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Porosity of microporous polyethylene membranes modified with polypyrrole and their diffusion permeability to low-molecular weight substances

G. Tishchenko [a,b,*], E. Rosova [a,b], G.K. Elyashevich [b], M. Bleha [a]

[a] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*
[b] *Institute of Macromolecular Compounds, Academy of Sciences of Russia, Bolshoj pr. 31, 199004 St. Petersburg, Russia*

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Abstract

Diffusion permeability of the composite polypyrrole/polyethylene (PPy/PE) membranes in relation to various low-molecular weight electrolytes (hydrochloric acid, potassium chloride or sodium hydroxide) was studied. PPy/PE membranes were prepared by oxidative polymerization of pyrrole in the presence of $FeCl_3$. They differed in the thickness of PPy layers deposited on both the membrane and pore surfaces and in porosity. It was shown that changes of porous, hydrophilic and ion exchange properties of the membranes affect their diffusion permeability to electrolytes in the same way as was demonstrated earlier for diffusion permeability of microporous ion exchange Neosepta membranes in relation to proteins [M. Bleha, G. Tishchenko, Y. Mizutani, N. Ohmura, in: A. Dyer, M.J. Hudson, P.A. Williams (Eds.), Progress in Ion Exchange. Advances and Applications, Cambridge, 1997, pp. 211–218]. It means that there is an optimum combination of PPy content and membrane porosity ensuring the maximum fluxes of electrolytes through the membranes. At low (<2 h) and high (>6 h) duration of pyrrole polymerization the diffusion permeability of PPy/PE membranes is low. In the first case, PPy covers mainly the outer membrane surfaces; the surface of pores remain hydrophobic because pyrrole has no time for penetrating into them. In the second case, PPy forms thick layers on both the membrane and pore surfaces resulting in their blocking. It was found that the diffusion transport of acid and alkali accompanied with removing of Fe from the PPy/PE membranes. The influence of Fe-containing compounds presenting in the PPy/PE membranes on their diffusion permeability in alkaline or acidic conditions is discussed.

Keywords: Polypyrrole/polyethylene membranes; Diffusion permeability; Oxidative polymerization

1. Introduction

Chemical modification of transport channels in membranes is a very powerful mean for changing their permeability. In particular, initially hydrophobic microporous polyethylene (PE) membranes become hydrophilic anion-exchange membranes possessing good conductance after surface modification of their pores with polypyrrole (PPy) and polyaniline (PANI) [1,2]. Good compatibility of deposited polymer layers within the porous membranes provides their good stability under drastic chemical conditions which is required in many specific technological applications such as antistatic and magnetic coatings, sensors and actuators, batteries, molecular devices or modified electrodes [3–6]. There is a suggestion that such membranes with facilitated electron transfer through the membrane phase can provide some advantages in comparison with the traditional ion exchange membranes in electrodialysis processes.

It is well known that PPy covers both the membrane and pore surfaces resulting in the oxidative polymerization of pyrrole onto the microporous PE membrane [1]. Moreover, diameter of pores and their size distribution can be considerably changed after pyrrole polymerization. The average pore diameter can diminish from 100 to 180 nm to absolute closing the pores. Therefore, investigation of the conditions of pyrrole polymerization is very important for preparing the membranes with optimum transport, selective and conducting properties. On the other hand, knowledge of these membrane properties can give the necessary information for controlling the modification process.

The aim of the study consists in investigation of diffusion permeability of PPy/PE membranes in relation to low-molecular weight electrolytes and its dependence on the

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[*] Corresponding author. Tel.: +42-2-403-253; fax: +42-2-367-981.
E-mail address: tiscenko@imc.cas.cz (G. Tishchenko).

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membrane porosity and PPy content. In order to compare permeability of the membranes with PPy being in conducting and non-conducting states, the solutions of potassium chloride, hydrochloric acid and sodium hydroxide were used as feed media. The two latter electrolytes were chosen for evaluation of the chemical stability of PPy layers in acidic and alkaline conditions which are usually recommended for regeneration of ion exchange membranes.

2. Experimental

2.1. Membranes

PE microporous membranes were prepared and modified with PPy as described in [1]. Duration of pyrrole polymerization varied in the range (30, 60, 120, 240, 360 min, 96 and 144 h) in order to prepare the membranes differing in PPy content and dimensions of pores. After pyrrole polymerization the modified membranes were treated several times with 4 M hydrochloric acid throughout 12 h for extracting the excess of Fe-containing compounds.

Then the membranes were thoroughly washed with redistilled water and dried. The content of Fe in PPy/PE membranes was determined by atom adsorption spectrometry using Atomic Absorption Spectrometer 3110 (Perkin-Elmer, USA). The content of PPy in modified PE membranes was calculated from the data of elemental (nitrogen) analysis carried out by using Elemental Analyzer 240 CHN (Perkin-Elmer, USA).

The disks of membranes with diameter 3.5 cm were equilibrated with 0.1 M sodium hydroxide (10 ml) during 24 h and the concentration of hydroxyl and chloride ions was determined by microtitration of aliquots of the equilibrium solutions with 0.1 M hydrochloric acid or 0.01 M mercury tetrachloride.

Specific surface of pores in the initial PE and modified PPy/PE membranes was measured by gas (nitrogen) adsorption using a Quantasorb (Quantachrome Corp., USA) apparatus. The characteristics of the PPy/PE membranes are presented in Table 1.

2.2. Diffusion permeability experiments

Permeability of PPy/PE membranes with respect to electrolytes (hydrochloric acid, potassium chloride or sodium hydroxide) was investigated in a two-compartment cell (compartment volume 50 cm^3) separated by a membrane with the window diameter of 2 cm. The compartments of the cell were thermostatted at 25±0.1°C. The compartments were filled with 1 M HCl, KCl or NaOH (feed) and redistilled water (receiver). The change in pH and conductivity in the receiving compartment was measured throughout the experiment after 30 min with glass microelectrode and pH-meter (Radiometer, Denmark) or conductivity electrode and Digital Conductivity Meter (Philips, USA). After finishing the experiment the concentration of Fe in the feed and receiving solutions was determined by atom adsorption spectrometry. Each permeability experiment was repeated four times by using the same membrane after its thorough washing with redistilled water. The permeability coefficients of electrolytes were calculated from their fluxes for the steady stage of diffusion transport using the equation [7]

$$P = J_i \times \frac{l}{C_0} = \left[(C_j - C_i) \times \frac{V}{S} \right] \times \frac{l}{C_0}, \qquad (1)$$

where P is the permeability coefficient ($\mathrm{cm}^2\,\mathrm{s}^{-1}$); J_i is the flux of electrolyte in the steady stage of diffusion transport ($\mathrm{meq\,cm}^{-2}\,\mathrm{s}^{-1}$); l and S are the thickness and working area of a membrane, respectively (cm); C_0 is the initial concentration of electrolyte in the feed solution; C_j (C_i) is the concentration of electrolyte in the receiving solution in a time-moment j (i) throughout the steady stage of the transport process.

3. Results and discussion

Under oxidative polymerization of pyrrole with $FeCl_3$, the polymerizing PPy captures Cl-anions and the reaction can be described by the following stoichiometric equation [8]:

Table 1
Characteristics of microporous polyethylene membranes modified with polypyrrole[a]

Duration of pyrrole polymerization (min)	Content of polypyrrole in membranes ($\mathrm{meq\,g}^{-1}$)		Adsorption capacity of membranes to OH-ions ($\mathrm{meq\,g}^{-1}$)		Desorption capacity of membranes to Cl-ions ($\mathrm{meq\,g}^{-1}$)		Content of $FeCl_3$ in membranes after regeneration with 4 M HCl ($\mathrm{meq\,g}^{-1}$)		Specific surface of pores in membranes ($\mathrm{m}^2\,\mathrm{g}^{-1}$)	
	I	II	I	II	I	II	I	II	I	II
30	1.29	1.62	1.16	1.13	0.254	0.278	0.0477	0.0127	27	24
60	1.40	1.82	1.38	1.39	0.273	0.298	0.0278	0.0143	29	32
120	1.53	2.11	1.54	1.63	0.295	0.306	0.0309	0.0157	29	20
240	2.30	2.48	1.95	1.91	0.338	0.292	0.0407	0.0279	14.2	14.8
360	2.34	–	1.60	–	0.366	–	0.0416	–	13.2	–
5760	–	6.35	–	3.05	–	0.748	–	0.425	–	1.1
8640	–	7.40	–	3.00	–	0.802	–	0.681	–	0.6

[a] The specific surface of pores in the initial PE membrane was 33.2 $\mathrm{m}^2\,\mathrm{g}^{-1}$.

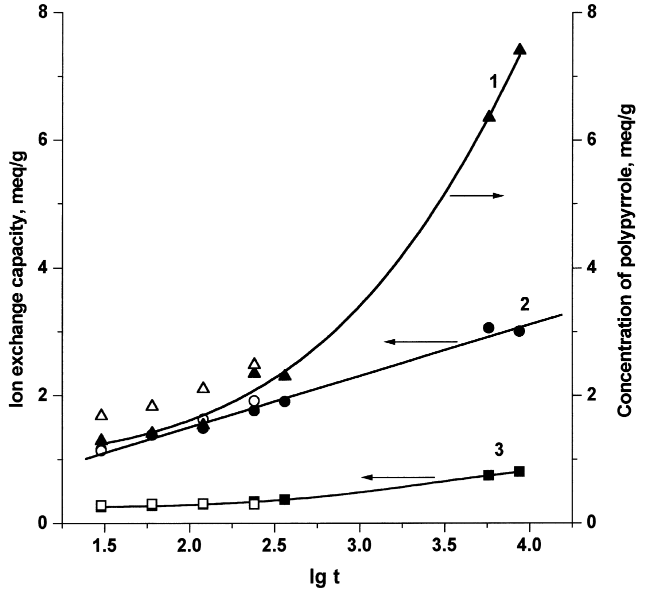

Fig. 1. Influence of duration of pyrrole polymerization within microporous polyethylene membranes on polypyrrole content (1) and ion exchange capacity (IEC) of modified membranes. Curves 2 and 3 correspond to the IEC determined from the data of adsorption of NaOH and desorption of Cl-ions, respectively. Solid and open symbols correspond to two series of membranes modified under the same conditions of pyrrole polymerization.

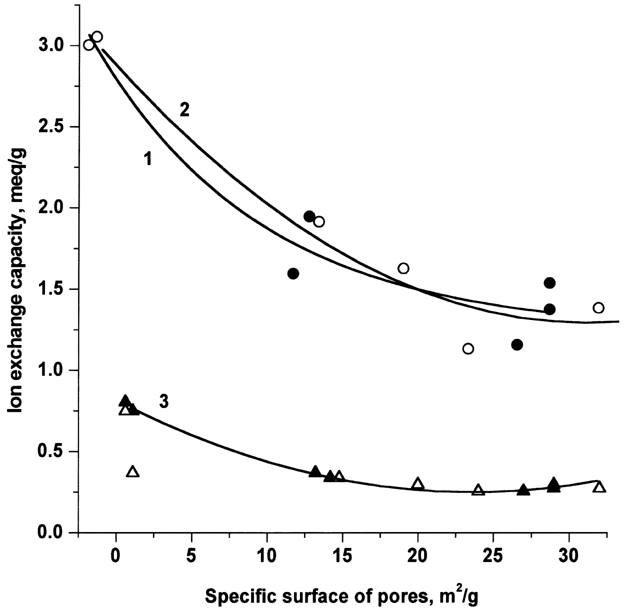

Fig. 2. Correlation between specific surface of pores of the composite PPy/PE membranes and their ion exchange capacity. Curves 1, 2 and 3 correspond to the IEC determined from the data of adsorption of NaOH and desorption of Cl-ions, respectively. Solid and open symbols correspond to two series of membranes modified under the same conditions of pyrrole polymerization.

$$n\,C_4H_5N + (2+y)_n\,FeCl_3 \rightarrow [(C_4H_5N)_n\,ny\,Cl^-] + (2+y)n FeCl_2 + 2n HCl, \qquad (2)$$

where y is the degree of PPy oxidation defining its ion exchange properties.

The relation of the contents of chloride and nitrogen varies as usually in the range 0.21–0.34. It was shown that PPy composite polymers include Fe-containing compounds such as $FeCl_2$, $FeCl_3$ and $FeCl_4$-anions. Moreover, chloride is present in PPy polymers in three states: ionic, covalent and medium being close to the state of Cl-ions in the salts ($FeCl_2$, $FeCl_3$). It has also been found that in spite of a large quantity of captured Cl-ions, only 25% of it is present in the ionic state. It means that this quantity of Cl-anions is able to participate in ion exchange reactions.

As shown in Table 1, the PPy content in PPy/PE membranes increases from 1.29 to 1.68 meq g^{-1} to 7.4 meq g^{-1} with increasing the pyrrole polymerization from 30 min to 144 h. The content of PPy in two series of PE microporous membranes modified with pyrrole by the same conditions has increased according to the logarithmic law (Fig. 1). Adsorption of sodium hydroxide with the PPy/PE membranes modified during 30–360 min achieves 98–80% of PPy content within them and decreases to 40% of PPy content, if the pyrrole polymerization proceeds for 96–144 h. At the same time the quantity of desorbed Cl-anions is considerably lower. It corresponds to 20–15 and 11–12% of PPy content in the former and in the latter membranes, respectively. Namely this quantity of Cl-anions is accessible to exchange with counterions. It has been observed also that Fe-containing compounds desorb from the membranes in alkaline medium and their quantity is higher for the membranes with lower duration of pyrrole polymerization. These results show that the catalyst is bound strongly within the membranes and more drastic conditions (than extraction with 4 M HCl) are required for its removing from the PPy layers. In contrast to the increase of ion exchange capacity of PPy/PE membranes, the specific surface of pores decreases according to the logarithmic law from 29–32 to 0.6 $m^2\,g^{-1}$ (Fig. 2) with increase of the pyrrole polymerization.

It is obvious that structural changes of modified membranes and hydrophilization of the surface of transport channels will influence their permeability. As can be seen in Fig. 3, the curves of the dependence of permeability coefficients of the PPy/PE membranes to hydrochloric acid on the duration of pyrrole polymerization have a maximum. At first the permeability of the membranes increases due to increasing the hydrophilicity of pore surface resulting in the deeper penetration of pyrrole into the pores. Then the permeability of the membranes drops sharply because of the blocking the pores with increasing the duration of pyrrole polymerization. At repetition of the experiment the shift of the curves to the higher values of permeability coefficients was observed. This unusual fact can be associated with desorption of the excess of the catalyst from the membranes (Fig. 4). And moreover, three or more times higher quantity of Fe desorbs into the feed solution (6×10^{-4} mM) in comparison with that penetrating into the receiving solution (2×10^{-4} mM). As a result the additional transport pores

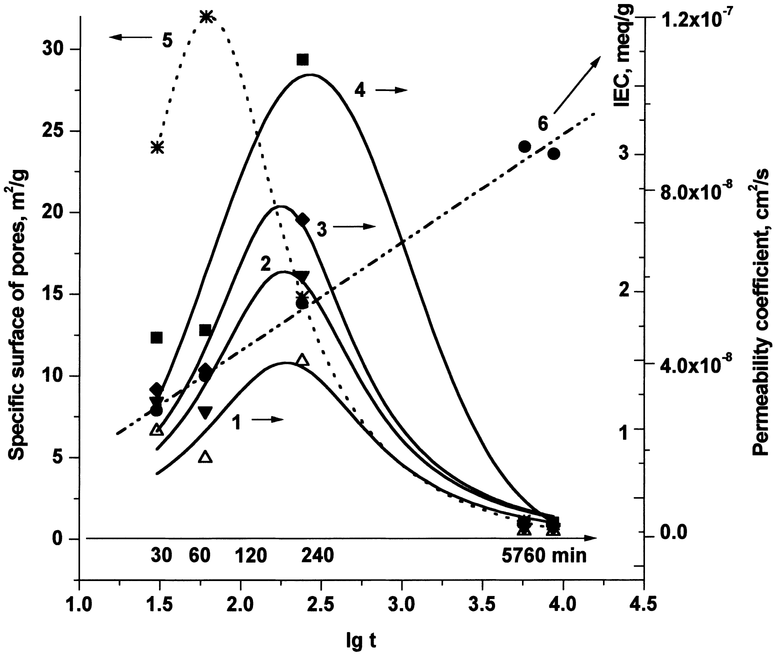

Fig. 3. Dependence of permeability of PPy/PE membranes to hydrochloric acid (1, 2, 3, 4) on polymerization time of pyrrole within microporous polyethylene membranes. Curves 5 and 6 correspond to specific surface of pores (5) and IEC (6). Second series of modified membranes.

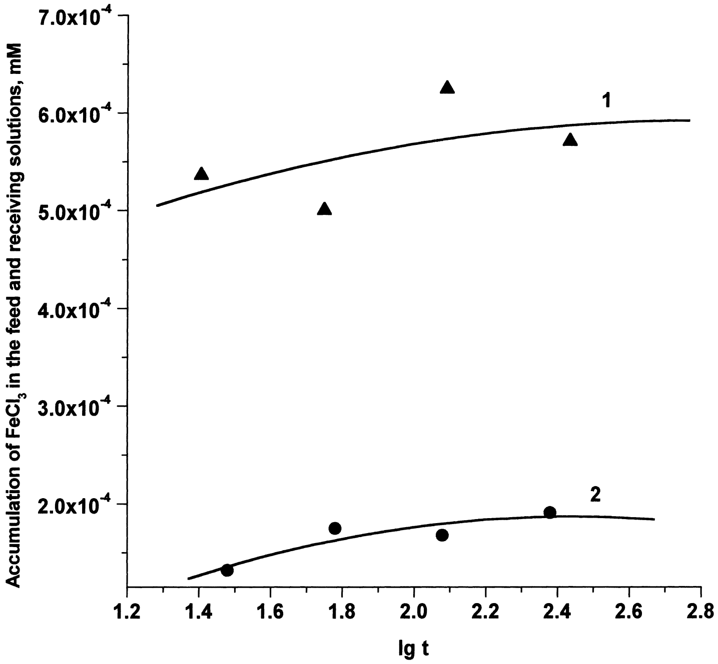

Fig. 4. Dependence of desorption of $FeCl_3$ from composite PPy/PE membranes on polymerization time of pyrrole within microporous polyethylene membranes. Curves 1 and 2 correspond content of $FeCl_3$ in the feed (1 M HCl) and the receiving (distilled water) solutions, respectively.

appear in the PPy layers. Counter flux of Fe-containing compounds into the feed solution can contribute to hindering the flux of electrolyte into the receiver solution. The same results were obtained in the experiments by using both series of PPy/PE membranes (Fig. 5) and other types of electrolytes (Fig. 6). The PPy/PE membranes showed the highest permeability in relation to sodium hydroxide and the lowest permeability in relation to potassium chloride. It can be suggested that not only the loss of membrane charge under transforming the PPy into the non-conducting state but also changes of their hydrophilicity and secondary interactions with Fe-containing substances affects these

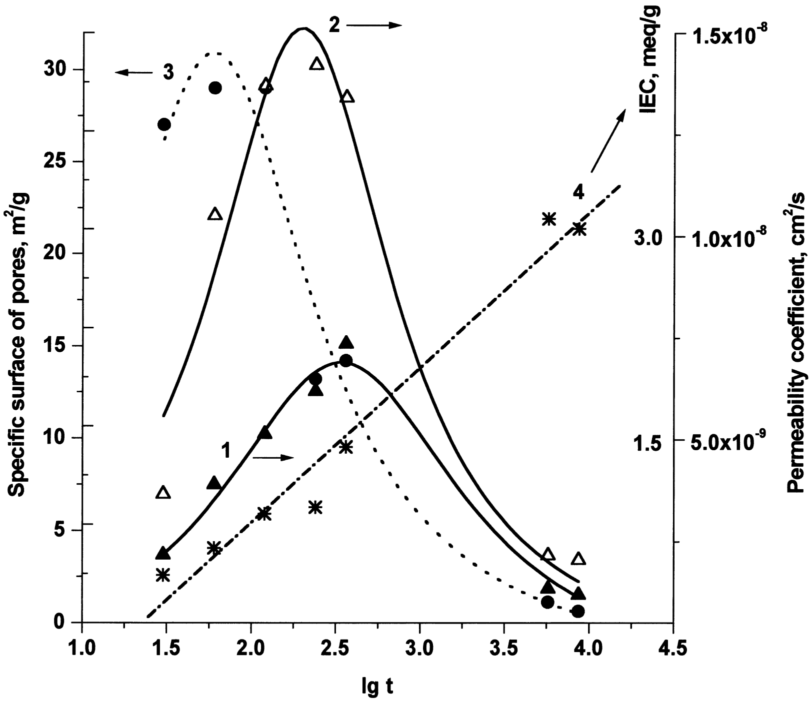

Fig. 5. Dependence of permeability of PPy/PE membranes to hydrochloric acid (1, 2) on polymerization time of pyrrole within microporous polyethylene membranes. Curves 3 and 4 correspond to specific surface of pores and IEC, respectively. First series of modified membranes.

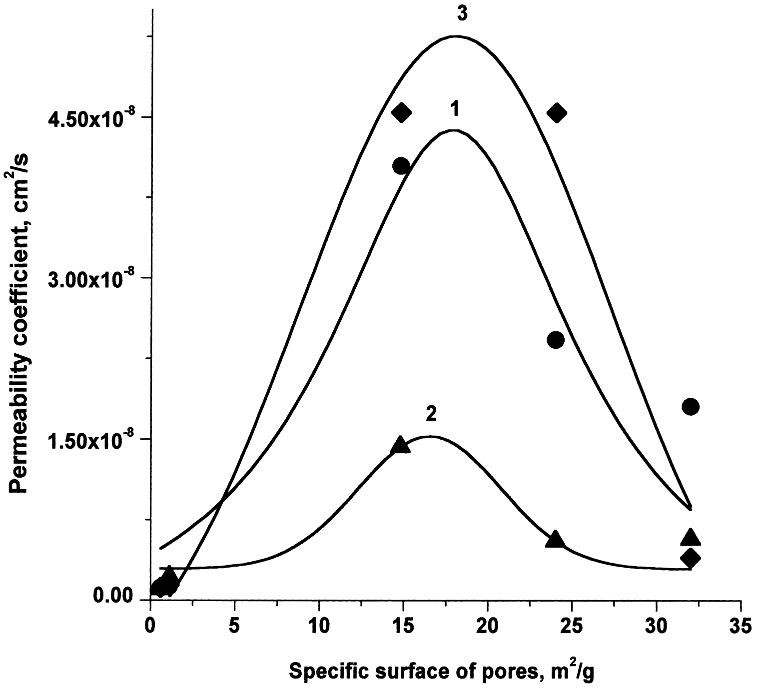

Fig. 6. Dependence of the permeability coefficient of the composite PPy/PE membranes on electrolyte nature (1 M solutions): hydrochloric acid (1), potassium chloride (2) and sodium hydroxide (3).

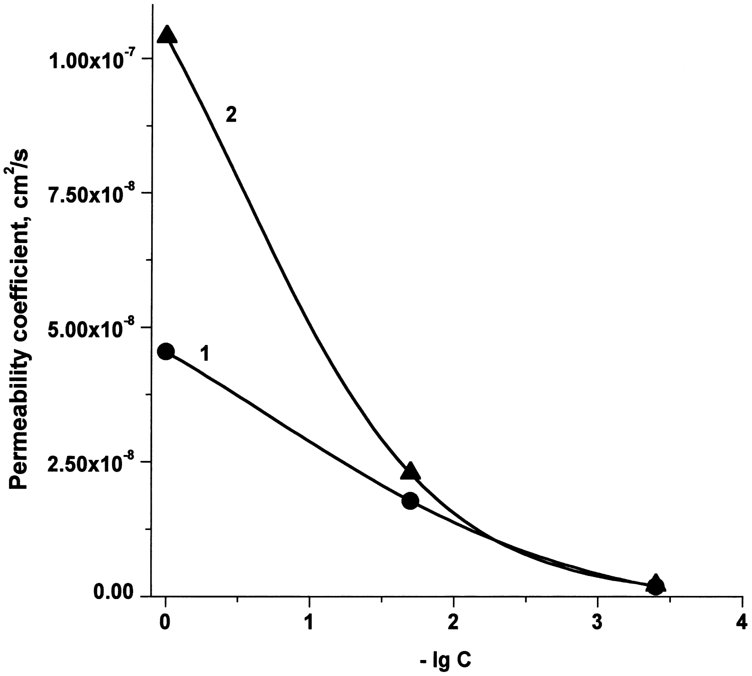

Fig. 7. Permeability of the composite PPy/PE membrane modified with polypyrrole during 4 h in dependence on the concentration of penetrant (NaOH). Figures on the curves indicate the sequence of the repeated experiments using the same membrane.

phenomena. The influence of sodium hydroxide concentration on the permeability of modified membranes was studied for the PPy/PE membrane that has demonstrated the highest permeability coefficients in relation to all used electrolytes. The concentration of sodium hydroxide varied in this case in the range 4×10^{-4} to 1×10^{-4} M. It is seen that the lower concentration of sodium hydroxide in the feed solution the lower difference between the membrane permeability coefficients determined from two repeated experiments using the same membrane (Fig. 7). At low concentration of electrolyte the PPy/PE membranes have displayed their ion exchange nature, i.e. the higher volume concentration of ionogenic groups in comparison with electrolyte concentrations became the obstacle for dialysis penetration of electrolyte molecules through them.

4. Conclusions

The results of the study can be summarized as follows:

The relationship between two main competitive membrane characteristics defining its permeability should be taken into account at preparing the PPy/PE membrane with desired correlation of transport and selective properties: ion exchange capacity and pore dimensions. For the dialysis application of microporous PPy/PE membranes the process of pyrrole polymerization should be controlled in order to provide the hydrophilization of pore surfaces and at the same time do not blocked them for transporting species.

It was shown that the study of the diffusion permeability of PPy/PE membranes in relation to various types of electrolytes allows predict their behavior under certain conditions of exploitation. The knowledge of the relationship between the permeability coefficients and both of the ion exchange capacity and of specific surface of pores ensure the necessary information for preparation of the PPy/PE membrane with desired properties for its target application. Despite the changes of PPy conductivity affected by the nature of electrolytes the found relationship appears to be universal for used PPy/PE membrane.

The duration of pyrrole polymerization does not exceed 120–240 min for the given initial PE membrane if the membrane will be used in the dialysis process. As found, the PPy/PE membranes with the PPy content 0.3–0.34 meq g^{-1} and with the specific surface of pores 15–18 $m^2 g^{-1}$ are more suitable for these purposes. The duration of pyrrole polymerization has to be increased up to 150 h for preparing the composite membranes with transport selectivity for ions.

It was shown that PPy layers onto microporous PE have the sufficient chemical stability. However, their diffusion permeability can be considerably changed under the drastic conditions (acidic or alkaline pH).

Acknowledgements

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References

[1] M. Bleha, V. Kudela, E.Yu. Rosova, G.A. Polotskaya, A.G. Kozlov, G.K. Elyashevich, Eur. Polym. J. 35 (1999) 613–620.

[2] J. Stejskal, M. Spirkova, O. Quadrat, P. Kratochvil, Polym. Int. 44 (1997) 283–287.

[3] Ch. Dridi, A. Chaieb, F. Hassen, M. Majdoub, M. Gamoudi, Synth. Met. 90 (1997) 233–237.

[4] N. Arsalani, K.E. Geckeler, Reactive Func. Polym. 33 (1997) 167–172.

[5] T. Osaka, S. Komaba, A. Amano, J. Electrochem. Soc. 145 (1998) 406.

[6] S. Cosnier, I.C. Popescu, Anal. Chim. Acta 319 (1996) 145–151.

[7] J. Crank, The Mathematics of Diffusion, 2nd Edition, Claredon Press, Oxford, 1975, p. 51.

[8] S. Machida, S. Miata, A. Techagumpuch, Synth. Met. 31 (1989) 311.