Chemical Modification of Dialysis Membrane Based on Poly(Acrylonitrile–Methylmethacrylate–Sodium Vinylsulphonate)

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SYNOPSIS

Poly(acrylonitrile–methylmethacrylate–sodium vinylsulphonate) membranes were subjected to modification with a view to improve their dialysis properties. Hydroxylamine and diethylaminoethylmethacrylate were used as modifying agents. As a result of the modification, nitrile groups depending on the modifying agent were partially converted to primary amine, oxime, and tertiary amine groups. The newly formed functional groups provide the membrane more hydrophylic properties and the permeability of the membranes substantially increases. The appearances of the $-NH_2$ and oxime groups were identified by IR spectroscopy. The primary as well as tertiary amino groups were determined quantitatively by potentiometric titration. The pore size distribution of the initial as well as modified membranes were compared. The mentioned modifying agents appeared to be very prospective to improve the dialysis characteristics of the ter-PAN membranes.

INTRODUCTION

Most dialysis membranes with medical application are based on regenerated cellulose,[1] poly(vinyl pyrrolidone),[2] poly(vinyl alcohol),[3] poly(methylmethacrylate),[4] and others. The reported results concerning the permeability characteristics of the membranes show that the degree of hydrophylicity plays a vital role to improve their performance. Inspite of the high hydrophylicity of PAN-polymer, the hollow fiber membranes based on it are subjected to further modification with amines to increase their hydrophilicity and thus improve their permeability.[5]

EXPERIMENTAL

Materials

Poly(acrylonitrile–methylmethacrylate–sodium vinylsulphonate) membranes, mol wt cut off 10,000, supplied by Spartak, Bulgaria, were used in our experiments. The modification of ter-PAN membranes has been carried out with following chemical agents: sodium hydroxide and hydrogen peroxide, p.a, Bulgaria; hydroxylamine, dimethylformamide, diethylaminoethylmethacrylate, p.a. Fluka, Germany; ferroammonium sulphate, p.a. Reachim, USSR. Aqueous solutions of vitamin B_{12} (p.a., Fluka, Germany) were used for studying the membranes permeability.

Modification of ter-PAN Membranes with HA

The membranes were swelled in 5 vol % aqueous solution of dimethylformamide.[6] Then, they were immersed in aqueous solution of hydroxylamine (HA) with concentration of 1.5–15 wt % and placed in a thermal chamber at a temperature of 298, 313, and 343 K for 30–180 min.

Modification of ter-PAN Membranes with DEAEM

The membranes were partially hydrolized with aqueous solution of NaOH with a concentration of 1.5–20 wt % at a temperature of 323 K for 20 min. The hydrolyzed membranes were treated subsequently with diluted solution of HCl and sufficient

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amount of water. Then, they were immersed in an aqueous solution of dimethylaminoethyl methacrylate (DEAEM) with a concentration of 10 vol %. The grafting reaction was initiated by an oxidation reduction system of H_2O_2–Fe(II) with molar ratio 10 : 1. The basic parameters of this reaction were well studied by Hydojadov et al.[7] The authors established that at the mentioned monomer concentration and oxidation-reduction system, the amount of homopolymer formed is negligible.

Determination of Hydrophilicity of Membranes

The degree of swelling in water was taken as a measure for the hydrophilicity of the membranes. It was determined as the amount of absorbed water for unit mass membrane.[8]

Determination of Permeability Coefficient (*P*)

The permeability coefficient was determined with a laboratory dialysis cell[9] with respect to vitamin B_{12} at a temperature of 298 K under static conditions. Samples with a volume of 1 mL were withdrawn from both chambers simultaneously at a predetermined period of time, and after the determination of the concentrations the solution were returned quickly to the chambers. The concentration of the solution was determined spectrophotometrically (Specol, Carl Zeiss-Iena, Germany) at 361 nm.

The permeability coefficient was calculated by the following relationship:

$$p = \frac{2.303\ V_1V_2}{At(V_1 + V_2)} \lg \frac{(C_1 - C_2)_0}{(C_1 - C_2)_t}, \text{ cm/min},$$

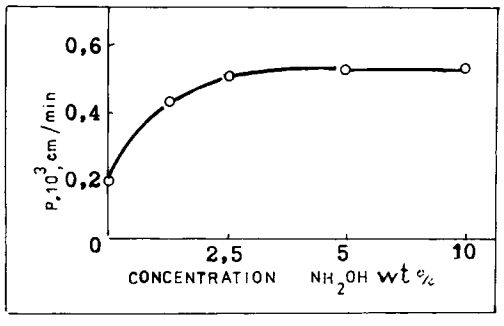

Figure 1 Permeability coefficient (with respect to 0.01 wt % aqueous solution of vitamin B_{12}) of the ter-PAN membrane modified by hydroxylamine as a function of the concentration of the modifying agent. Reaction temperature and time = 313 K and 120 min, respectively.

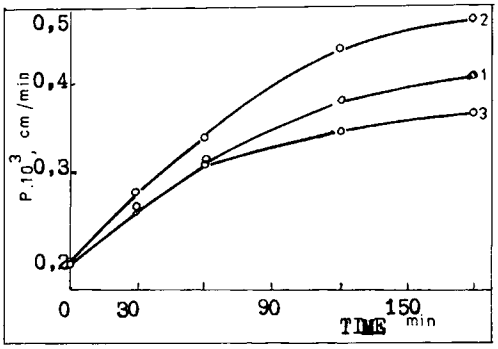

Figure 2 Permeability coefficient (with respect to 0.01 wt % aqueous solution of vitamin B_{12}) of modified membrane as a function of modification time and temperature. Concentration of HA is 2.5 wt %. Reaction temperature: (1), 298; (2), 313; (3), 343.

where:

V_1 and V_2 are the volumes of the chambers, cm^3; A = the effective membrane area, cm^2; C_1, C_2 = the concentrations of the solute in the donor and receptor compartments, respectively; t = dialysis time.

RESULTS AND DISCUSSION

The permeability coefficient (with respect to vitamin B_{12}) of the modified membrane as a function of the concentration of the modifying agent (HA) is represented in Figure 1. It is established that up to a HA concentration of 2.5 wt % the permeability coefficient monotonously increases. On the basis of the observed phenomenon, the further experiments were carried out with above-mentioned concentrations of HA. The changes in the permeability coefficients for a 0.01 wt % solution of the vitamin B_{12}, as a function of the modification time with HA at a temperature of 298, 313 and 343 K, are represented in Figure 2. The permeability coefficient monotonously increases up to a reaction time of 120 min. Beyond that, the increase is negligible. The permeability coefficients follows the order $P_{313K} > P_{298K} > P_{343K}$. The pore size distributions of the membranes modified at temperatures of 313 and 343 are compared to that of the unmodified one (Figure 3). It is seen from the figure that the pore size distribution of the initial as well as that of the membrane modified at 313 K are almost the same. The membrane modified at 343 K shows some compaction of the porous structure. The lower value of the permeability coef-

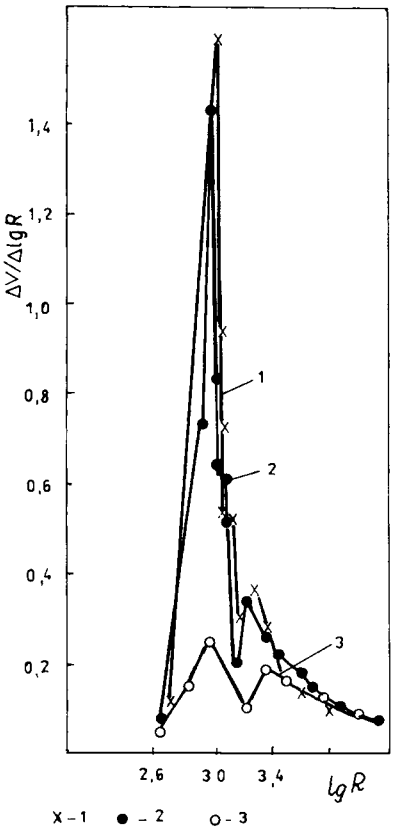

Figure 3 Differential pore size distribution of the initial membrane (1) and those of the modified ones treated with 2.5 wt % hydroxilamine for 120 min at (2) 313 and (3) 343 K.

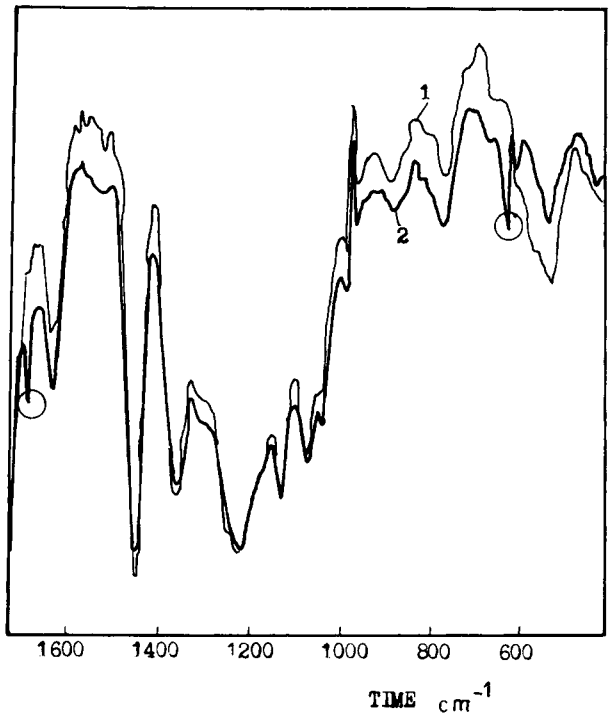

Figure 4 Infrared spectrum of (1) the initial membrane and (2) that of the membrane modified with 2.5 wt % hydroxylamine at a temperature of 313 K for 120 min.

ficient at a temperature of 343 K may be attributed to the contraction of the pores of the membranes.

The increase in the permeability coefficient up to a temperature of 313 K is attributed to the appearance of the new hydrophilic groups in the membrane. The formed $-NH_2$ and oxime groups are about several times more hydrophilic than —CN groups.[10] Infrared spectra of the initial and modified membranes are presented in Figure 4. The adsorption peaks at wave numbers 630 and 1,690 cm^{-1} correspond, respectively, to the deformational vibration of N—H bond of the primary amino groups and the valency bond vibration of C=N of the oxime groups. Such peaks are absent in the spectra of the initial membrane. Elementary analysis shows an increase in *N*-contents in the modified membranes (*N*-contents in initial and modified membranes are, respectively, 22.5 and 24.5 wt %). The primary amino groups were determined quantitatively by the potentiometric titration.[11] It is obvious from Figure 5 that the quantity of the amino groups also increases with the increase in the reaction time and HA concentration. After a reaction time of 120 min, the increase in NH_2 groups is negligible for the modification with 2.5 wt % HA.

The influence of —COOH concentration (obtained as a result of the partial hydrolysis) on the degree of grafting and tertiary amino group contents, as well as the permeability coefficient of the DEAEM-grafted ter-PAN membrane, is represented in Figure 6. The —COOH and tertiary amino

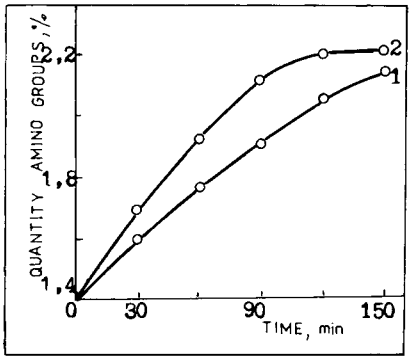

Figure 5 Influence of the reaction time on the amount of $-NH_2$ groups formed at a temperature of 313 K and hydroxylamine concentration of (1) 1.5 and (2) 2.5 wt %.

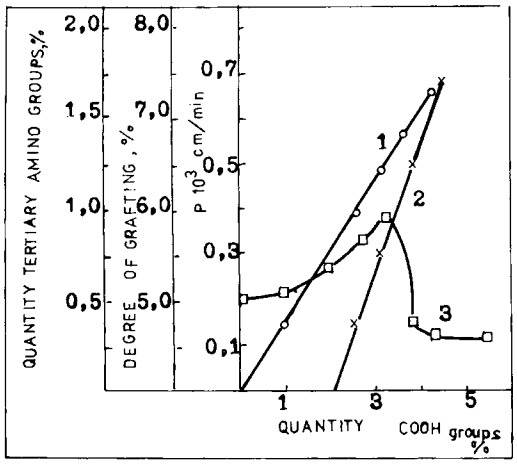

Figure 6 The influence of —COOH concentration on (1) quantity of the tertiary amine groups formed, (2) degree of grafting, (3) and permeability coefficient with respect to 0.01 wt % vitamin B_{12}. Modification condition: 10 vol % DEAEM; H_2O_2–Fe(II) = 10; 313 K, 120 min.

groups are determined by potentiometric titration.[11] The grafting on the partially hydrolyzed membranes is done with a DEAEM concentration of 10 vol % at a temperature of 313 K for 120 min. Suitable reaction time and temperature were determined experimentally. The degree of grafting of DEAEM to the initial membrane was calculated taking into account the tertiary amino group content. It is evident from the figure that the tertiary amino group contents and the degree of grafting increase with increase in the —COOH content of the hydrolized membranes. However, the permeability coefficient passes through a maximum at a —COOH concentration of 3.21%. Such a degree of hydrolysis was obtained treating the ter-PAN membranes with an aqueous solution of 6 wt % NaOH at a temperature of 323 K for 20 min. To explain the decrease in the permeability coefficient of the grafted membranes with the initial —COOH concentration more than 3.21%, the porous characteristics of the membranes with initial —COOH concentration more and less 3.21% were compared to those of the initial one (Figure 7). It is evident from Figure 7 that the porous characteristics of the grafted membranes with the initial —COOH concentration of 2.7% differ negligibly from that of the initial membrane. On the contrary, the selective layer is completely densed for a membrane grafted with DEAEM with the —COOH concentration of 3.7%. Thus, the decrease in the permeability coefficient for membrane 3 is due to the densification of the pores of the selective layer.

A comparison is made between the hydrophilicity and the permeability coefficient of the membranes modified under different conditions (Table I). It is evident from the table that the increase in hydrophilicity leads to an increase in the permeability coefficient, with an exception in the case with DEAEM-grafted membrane, while the increase in hydrophilicity does not lead to the expected increase in permeability coefficient, an effect attributed to the negligible decrease in the pore volume in the selective layer (Figure 7, curve 2).

CONCLUSIONS

Poly(acrylonitrile–methylmethacrylate–sodium vinylsulphonate) membrane modified by hydroxylamine and DEAEM shows better performance in the dialylis process than unmodified one. The improvement in the permeability is attributed to the appearance of the new functional groups as primary

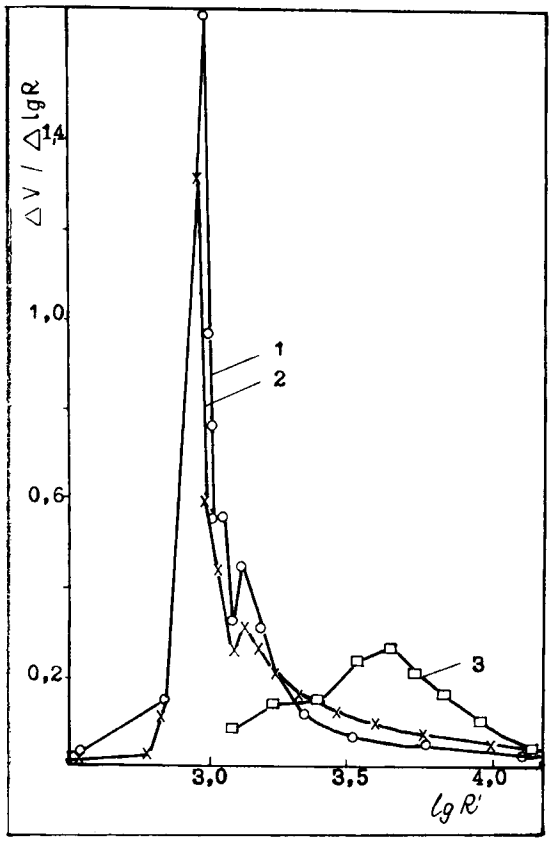

Figure 7 Differential pore size distribution of (1) the initial membrane and (2) modified with 10 vol % DEAEM at a temperature of 313 K for 120 min with initial —COOH concentration 2.7% and (3) 3.7%.

Table I Hydrophilicity and Permeability Coefficient of Initial and Modified (under Optimal Condition) Membranes

Number	Membrane	Modifying Agent	Degree of Hydrophilicity gH_2O/g membrane	Permeability Coefficient with Respect to 0.01 wt % Vitamin B_{12} ($P \times 10^3$ cm/min)
1	Initial	—	0.4682	0.20
2	Modified	HA, 1.5 wt %	0.4782	0.37
3	Modified	HA, 2.5 wt %	0.4823	0.45
4	Modified	DEAEM, 10 vol %; NaOH, 3 wt %	0.5281	0.27
5	Modified	DEAEM, 10 vol %; NaOH, 6 wt %	0.5618	0.37

amine, oximes, and tertiary amine, which are more hydrophilic than the nitrile groups present in the initial membrane. It is found that the increase in the degree of hydrophilicity does not always lead to the expected increase in the permeability coefficients. The modification conditions should be chosen such that the pore size remains unaltered.

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