
CHANGES IN MORPHOLOGY, PHYSICAL AND CHEMICAL PROPERTIES OF THE POLYACRYLONITRILE MEMBRANES SELECTIVE LAYER AFTER MODIFICATION BY POLYELECTROLYTE SOLUTIONS

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Introduction

It is important for obtaining of the composite nanofiltration structures to choose an optimal initial membrane matrix for formation of the tight selective layer by means of the interfacial polycondensation reaction. In this work we studied changes in the morphology, physical and chemical properties of the ultrafiltration membranes made of various acrylonitrile copolymers after applying of dilute polyelectrolyte solutions as modification agents. This modification method can be used both as for obtaining of tight ultrafiltration membranes (MWCO = 1–5 kDa) [1] and as an intermediate stage in the production of composite nanofiltration membranes.

Experiments

The following copolymers of acrylonitrile have been used to produce the initial membrane matrix: **PAN-IA-1** - poly(acrylonitrile-co-itaconic acid) (99:1), **PAN-IA-2** - poly(acrylonitrile-co-itaconic acid) (96:4), both from JSC “VNIISV” (Russia) and **PANMAAM** - poly(acrylonitrile-co-methylacrylate-co-2-acrylamide-2-methylpropanesulfonic acid) (91:8:1) from plant “Polymir” (Belarus). The membranes were formed from 12% casting solutions of PAN-IA-1 and a mixture of PAN-IA-2 (80%) and PANMAAM (20%) in dimethyl sulfoxide (DMSO). Dilute aqueous solutions of the following polyelectrolytes: poly-[N, (2-aminoethyl) acrylamide] (PAEAA) and copolymer of polystyrenesulfonic and maleic acids (PSMA) were used for surface modification of the initial membranes. Modification procedure was conducted in the dynamic mode. Glutaraldehyde (GA) was used as a crosslinking agent. IR spectra (Nicolet Is50 spectrometer, Thermo Fisher Scientific, USA) were used to investigate the chemical composition of initial and modified membranes. Contact angles were measured in the membrane-air-water system at 20°C. Scanning electron microscopy (SEM) was used to study of the membrane morphology.

Results and Discussion

The study of membranes obtained from PAN-IA-1 and a mixture of PAN-IA-2 and PANMAAM showed that its transport characteristics and contact angles are almost the same (Table). Modification of membranes by dilute polyelectrolyte solutions led to significant changes in transport characteristics and lead to increasing of the surface hydrophilicity. After modification procedure membrane permeability was decreased by 10-20 times. At the same time the rejection coefficients of PEG-1000 were almost the same (94-96%) for all modified membrane samples. Only calibration by 0.2% MgSO₄ solution showed some differences between these ones. With a decrease in the membrane permeability its rejection ability to MgSO₄ increased. For the membrane sample from a mixture of PAN-IA-2 and PANMAAM a lower value of the rejection coefficient was observed after the modification by PAEAA - PSMA complex in comparison with the modification by PAEAA. Comparison of the IR spectra of the membranes showed that the chemical composition on the membrane surface changes during the modification procedure (Figure 1). In the IR spectra of PAN-IA-1 membranes and a mixture of PAN-IA-2 and PANMAAM modified by PAEAA absorption band appears at 3300 cm⁻¹ which can be explained by presence of amide groups. Intense bands at 1650 cm⁻¹ are characteristic for bond formation - C=N- and bands at 1550 cm⁻¹ are characteristic for secondary amines. Decrease in the vibration intensity of the nitrile group (2200 cm⁻¹) is also observed. In the IR spectrum of the membrane from a mixture of PAN-IA-2 and PANMAAM modified by PAEAA-PSMA complex the same bands are observed but with a lower intensity. Probably this explains the lower value of the salt rejection coefficient of the membrane modified by PAEAA-PSMA complex compared to the membrane modified by PAEAA.

Table: Characteristics of initial and modified membranes

Membrane polymer	Way of modification	J*, l m ⁻² h ⁻¹	R** (%)			Θ***, °
			PVP K 30	PEG-1000	MgSO ₄	
PAN-IA-1	-	155	68	<2	0	39
	GA,PAEAA	14	>99	96	24	29
80% PAN-IA-2 and 20% PANMAAM	-	150	70	<2	0	38
	GA,PAEAA	6	>99	94	37	30
	GA,PAEAA, PSMA	6	>99	96	32	29

* J (water flux) at 0.1 MPa and 293 K

** R (rejection coefficients): at 0.1 MPa for PVP and PEG, at 0.5 MPa for MgSO₄, 293 K and ω = 5 s⁻¹. Concentrations: PVP and PEG – 3 g/l, MgSO₄ – 2 g/l.

*** Θ (contact angle) in the membrane-air-water system.

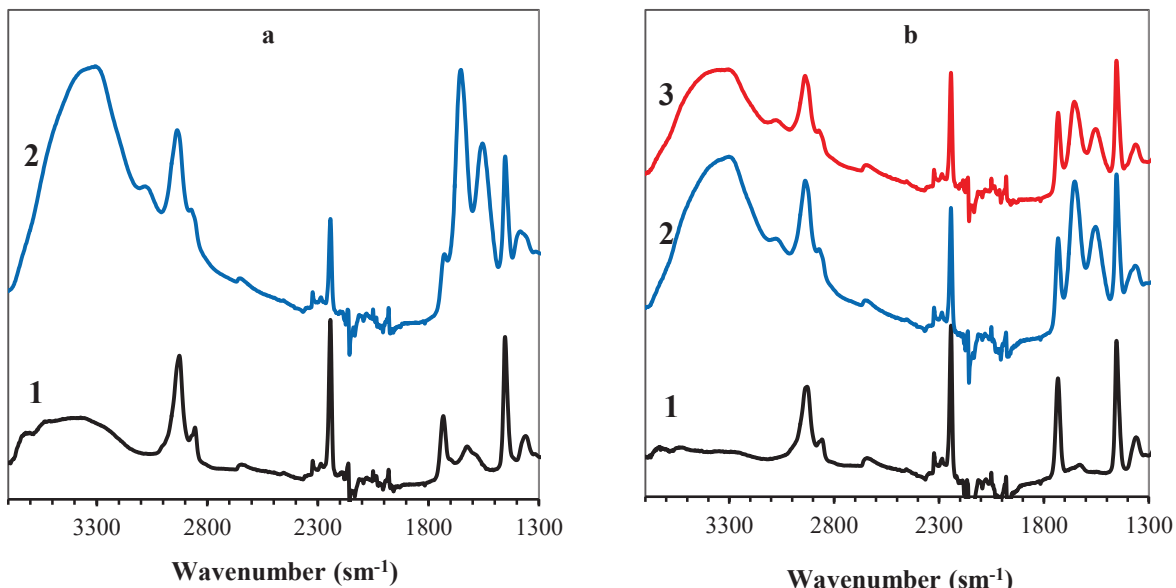


Figure 1. a - IR spectra of initial membrane PAN-IA-1 (1) and membrane modified (2) by PAEAA, b - IR spectra of initial membrane from a mixture of PAN-IA-2 and PANMAAM (1), membranes modified by PAEAA (2) and by PAEAA-PSMA complex (3).

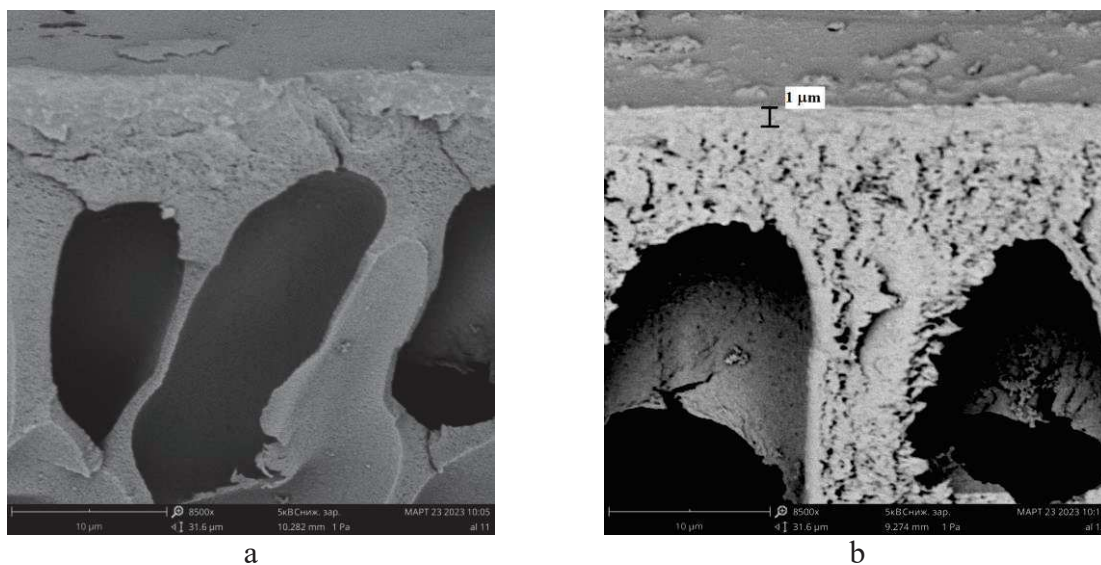


Figure 2. SEM microphotographs of the initial PAN-IA-1 membrane (a) and membrane modified by PAEAA (b).

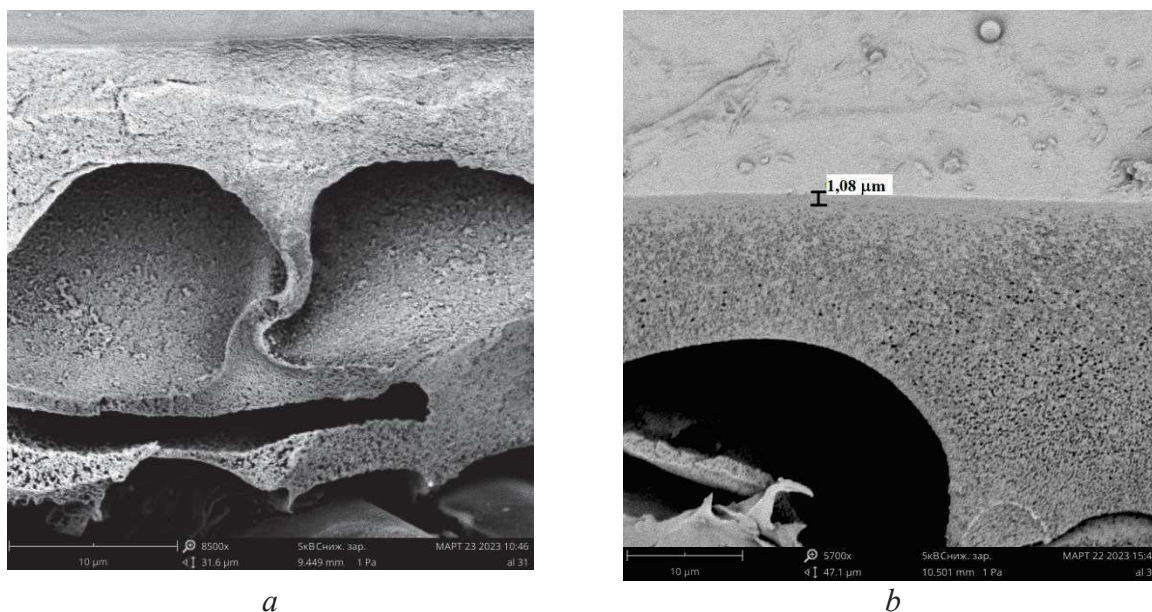


Figure 3. SEM microphotographs of initial membrane from a mixture of PAN-IA-2 and PANMAAM (a) and membrane modified by PAEAA.

The study of membrane cleavages by SEM showed that after modification procedure the roughness of the outer surface of the membranes increases and outgrowths appear inside the large-pore supporting layer (Figures 2, 3). On the surface of membranes modified by PAEAA the formation of a dense layer about 1 μm thick was observed which apparently plays the role of a selective membrane layer (Figures 2b, 3b).

Thus the deposition of polyelectrolytes from dilute aqueous solutions using a crosslinking agent (GA) makes it possible to control the porous structure and properties of the membrane surface in modification process. The formation of an additional selective layer significantly increases the rejection ability of initial membranes. From the other hand the functional groups formed on the surface of the membrane can be used for polycondensation reaction in further process of obtaining of composite nanofiltration structures.

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References

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