reduced by 80%. This was because of the deprotonizing effect of NaOH , according to reaction (2).

The results of the dialysis are shown in tab. 2.

The plots $\ln c_0/c_t$ are shown in figs. 3 and 4. EF_{\max} (the highest efficiency coefficient and the time of reaching it) and t_{\max} were determined from plots EF vs. time (figs. 5 and 6).

Table 2

Transport properties of weak base anion exchange membranes

Sample* A-a/b	Molar concentration ratio $\text{NH}_4\text{OH}:\text{HNO}_3$	Acid transport rate constant $10^4 k$ s^{-1}	Efficiency coefficient EF_{\max}	Time of dialysis $10^{-3} t_{\max}$ s	Acid flux $10^8 J$ $\text{mol}/\text{cm}^2\text{s}$
A-30/1	100:1	4.3	0.710	28.8	4.31
	50:1	3.0	0.690	21.6	1.96
A-30/3	100:1	24.7	0.730	15.6	8.29
	50:1	6.8	0.655	9.6	2.27
A-30/4	100:1	9.3	0.676	15.6	9.59
	50:1	3.8	0.665	21.6	1.02
A-30/6	100:1	8.4	0.705	36.0	3.03
	50:1	3.2	0.715	43.2	0.98

*For designation see tab. 1.

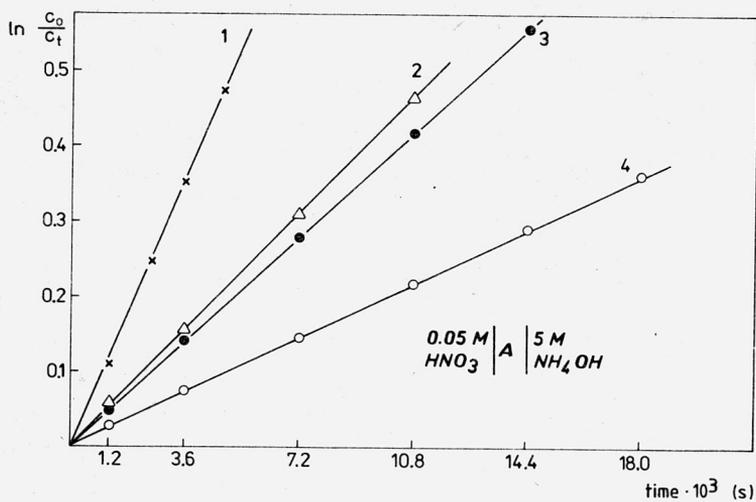


Fig. 3. Plots of $\ln \frac{c_0}{c_t}$ vs. time for HNO_3 transport through weak base membranes
 1 - membrane A-30/3, 2 - membrane A-30/4, 3 - membrane A-30/6, 4 - membrane A-30/1

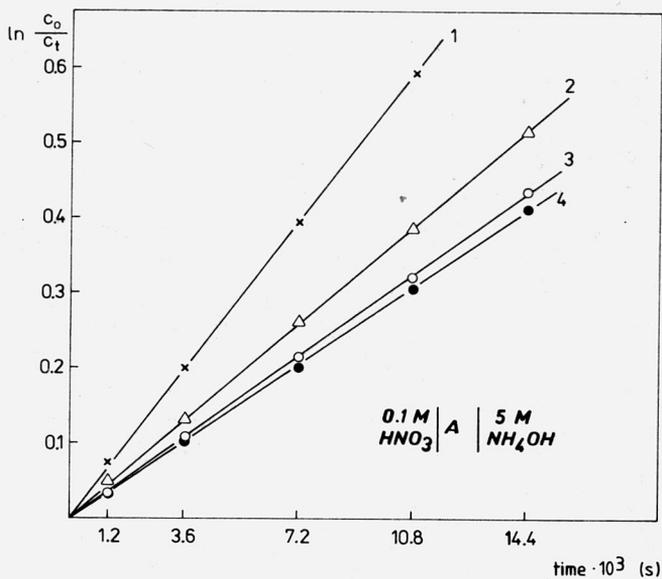


Fig. 4. Plots of $\ln \frac{c_0}{c_t}$ vs. time for HNO_3 transport through weak base membranes
 1 - membrane A-30/3, 2 - membrane A-30/4, 3 - membrane A-30/6, 4 - membrane A-30/1

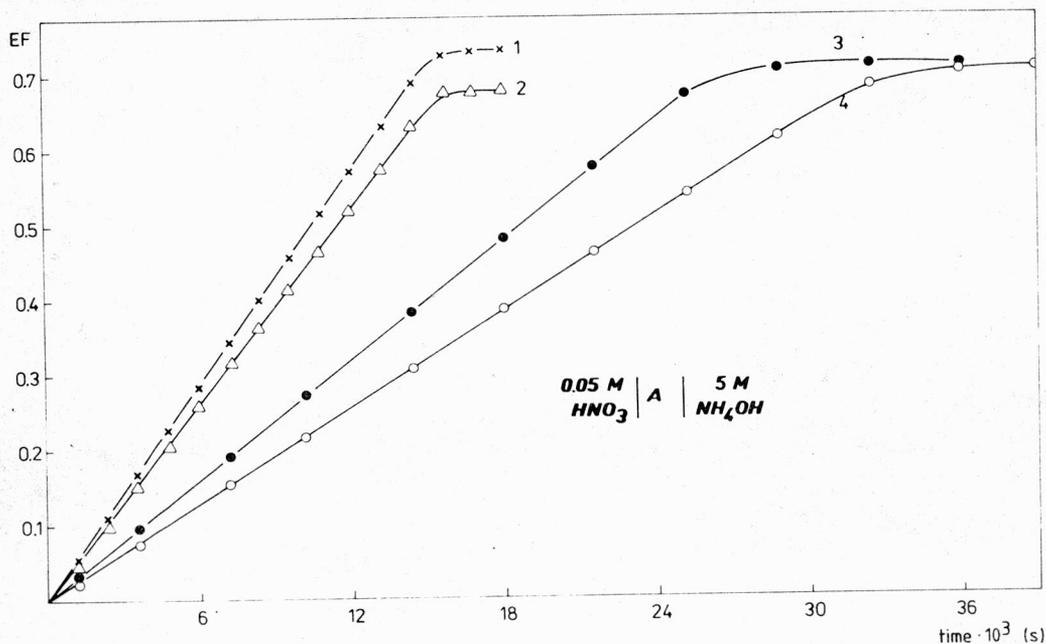


Fig. 5. Plots of efficiency coefficient vs. time for HNO_3 dialysis through weak base membranes
 1 - membrane A-30/3, 2 - membrane A-30/6, 3 - membrane A-30/1, 4 - membrane A-30/4

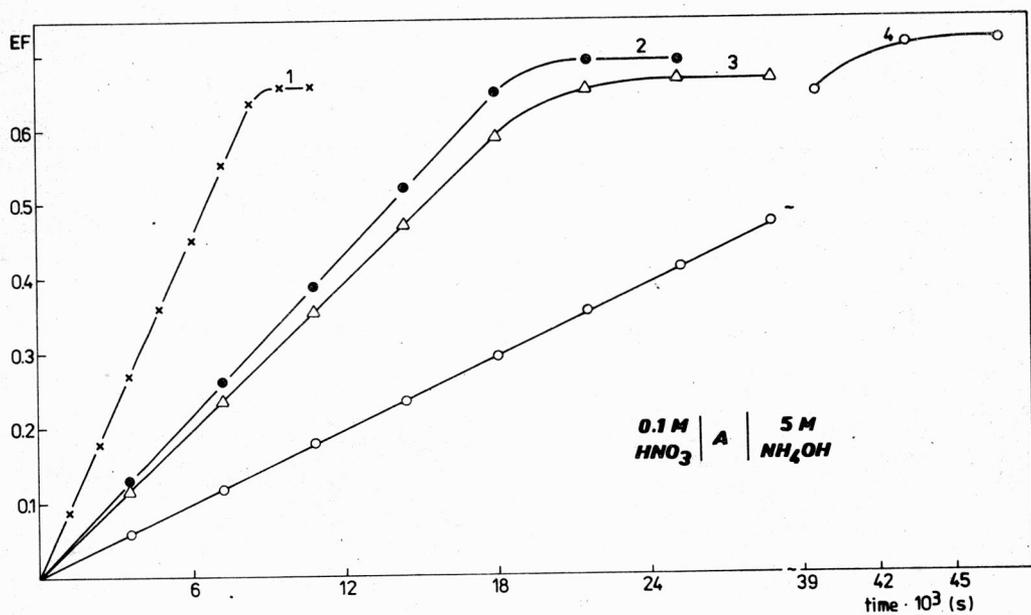
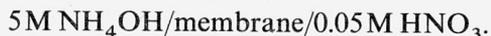


Fig. 6. Plots of efficiency coefficient vs. time for HNO_3 dialysis through weak base membranes
 1 - membrane A-30/3, 2 - membrane A-30/1, 3 - membrane A-30/4, 4 - membrane A-30/6

No significant changes in volumes of the solutions were observed during experiments.

As expected, the acid transport proceeds more effectively for the higher ratio of solution concentrations, i.e., for the system:



The data shown in tab. 2 suggest that the transport properties of the membranes depend on the crosslinking degree of the starting IPN systems. The membranes containing more DVB have higher molar concentration of ionic groups and therefore the Donnan potential, the driving force for NO_3^- ions transport, becomes smaller.

By comparing the values of HNO_3 transport rate constant, efficiency coefficient, and HNO_3 flux it becomes apparent that the membrane A-30/3 is the most effective one for dialytic removal of nitric acid from dilute aqueous solutions.

The known poor resistance of PE to oxidation required testing whether or not the properties of the membranes changed in the HNO_3 environment. To verify the seriousness of the danger, the membrane A-30/3 was kept in 1 M HNO_3 solution for 3, 6, and 9 weeks. The changes in some properties of the membrane are shown in fig. 7. It can be seen that the long contact of the membrane with HNO_3 solution does

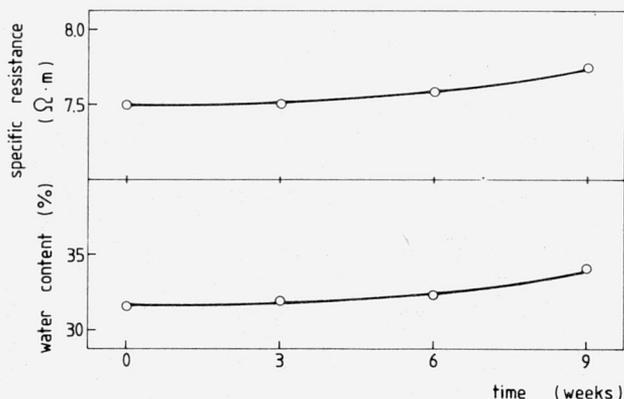


Fig. 7. Characteristics of membrane A-30/3 after exposure in 1 M HNO_3 solution

not seriously affect the properties of the membrane. The specific resistance and water content increase not more than by 10%.

4. CONCLUSIONS

It is possible to remove nitric acid from dilute aqueous solutions in the Donnan dialysis process by using the weak base anion exchange membranes obtained from

polyethylene/poly(styrene-co-divinylbenzene) composites. The dialytic system applied to this study has the advantage of removing nitric acid from wastewaters and its immediate utilization to form an ammonium salt — valuable fertilizer.

The best results can be obtained with the membrane containing 3 wt.-% of DVB in the aromatic component of the polymeric material. This membrane is characterized by a high selectivity, negligible osmotic flow of water and good resistance to oxidation by diluted nitric acid. It is sufficiently elastic and mechanically stable to be used in tubular dialytic modules where a high ratio of the active surface to the volume of a device can be achieved.

REFERENCES

- [1] GRAHAM T., *Phil. Trans. Roy. Soc., London*, 144, 177 (1854).
- [2] WALLACE R. M., *Ind. Eng. Chem. Process Design. Develop.*, 6, 423 (1967).
- [3] DONNAN F. G., *Chem. Rev.*, 1, 73 (1925).
- [4] MIKA-GIBAŁA A. et al., Report of the Institute of Environment Protection Engineering, Technical University of Wrocław, PWr I-15/SPR-12/80.
- [5] NG P. K., DEXTER D., *J. Electrochem. Soc.*, 128, 1714 (1981).
- [6] HAMIL H. F., *Annu. Tech. Conf. Proc.-Am. Electroplat. Soc.* 69th, Paper C-1, 1982.
- [7] WEN C. P., HAMIL H. F., *J. Membr. Sci.*, 8, 51 (1981).
- [8] ODA Y., NISHIHARA A., HANI H., YAWATAYA T., *Ind. Eng. Chem., Prod. Res. Dev.*, 3, 244 (1964).
- [9] POŹNIAK G., TROCHIMCZUK W., *Angew. Makromol. Chem.*, 92, 155 (1980).
- [10] POŹNIAK G., TROCHIMCZUK W., *Angew. Makromol. Chem.*, 104, 1 (1982).
- [11] MIKA-GIBAŁA A., Dissertation, Technical University of Wrocław, 1977.
- [12] ADAMS G., JONES P. M., MILLAR J. R., *J. Chem. Soc. A*, 2543 (1969).
- [13] OKE R. B., MILLAR J. R., *Israel J. Chem.*, 10, 911 (1972).
- [14] SMIRNOVA N. M., LASKORIN B. N., KABANOVA S. D., GOLOVNIYA V. A., *Zh. Prikl. Khim. (Leningrad)*, 47, 456 (1974).
- [15] NARĘBSKA A., KOSTECKA J., *Roczniki Chem.*, 39, 1075 (1965).
- [16] HATCH J. M., DILLON J. A., *Ind. Eng. Chem., Process Design.*, 2, 253 (1963).
- [17] SPERLING L. H., *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York 1981.
- [18] POŹNIAK G., TROCHIMCZUK W., *Angew. Makromol. Chem.*, 127, 171 (1984).
- [19] POŹNIAK G., TROCHIMCZUK W., *J. Appl. Polym. Sci.*, 27, 1833 (1982).
- [20] HECKER H., *J. Chromatogr.*, 102, 135 (1974).
- [21] GRYTE C. C., GREGOR H. P., *J. Polym. Sci., Polym. Phys. Ed.*, A 14, 1839 (1976).

OTRZYMYWANIE TUBULARNYCH SŁABO ZASADOWYCH MEMBRAN ANIONOWYCH I ICH WŁAŚCIWOŚCI TRANSPORTOWE

Serię tubularnych membran słabo zasadowych z grupami dietyloaminy uzyskano z układu polietylen/poli(styren-co-diwinylbenzen), zawierającego różną ilość DWB (od 1 do 6% wag. w składniku aromatycznym układu polimerowego). Membrany te mają podobną pojemność wymienną (ok. 1,6 mmol/g), lecz różne stężenie molarne grup jonowych (od 4,5 do 7,6 mmol/cm³).

Właściwości transportowe tych membran określano w układzie: rozcieńczony HNO₃/membrana/stę-

zony NH_4OH . Stwierdzono, że membrany te są przydatne do dialitycznego usuwania kwasu azotowego z roztworów wodnych. Najlepsze właściwości wykazuje membrana z układu zawierającego 3% wag. DWB, dla której strumień kwasu wynosi $8,3 \times 10^{-8} \text{ mol/cm}^2\text{s}$, stała szybkości transportu kwasu $24,7 \times 10^{-4} \text{ s}^{-1}$, a współczynnik efektywności 0,730.

ПОЛУЧЕНИЕ ТУБУЛЯРНЫХ СЛАБО ОСНОВНЫХ АНИОННЫХ МЕМБРАН И ИХ ТРАНСПОРТНЫЕ СВОЙСТВА

Серию тубулярных слабо основных мембран с группами диетилоamina получено из системы полиэтилен/поли(стирен-ко-дивинилбензон), содержащего разное количество DWB (от 1 до 60 вес. в ароматическом компоненте полимерной системы). Эти мембраны обладают похожей заменимой ёмкостью (ок. 1,6 ммол/г) но разной молярной концентрацией ионных групп от 4,5 до 7,6 ммол/см³).

Транспортные свойства этих мембран определены в системе: разбавленная HNO_3 /мембрана/концентрированный NH_4O_3 . Доказано, что эти мембраны могут пригодиться для диалитического устранения азотной кислоты из водных растворов. Наилучшие свойства проявляет мембрана из системы содержащей 3% вес. DWB, для которой поток кислоты $8,3 \times 10^{-8} \text{ мол/см}^2\text{с}$, постоянная скорости транспорта кислоты $24,7 \times 10^{-4} \text{ с}^{-1}$ а коэффициент эффективности 0,730.