Modification of Hollow Fiber Ultrafiltration Membranes by Interfacial Polycondensation: Monomer Ratio Effect

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Abstract—The effect of the component ratio on the permeability and contact angle of ultrafiltration polysulfone hollow fiber membranes modified by interfacial polycondensation of triethylenetetramine (TETA) and isophthaloyl chloride (IPC) has been studied. It has been found that the dependence of the rejection factor on the monomer ratio in the TETA : IPC range from 1 : 28 to 20 : 1 has two peaks. The first rejection peak is observed in a narrow range of TETA : IPC ratios close to 7 : 1. The second peak is observed in a rather broad range of isophthaloyl chloride excess, at TETA : IPC equivalent ratios 1 : (5–15). The membrane pure water flux was shown to change conversely to the rejection coefficient. The influence of the average functionality of the system on the change in the selectivity of the modified membranes was studied. A correlation between hydrophilicity and permeability of the modified membranes was revealed: with decreasing contact angle the pure water flux enhances, and the rejection coefficient decreases.

Keywords: polysulfone, hollow fiber membrane, permeability, interfacial polymerization, modification, hydrophilization

INTRODUCTION

The vast majority of commercial reverse osmosis (RO) and nanofiltration (NF) membranes are prepared by the formation of a barrier layer of polyamides, polyesters or polyurethanes on ultrafiltration polyethersulfone or polysulfone membrane substrates using interfacial polycondensation [1]. The method makes it possible to obtain ultrathin selective layers with varying crosslink density, hydrophilicity, and permeability [2], which gives an opportunity to create highly permeable membranes with high salt retention compared with membranes prepared by phase inversion. The use of polysulfone membrane substrates is due to a high chemical resistance and thermal stability of these polymers and the ability to control their porosity. Despite a wide variety of polymeric materials suitable for the preparation of barrier layers, some commonality in their chemical structure can be noted. A material of the separation layer having high selectivity and permeability should contain a high mole fraction of groups or atoms capable of hydrogen bonding with water molecules. The imparting of positive (an excess of amino groups) or negative (an excess of carboxylic or sulfonic acid groups) charge to the barrier layer is an additional factor that enables to control the separation properties of the membranes. In particular,

this allows to create materials which are effective in membrane separation of single and doubly charged ions, as well as solutions containing natural organic substances [3]. In recent years, attempts were made to obtain membranes for direct osmosis and pervaporation by this method [4, 5].

Mechanism of the synthesis of aromatic polyamides at the interface of two immiscible liquids is not completely revealed. In general, it is believed that the interfacial polycondensation reaction takes place in the organic phase to form a thin film [6]. Further increase in the polyamide film thickness occurs also from the organic phase and is determined by the diffusion of water-soluble (amine) component into the organic phase, because the anhydride component is hydrolyzes in contact with water. It is believed that in the preparation of polyamides by interfacial polycondensation the use of high purity monomers and precise stoichiometric ratios of reactants is not required [7]. The ratio of starting reactants in almost all cases does not affect the molecular weight of the resulting polymers. So, it was determined [8] that upon the preparation of polyamides an excess of any of the reaction components up to 100% excess does not reduce the molecular weight of the resulting polyamide. This is caused by the fact that due to a high rate of interaction

of the starting materials the molecular weight is determined by the rate of diffusion of the monomers through the polymer film formed. Therefore, the reactions of chain termination are the main factor determining the molecular weight of the polyamide. Due to the diffusion of the components the supply of starting components to the interface is constantly ensured, and the stoichiometry is automatically maintained at the interface.

On the other hand, to achieve the maximum values of monomer conversion and the molecular weight of the resulting polymer an equivalent ratio of functional groups of different types in the polycondensation reaction zone is necessary. With an excess of one of the components the polycondensation process proceeds until monomer present in lesser amount is consumed. As a result, all the macromolecules will contain at both ends functional groups of the excess component, which would stop the process. However, in the systems of two immiscible liquids with polyamine partition coefficient less than unity an excess of the amine component corresponds to the maximum viscosity (molecular weight) of the resulting polymer. These provisions are valid from the point of view of the synthesis of structural materials by emulsion polycondensation. In forming the barrier layers of semi-permeable membranes the situation is more complicated, since in this case not so much the molecular weight of the resulting polymer, but its structure (linear, branched), crosslink density, the total and relative amounts of NH_2- and COOH groups are important. Thus, the properties of the resulting membranes will depend on the chemical nature of polyamine that determines its distribution coefficient between organic and aqueous phases, as well as on the initial concentrations of polyamine and crosslinking agent [9–11]. Thus, when studying polycondensation with the use of polyethyleneimine, the conclusion was made on the impossibility of the occurrence of polycondensation reaction in the organic phase because of the impossibility of polymeric amine diffusion through the formed polyamide film for steric reasons [12]. As the result, a very thin layer of polymer is formed in the reaction. To increase the flux and salt retention, a larger amount of amine should be reacted with acyl halide groups at the interface, but not diffuse into the bulk of the organic phase [13].

Despite the abundance of works aimed to the production of RO and NF membranes by interfacial polycondensation, the effect of the initial monomer ratio on the properties of the resulting membranes has hardly been covered. Previous studies primarily were focused on the selection of monomers, reaction conditions and post-processing of the obtained membranes. In the studies, as a rule, researchers use a specified ratio of monomers. Thus, in [14–18] a 2 wt % aqueous solution of *m*-phenylenediamine (PDA) and 0.1 wt % trimesoylchloride (TMC) solution in hexane as an acyl component were used. These concentrations of reactants correspond to the PDA : TMC equivalent ratio = 49 : 1, i.e., a large excess of polyamine is used. There are scarce exceptions. For example, in [19] a 1.0 wt % tetraethylene pentamine (TEPA) aqueous solution and 0.5 wt % TMC hexane solution were used. The ratio of the components in this case was TEPA : TMC = 0.74. In the study of regularities of the synthesis of polyamides by interfacial polycondensation it was found that the maximum molecular weight of the polymer is achieved at non-equivalent ratio of the monomers in the aqueous and organic phases. Thus, for polyhexamethylene sebacamide the maximum viscosity (molecular weight) corresponds to a diamine : acid chloride mole ratio of (5–6) : 1, with curves of the dependences of the molecular weight and the number of $-NH_2$ and $-COOH$ groups on the excess of one of the monomers have asymmetric branches [20].

The structure and surface properties of membranes play a crucial role in membrane separation processes. Therefore, at present, intensive studies are in progress on the development of practically feasible approaches to membrane surface modification, which make it possible to impart desired physical and chemical properties (hydrophilicity, surface charge, etc.) to membranes and thus to obtain membranes with required performance [21]. An urgent issue is the creation of ultrafiltration membranes with low cut-off (ca. 1000–5000 Da). This is caused by some difficulties in obtaining such materials by phase inversion and in monitoring their quality characteristics. In [1] the difficulties in obtaining nanofiltration membranes with cut-off more than 500 Da using interfacial polycondensation are pointed out.

We have previously proposed a technique and laboratory equipment for the modification of polysulfone hollow fiber "inside-out" filtration type membranes by the interfacial polycondensation method, conducted its testing, and showed that using this technique and the equipment it is possible to obtain membranes with reproducible parameters [22]. Varying concentrations of starting monomers at the same their molar ratio it is possible to obtain hollow fiber ultrafiltration membranes with different cut-off.

The aim of this study was to investigate the effect of monomer ratio on the structure, permeability, and hydrophilicity of the surface of hollow fiber ultrafiltration membranes modified by interfacial polycondensation of triethylenetetramine and Isophthaloyl chloride.

EXPERIMENTAL

The objects of the research were PS-PV-100 hollow fiber "inside-out" filtration type ultrafiltration mem-

branes (TU BY 100185198.091-2008). The membrane samples had the following parameters:

Membrane material	hydrophilized polysulfone
Inner diameter	1.0 mm
Outer diameter	1.5 mm
Water flux at $P = 0.1$ MPa	270–330 L/m^2 h
Retention coefficient*, 12–18%	12–18

*Calibrant, polyvinylpyrrolidone K-15 (PVP)

To modify the hollow fiber membranes the following reagents were used: triethylenetetramine (TETA, ≥99%, Sigma–Aldrich), isophthaloyl chloride (IPC, ≥99%, Sigma–Aldrich). For the preparation of solutions of the amine components deionized water (Milli-Que, Millipore) was used; as an organic solvent for IPC, heptane (≥99%, Kriohrom) was used.

The used starting reagent concentrations and their equivalent ratios are listed in Table 1.

By this way, 19 samples of modified membranes were obtained, their structure and properties were studied.

The measurement of the flux (J, L/(m^2 h)) for individual fibers before and after the modification was carried out on a test bench comprising a gear pump (DGS.68PPT type, Tuthill corp.), and a flow-through cell consisting of inlet and outlet capillaries and a sample of the fiber 0.6 m in length strung on them. The pressure at the inlet capillary was 1.1 atm, at the outlet one, 1.05 atm. The pressure difference was monitored with gages. The volumetric rate of the feed of the solution to the fiber was 4 L/h. The value of the flux for the membranes was calculated using the formula:

$$J = \frac{V}{t\pi dl} = \frac{V}{St},\tag{1}$$

Where V is the volume of liquid (m^2) passed through the membrane during time t (s);

d is the inner diameter of the fiber (m);

l is the length of the fiber (m);

S is the area of the hollow fiber membrane (m^2).

To determine the retention capability of the membranes, a 0.3 wt % aqueous solution of polyvinylpyrrolidone K-15 ($M_w = 10000$ g/mol, Fluka, Germany) was used as a calibrant.

The value of the retention coefficient (R) was calculated by the formula:

$$R = \left(1 - \frac{C_f}{C_0}\right) \times 100\%,\tag{2}$$

where C_f is calibrant concentration in the filtrate;

C_0 is calibrant concentration in the initial solution.

concentrations of PVP in the initial solution and filtrate were measured on an ITR-2 interferometer using a calibration curve measured beforehand.

Table 1. Initial concentrations of reagents used in the preparation of the hollow fiber membranes

TETA concentration in the aqueous phase, wt %	IPC concentration in heptane, wt %	TETA : IPC equivalent ratio
0.3	0.207	1 : 1
0.3	0.415	1 : 2
0.3	0.83	1 : 4
0.3	1.245	1 : 6
0.3	1.66	1 : 8
0.3	2.905	1 : 14
0.3	3.32	1 : 16
0.3	3.53	1 : 17
0.3	3.735	1 : 18
0.3	3.95	1 : 19
0.3	4.15	1 : 20
0.3	4.98	1 : 24
0.3	5.81	1 : 28
0.45	0.207	1.5 : 1
0.6	0.207	2 : 1
1.2	0.207	4 : 1
2.1	0.207	7 : 1
3.0	0.207	10 : 1
6.0	0.207	20 : 1

Measurements of the contact angle (θ) for the initial and modified membranes were carried out by the attached bubble method in the "membrane–0.02 M NaCl–air" system. An advantage of the attached bubble method as compared with the stationary droplet method is complete hydration of the membrane surface under study. Thus, one can expect that the surface energy of the water–membrane interface will not change during the measurement at the membrane–liquid interface [23].

To conduct the measurements, the hollow fiber was carefully cut along the axis, unrolled and fastened in the measuring cell by the outer surface with the selective (inner) layer down. The selective layer was directed to a 0.02 M NaCl solution. Using a microsyringe an air bubble 0.01 cm^3 in volume was carefully applied to the membrane surface.

The image of the bubble was recorded by a photographic camera with a focal length of 500 mm, after 1 minute from the time of the bubble attachment.

To determine the contact angle, an image processing program was used. A single-drop boundary integral equation was determined, which rather reliably is described by an elliptic curve of the second order [24].

The structure of the samples was investigated on an HT-206 atomic force microscope with standard silicon cantilevers with a stiffness of 3 N/m (MicroMash,
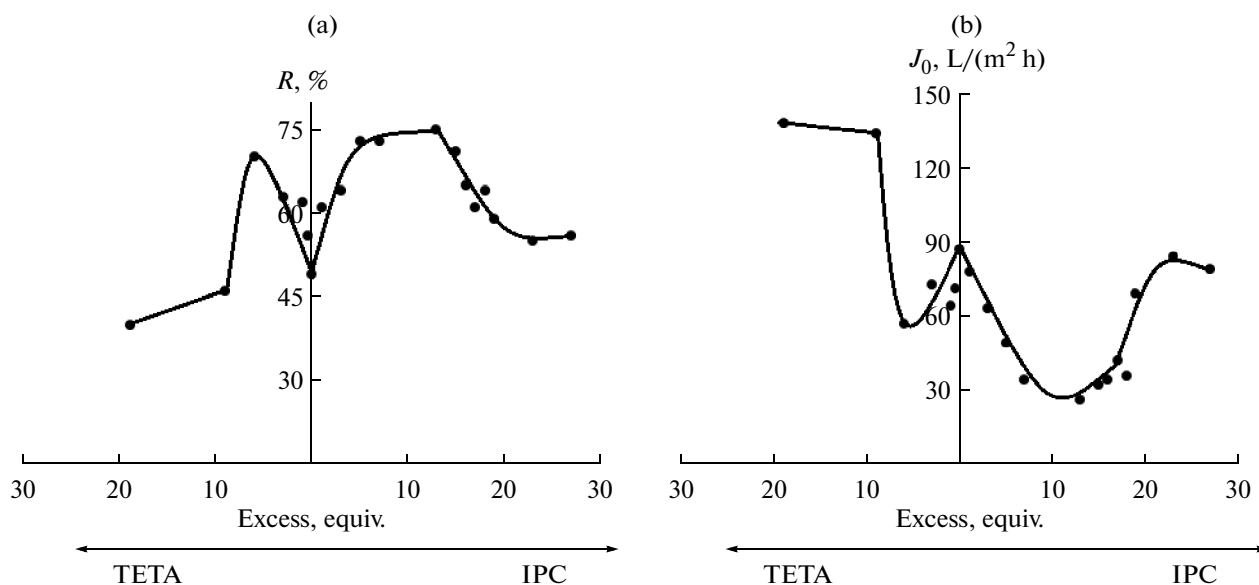
Fig. 1. The dependence of the retention coefficient and water performance of the modified membranes on the TETA : IPC ratio.

Estonia). Determination of the pore diameter and surface roughness of the membranes was performed on the basis of the surface profile of the sample.

RESULTS AND DISCUSSION

In [25] it was shown that in the preparation of nanofiltration membranes there is a rather narrow range of concentrations (0.1–0.75 wt %) of the interfacial polycondensation reaction components, within which the formed membranes have high values of permeability and selectivity for doubly charged ions, and this extreme dependence does not change when passing from one component to another and is not dependent on the type of the membrane substrate. The authors [26] attempted to vary the separation characteristics of nanofiltration membranes by changing the concentration of bisphenol A in an aqueous phase at a constant trimesoyl chloride concentration in hexane. It was found that increasing the initial concentration of bisphenol A from 0.5 to 2 wt % results in a sharp decrease in membrane performance at a simultaneous decrease in retention coefficient for vitamin B_{12} from 66 to 32%.

From our experimental data it follows (Fig. 1) that a change in the transport properties of the modified membranes in dependence on the equivalent ratio of the monomers is more complicated. The dependence of the retention coefficient has two peaks. The water flux performance of the membranes changes inversely to a change in the retention coefficient. One of the retention maxima is in a narrow range of TETA : IPC ratios close to 7 : 1, i.e., at rather large TETA excess. With further increase in TETA concentration the retention coefficient decreases and the water flux per-

formance of the membrane sharply increases. This may be due to a decrease in the degree of crosslinking of the formed polyamide. In [27] upon the preparation of reverse osmosis membranes it was found that an increase in the diffusion coefficient for the amine reactant results in an increase in the thickness and roughness of the formed layer. In this process due to a reduction in the degree of crosslinking the water flux for such membranes is higher compared with membranes modified by amines with a lower diffusion coefficient.

The second retention maximum is observed in a rather wide range of IPC excess, at an equivalent ratio of TETA : IPC = 1 : (5–15). At the equivalent ratio of the components = 1 : 1 the retention capability of the modified hollow fiber membranes takes a minimum value, and the hydraulic permeability passes through a maximum. The said extreme dependence is observed at an IPC excess up to the equivalent ratio IPC : TETA = 14 : 1, and at a TETA excess up to the TETA : IPC ratio = 7 : 1.

It is known that upon the condensation of tri- and tetrafunctional compounds the average functionality of the system is important

$$f_{av} = \frac{\sum f_i N_i}{\sum N_i}, \qquad (3)$$

where f_i is functionality (the number of functional groups) in the molecules of the starting monomer i;

N_i is the number of moles of monomer i with functionality f_i.

Equation (1) holds only in the case of the stoichiometric ratio of the components (functional groups). If one of the components is in an excess, the average functionality is equal to twice the functionality of the
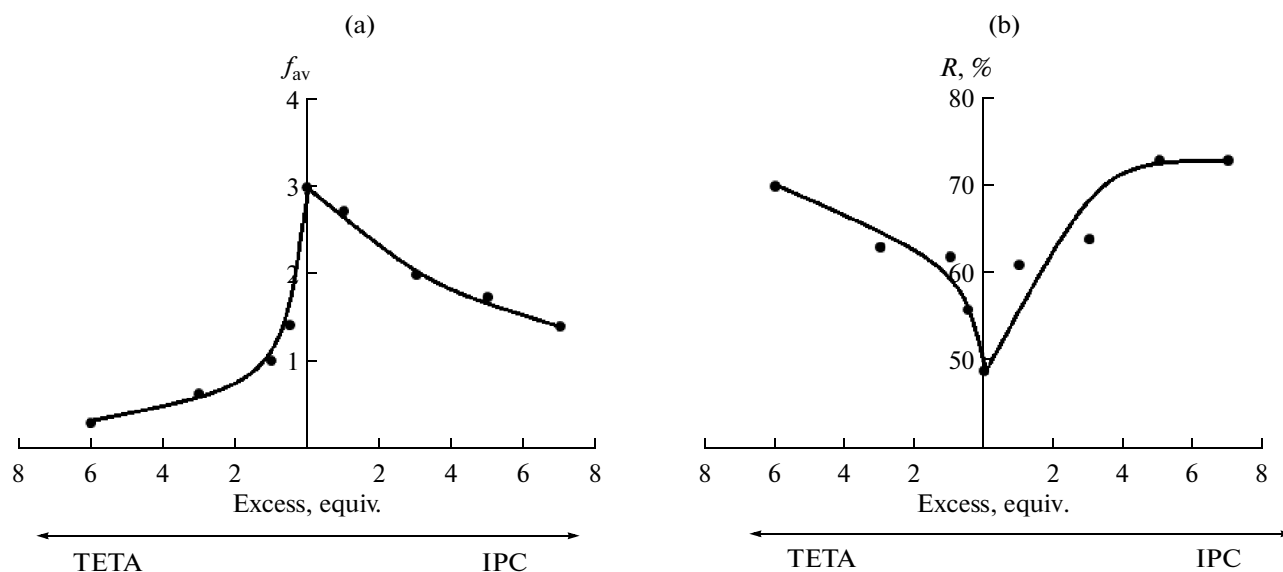
Fig. 2. The dependence of (a) the average functionality of the system and (b) the retention coefficient for the modified membranes on the TETA : IPC ratio.

substance present in a lower quantity divided by the total number of the molecules:

$$f_{av} = \frac{2f_A N_A}{N_A + N_B}, \qquad (4)$$

where N_A is the number of moles of a monomer present in deficiency;

N_B, the number of moles of a monomer present in excess.

If $1 < f_{av} \leq 2$, then linear polymers are formed upon polycondensation, and if $f_{av} > 2$, then three-dimensional crosslinked polymers are formed.

A comparison of the obtained dependences of R with the average functionality of the system in the range of component ratios from 7 : 1 to 1 : 8 (Fig. 2) showed that the change in the selective properties of the modified membranes is of reverse type.

This may indicate that the maximum selectivity is achieved upon the formation of predominantly linear or weakly crosslinked layers of polyamide on the surface of the polysulfone matrix. Although it should be noted that the actual value of the f_{av}, as well as the ratio of the monomers in the reaction zone, which depend on the reaction conditions, may not coincide with the theoretical value. The second possible reason for the revealed patterns may be the differences in the structure, charge or hydrophilicity of the formed modifying layer.

The material of the initial membrane support is polysulfone hydrophilized with polyvinylpyrrolidone (PVP). The introduction of PVP into the membrane matrix results in the reduction in the contact angle of the starting polysulfone from 75° to 47°–49°. As seen in Fig. 3, in the range of equivalent TETA : IPC ratios of 1–1.5 : 1 the contact angle decreases to 21°–27° and

has minimum values. At a five- to sevenfold excess (in equivalents) of one of the components its values rise to 44°–48°, i.e., to the values typical of the original matrix. In this area, there is a fairly clear correlation between the hydrophilicity and permeability of the modified membranes: at a decrease in the contact angle the water performance is increased, and the retention coefficient is decreased.

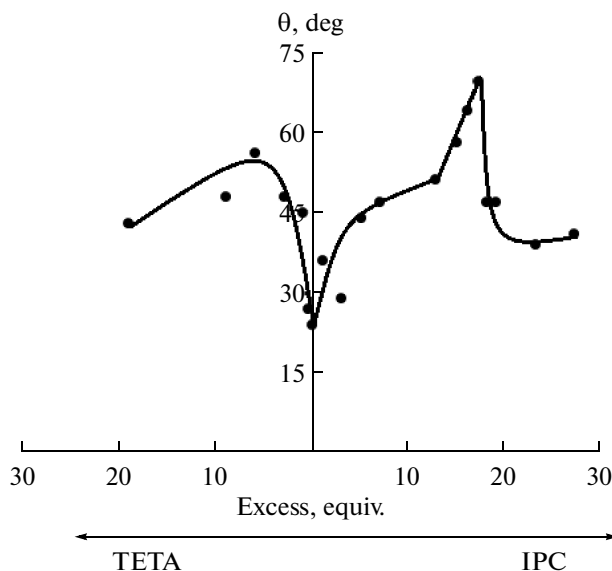The largest contact angle (64°–73°) is observed in a narrow range of TETA : IPC ratios of 1 : (16–17),

Fig. 3. The dependence of the contact angle of the modified membranes on the TETA : IPC ratio.

Table 2. Characteristics of the surface topography of the initial and modified membranes. Ra, arithmetic average roughness; Rq, mean square roughness; d, pore diameter

Equivalent ratio	Ra, nm	Rq, nm	d, nm
–	1.0	1.3	14.3 ± 5.6
1 : 1	1.0	1.3	12.5 ± 4.0
7 : 1	1.7	2.1	10.3 ± 3.8
1 : 14	1.8	2.2	9.3 ± 2.4

which is quite an unexpected result, because hydrophobization of the initial matrix occurs.

The results of the studies on the structure of the original and modified membranes are shown in Figs. 4 and 5. As can be seen from the image 11×10 μm in size, the initial membrane has a structure consisting of interwoven linear aggregates oriented along the fiber axis. Smaller images (2.1×2.1 μm) exhibit uniform grainy texture with elongated elements $30-60$ nm in width and 400 nm in length.

Figure 5 shows the results of the study of the structure of the initial membrane and membranes modified by using different ratios of monomers. Samples prepared at TETA : IPC ratios 7 : 1 and 1 : 14 are characterized by the maximum values of the retention coefficient (70 and 75%, respectively), while the sample at the TETA : IPC ratio 1 : 1 has the minimum value of $R = 49\%$.

The sample treated with TETA : IPC at a ratio of 1 : 1 has clearly rather homogeneous fine-grained surface with the morphology identical to the original membrane. A completely different picture is observed
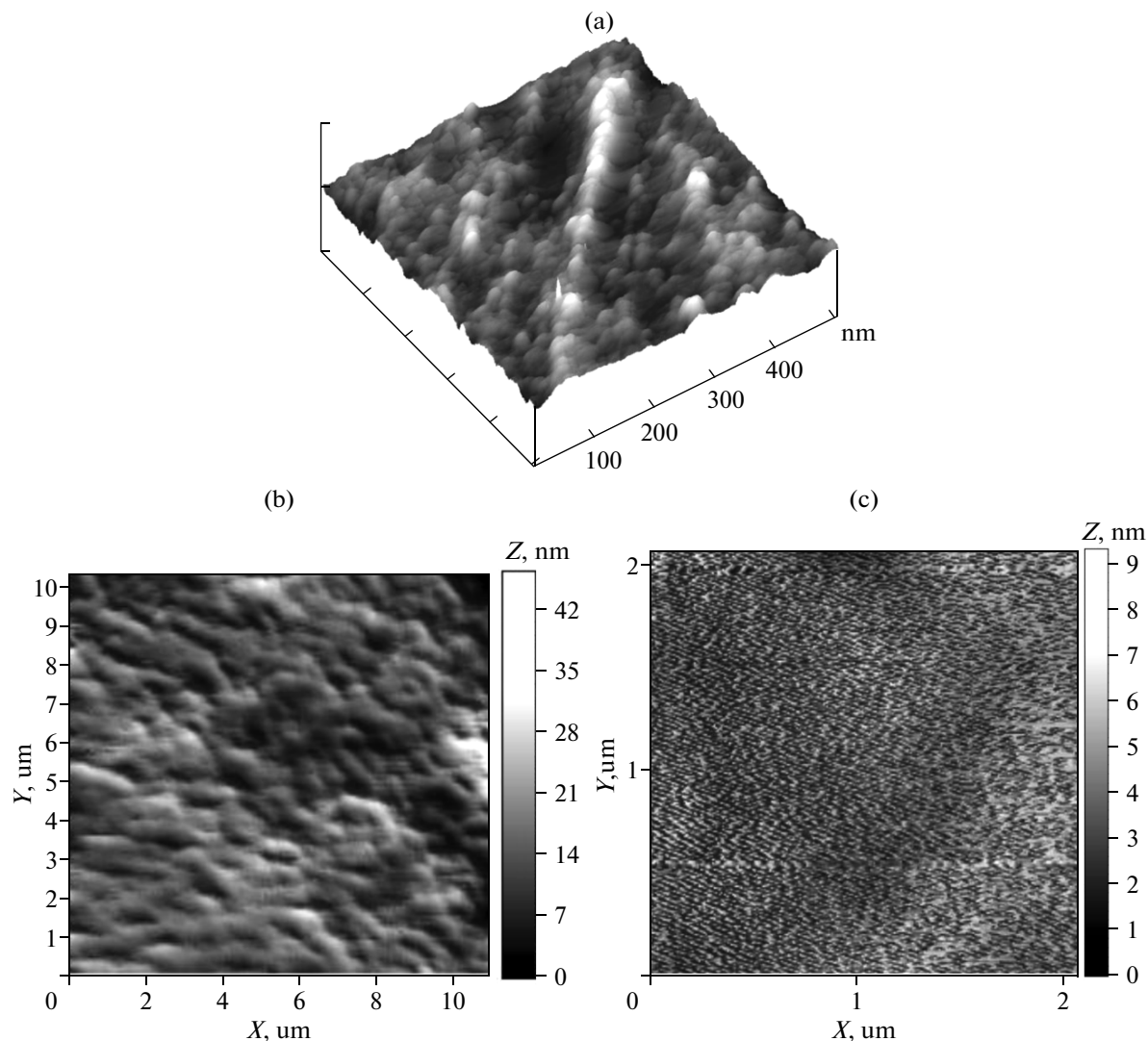

Fig. 4. The AFM image of the topography of the inner surface of the original PS-100 membrane: (a) the scanning area 0.5 × 0.5 μm 3D; (b) 11 × 10.4 μm; (c) 2.1 × 2.1 μm.
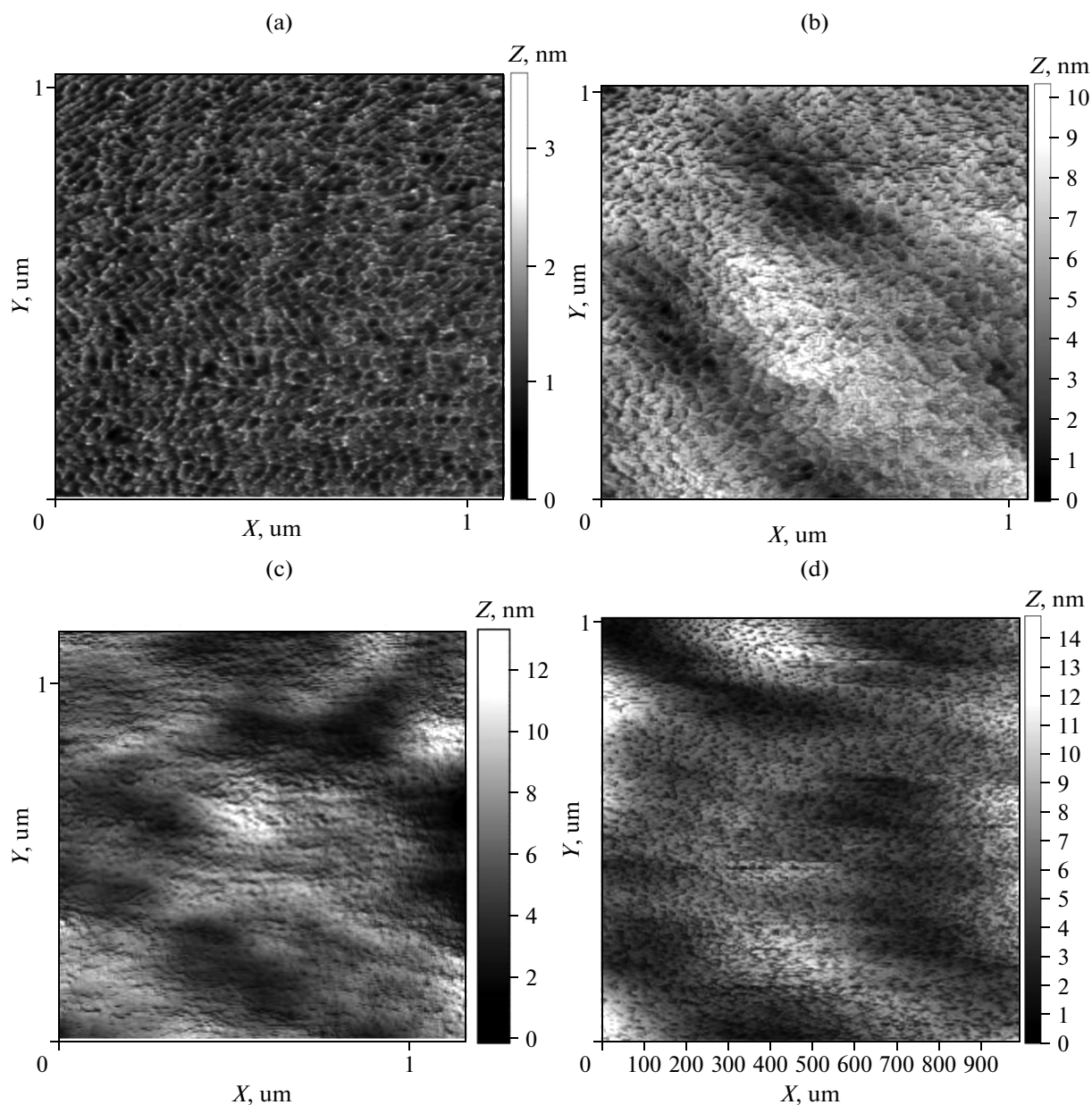
(a)

(b)

(c)

(d)

Fig. 5. The AFM image of the topography of the inner surface of (a) the original membrane and (b–d) modified membranes prepared at a TETA : IPC ratio of (b) 1 : 1; (c) 2 : 1; and (d) 1 : 14.

for the other two samples. They have a much more developed and rough surface than the original membrane, which can be estimated by the total difference of elevations in the images of the same size. There is a smoothing of the fine-grained surface typical of the original membrane, which indicates the consolidation of the surface structure. The results of the analysis of the images obtained are summarized in Table 2, from which it follows that there is a correlation between pore size and membrane retention capability, as well as substantial differences in the surface roughness of the samples prepared at the equivalent ratio of the monomers and at an excess of one of them.

CONCLUSIONS

The effect of monomer ratio on the permeability and hydrophilicity of polysulfone-based hollow fiber ultrafiltration membranes modified by interfacial polycondensation of triethylenetetramine and isophthaloyl chloride has been studied. It was revealed that the dependence of the retention coefficient on the ratio of the monomers in the range TETA : IPC from 1 : 28 to 20 : 1 has two maxima. The first maximum of the retention is in a narrow range of TETA : IPC ratios close to 7 : 1. The second maximum of the retention is observed in a rather wide range of IPC excess—at an equivalent TETA : IPC ratio = 1 : (5–15). It was

shown that the water performance of the membranes changes inversely with changes in the retention coefficient. The minimum value of the retention coefficient is observed at the equivalent ratio of the components = 1 : 1, and the hydraulic permeability at this ratio passes through a maximum. It was found that at component ratios from 7 : 1 to 1 : 8 the change in the selective properties of the modified membranes is reversed relative to the average functionality of the system. This may indicate that the maximum selectivity is achieved upon the formation of predominantly linear or weakly crosslinked layers of polyamide on the surface of the polysulfone matrix. The maximum productivity and minimum retention coefficient are observed for the membranes prepared at a large excess of one of the components.

A correlation between the hydrophilic and transport properties of the modified membranes was revealed: at a decrease in the contact angle the water performance is increased, and the retention coefficient is decreased. The maximum hydrophilicity ($\theta = 24°{-}27°$) is observed for the samples obtained at the equivalent reagent ratio, or at a slight TETA excess. At the TETA : IPC ratio = 1 : (17–18) hydrophobization of the surface of the modified membranes occurs compared with the original matrix.

The variation of the monomer ratio upon the modification of the UF polysulfone hollow fiber membranes by the interfacial polycondensation makes it possible to prepare membranes with a selectivity of 70-75% for PVP K-15, which is 4–5 times higher than that for the original membrane (retention coefficient, by 12–18%).

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