Selective Separation of Aromatics by Pervaporation of Azeotropic Toluene/Methanol Mixture Using Polymer Membranes with 2-Pyridyl-Quinoline Groups

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Abstract—Copolyamide coPA and its metal–polymer complex coPA–Cu^{2+} (MPC)—new polyheteroarylenes—have been synthesized and used to obtain dense nonporous membranes. Some physical properties of the membranes have been determined: density and glass transition temperature, as well as the water contact angle, which showed increased hydrophobicity in the MPC membrane. Thermogravimetric and differential thermal analyses have been used to assess the thermal stability of the membranes. Transport properties have been studied during pervaporation of a toluene/methanol mixture. The coPA and MPC membranes are predominantly permeable to toluene for all feed mixture compositions. In separation of the azeotropic toluene/methanol = 31 : 69 (w/w) mixture, the coPA membrane showed the best separation factor equal to 64, while the MPC membrane had a higher permeability of 26.7 g/(m^2 h) than the coPA membrane. Based on the sorption studies of membrane samples in toluene and methanol, the degree of equilibrium sorption has been determined. New membranes will be most cost-effective in separating toluene/methanol mixtures with a low toluene content.

INTRODUCTION

Membrane processes are traditionally considered to be the most significant energy- and resource-saving environmentally friendly technologies [1–3]. The membrane pervaporation process, in which a binary or multicomponent mixture of liquids is separated by partial evaporation through a dense nonporous membrane, is successfully used for dehydration of water–organic mixtures [4, 5], removal of organic compounds from aqueous solutions [6], separation of a mixture of organic liquids [7–10], and also for extraction of aromatic compounds from petroleum products [11]. The latter type of pervaporative separation as applied to mixtures of organic compounds is the least studied and described in the literature, since it requires membrane polymers resistant to organic solvents [12].

Heteroaromatic polymers are distinguished by excellent chemical resistance to aggressive organic media and hold promise as membrane materials [13–15]. The influence of the chemical structure of the monomer unit in polyheteroarylenes on the trans-

port parameters of membranes can be explained by changes in chain flexibility, macromolecular packing, interchain interactions, etc. Of particular interest are polyheteroarylenes containing organic ligands in the main chain or in side groups, such as 2,2'-biquinoline, *o*-phenanthroline, 2,2'-bipyridyl, and 2-(2-pyridyl)quinoline, capable of forming complexes with various transition metals [16, 17]. The formation of metal–polymer complexes makes it possible to introduce inorganic compounds into polymers and impart new properties to the polymers or regulate existing ones. It is known that 2-(2-pyridyl)quinoline and its derivatives can form coordination compounds with a wide range of transition metal ions, the most stable complexes being formed with Cu^{2+} salts [18]. Therefore, in the present work, we chose cupric chloride as a reagent for obtaining metal–polymer complexes based on macromolecular ligands with pyridylquinoline groups.

Metal–polymer complexes are promising materials for membrane technologies [19]. Gas separation membranes based on metal–polymer complexes of ethyl cellulose and platinum or rhodium acetylaceto-

nates demonstrated high permeability and good selectivity in the separation of oxygen/nitrogen mixtures [20]. A membrane based on a polycarbonate complex with salts of metals, such as Co^{2+}, Cu^{2+}, Fe^{3+}, and Zn^{2+}, was studied for pervaporation of aqueous solutions of alcohols [21].

In this work, two polymers were studied, an aromatic copolyamide containing 2-pyridyl-4,7-quinolinedicarboxylic acid (coPA) units in the main chain, and its metal–polymer complex (MPC) with $CuCl_2$. Membranes based on these polymers seemed promising for solving a pressing problem in the oil refining industry—separating a mixture of toluene and methanol, which is formed after catalytic reforming of gasoline fractions of oil [22, 23]. The mixture is characterized by an azeotropic point of 69 wt % methanol and 31 wt % toluene. The pervaporation method is the most advanced and cost-effective for separating azeotropic mixtures. Separation of toluene/methanol mixtures by pervaporation using hydrophilic and hydrophobic membranes has been studied in a number of works [24–33]. Selectivity to methanol was demonstrated by hydrophilic membranes based on chitosan [26, 27], polyacrylic acid and polyvinyl alcohol [28], polyphenylene isophthalamide [29, 30], and composites with polyaniline [31]. Selectivity for aromatics with recovery of toluene from toluene/methanol mixtures was noted for hydrophobic membranes made of polydimethylsiloxane and low-density polyethylene [24]; natural rubber mixed with carbon black, organophilic clay, or organophilic zeolite as fillers [32]; and polydimethylsiloxane/polyimide blends [33].

The aim of this work is to study the structure, physicochemical properties, and transport characteristics of new polyheteroarylenes: copolyamide with 2-pyridylquinoline ligand units (coPA) and its MPC (coPA-Cu^{2+}). A comparative analysis of the transport properties of membranes made of the new polymers was carried out in the pervaporative separation of a mixture of methanol and toluene.

EXPERIMENTAL

Materials

The copolyamide was synthesized using low-temperature polycondensation according to the procedure described in [34]. The coPA-Cu^{2+} MPC was obtained by reacting a 5% solution of the copolyamide in N-MP with a $CuCl_2$ solution in N-MP at room temperature for 10 h. Figure 1 shows the chemical structures of coPA and MPC, the objects of this study.

The molecular weight of coPA and MPC, determined using gel permeation chromatography [34], was 3.9×10^4 and 11×10^4 Da, respectively.

Preparation of Membranes

Dense nonporous membranes made of coPA and MPC were obtained by casting solutions of the respective polymers in N-MP onto a glass plate, followed by evaporation of the solvent at 100°C in air. The films were dried to constant weight in a vacuum at 50°C for 5 days. The thickness of the polymer film was about 30–40 µm.

Characterization of Membranes

The density of the membranes was determined by hydrostatic weighing (RADWAG 220 c/xc balance, Poland). The samples were weighed in air and in heptane at least five times each.

The glass transition temperature (T_g) was determined by the thermomechanical method using a Netzsch TMA 402 F1 Hyperion thermal analyzer. The sample heating rate was 5°C/min, and the constant tensile stress was as low as 25 kPa. All experiments were carried out in argon.

Thermal degradation processes in membranes were studied using a Shimadzu DTG-60 instrument, which provides simultaneous thermogravimetric (TGA) and differential thermal (DTA) analysis. Samples (about 5 mg) were heated to 600°C at a rate of 5°C/min. The experiments were carried out in air.

The water contact angles of the surface of the membranes under study were determined by the sessile drop method using a Krüss DSA 10 drop shape analyzer at atmospheric pressure and a temperature of 20°C.

Sorption Experiment

Liquid sorption was studied by immersing membrane samples in individual liquids (toluene and methanol) at atmospheric pressure and a temperature of 20°C. At certain intervals, the samples were removed from the liquid and weighed on a Mettler Toledo ME204 analytical balance with an accuracy of $\pm 10^{-4}$ g. The experiment continued until a constant weight was achieved, i.e. sorption equilibrium was established (4 days for methanol and about 2 weeks for toluene). After completion of the sorption experiments, the solvent was desorbed by holding the samples at 20°C in a desiccator containing a molecular sieve adsorbent.

The degree of equilibrium sorption (S, %) was calculated using the equation:

$$S = \frac{m_s - m_d}{m_d} \times 100\%, \qquad (1)$$

where m_s is the mass of the swollen membrane after reaching sorption equilibrium and m_d is the mass of the dry membrane after desorption experiments.
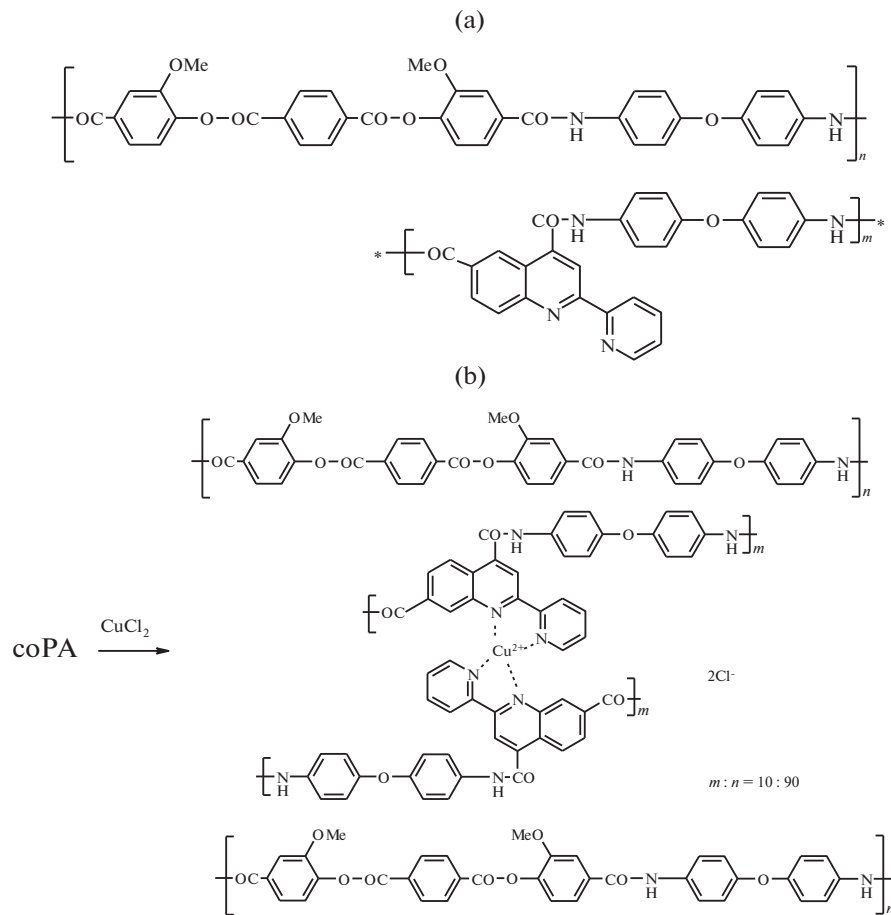
(a)

(b)

Fig. 1. Structural formulas of polymers (a) coPA and (b) MPC.

Pervaporation

The process of pervaporation of the toluene/methanol mixture was carried out on a laboratory setup with an effective membrane area of 14.8 cm^2 at a temperature of 40°C in vacuum mode at a residual pressure of 0.2 mbar [35]. A batch stainless steel cell equipped with a stirrer was used. The feed mixture and permeate compositions were determined using a Chromatec Kristall 5000.2 chromatograph (Russia) with a thermal conductivity detector and a Porapak Q 80/100 packed column.

The separation factor ($\alpha_{\text{Tol/MeOH}}$) was calculated using the formula:

$$a_{\text{Tol/MeOH}} = \frac{Y_{\text{Tol}}/Y_{\text{MeOH}}}{X_{\text{Tol}}/X_{\text{MeOH}}}, \tag{2}$$

where X and Y are the concentrations of the components in the feed mixture and in the permeate, respectively.

The membrane flux J (g/(m^2 h)) was determined by the amount of penetrant Q that passed through unit membrane area S per unit time t.

$$J = \frac{Q}{St}. \tag{3}$$

To assess the transport properties of the penetrant–membrane system, the permeability of toluene and methanol, as well as the membrane selectivity, were calculated using the method of R.W. Baker et al. [36]. The permeability of the ith component (P_i/l), where P_i is the permeability coefficient and l is the membrane thickness, was determined using the equation [36]:

$$\frac{P_i}{l} = \frac{j_i}{p_{i0} - p_{il}}, \tag{4}$$

where j_i is the molar flux of the ith component, cm^3(STP)/(cm^2 s), and p_{i0} and p_{il} are the partial pressures of the ith component on different sides of the membrane (subscript 0 refers to the surface on the feed side, and subscript l refers to the surface on the permeate side). Permeability was calculated in GPU (1 GPU = 1 × 10^{-6} cm^3(STP)/(cm^2 s cmHg).

The membrane selectivity $\beta_{\text{Tol/MeOH}}$ was determined through the permeability ratio using the equation:

$$\beta_{\text{Tol/MeOH}} = \frac{P_{\text{Tol}}/l}{P_{\text{MeOH}}/l}, \tag{5}$$

Table 1. Some physical properties of membranes

| Membrane	Density, g/cm^3	T_g, °C	Contact angle, °
coPA	1.26 ± 0.01	198 ± 5	81.1 ± 0.5
MPC	1.29 ± 0.02	228 ± 6	85.0 ± 0.7

RESULTS AND DISCUSSION

Copolyamide coPA was synthesized by low-temperature polycondensation, which allows obtaining polymers with a high molecular weight. The complex coPA-Cu^{2+} was synthesized by reacting coPA with CuCl$_2$.

To identify the specific features of coPA and MPC membranes, the density and glass transition temperature of the film samples were determined, which are presented in Table 1. The formation of MPC as a result of the interaction of coPA with CuCl$_2$ leads to a slight increase in density and a significant (by 30°C) increase in the glass transition temperature of MPC compared to coPA. It can be assumed that bulky complex groups including two 2-pyridylquinoline units linked by a Cu atom hinder the segmental mobility of polymer macrochains.

The surface properties of membranes made of the new polymers were characterized by the water contact angle of the surface of coPA and MPC films. The contact angle in the case of MPC increases significantly compared to coPA, indicating an increase in the hydrophobicity of the MPC membrane (Table 1).

The thermal stability of the coPA and MPC membranes was evaluated using thermogravimetric (TGA) and differential thermal analysis (DTA). Several weight loss regions can be identified in the TGA curves
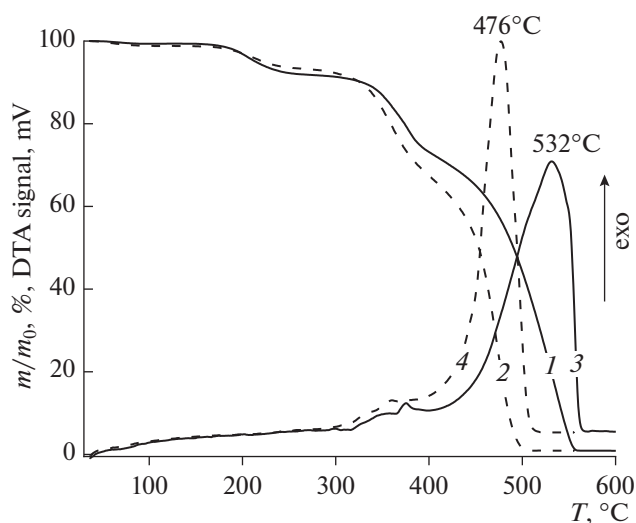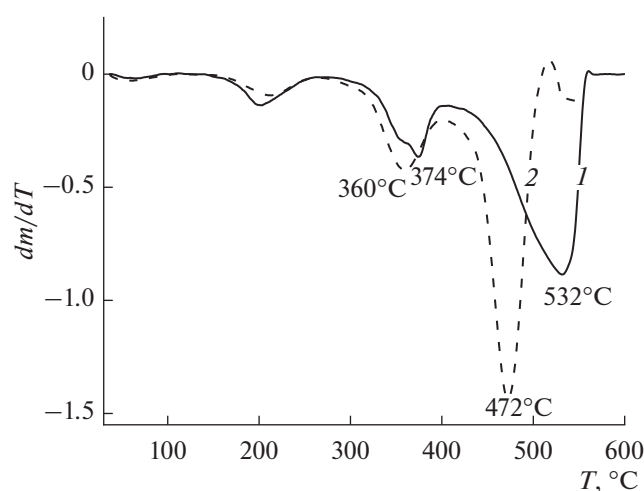
(Fig. 2). The low-intensity process in the temperature range up to 100−110°C is associated with the removal of water (~1%). The weight losses in the range of 180−260°C reflect the evaporation of residual solvent from the sample (7−8%).

Thermo-oxidative degradation of the test films occurs in two steps (Fig. 3). In the first step covering the range of 300−400°C with maximum intensity at 360−370°C, the material loses 20−25% of its mass. The main losses occur at the second step above 420−430°C, up to the complete degradation of the material at 500−550°C.

In MPC films, both degradation steps are observed earlier than in the initial coPA. The maximum rate of weight loss for MPC at the first step is recorded at 14°C lower than for coPA. At the second stage degradation step, this temperature difference increases to 60°C.

The observed shift of the thermo-oxidative degradation process of MPC toward lower temperatures is obviously due to the well-known effect of the catalytic action of copper and a number of its compounds in the decomposition reactions of various polymers [37]. It can be assumed that it is in the region of intense decomposition of the complex (above 300°C) that copper compounds appear in free form in the polymer volume, catalyzing the further development of degradation processes. Thus, it can be concluded that the indicated temperature characterizes the onset of thermally stimulated decomposition of the polymer−Cu complex. Note that similar behavior of MPC with copper was previously revealed in a study of complexes on other polymer carriers [38].

In all cases, two exothermic processes reflected in the DTA curves correspond to two steps of thermal degradation of the material. The low-temperature degradation step corresponds to low-intensity heat release, and a powerful exothermic effect is recorded

Fig. 2. TGA and DTA curves of coPA and MPC membranes: (*1*) TG curve of coPA, (*2*) TG curve of MPC, (*3*) DTA curve of coPA, and (*4*) DTA curve of MPC.

Fig. 3. DTG curves of (*1*) coPA and (*2*) MPC membranes.

at the second stage of degradation. The temperatures of the heat release maxima correspond well to the maxima in the DTG curves (Fig. 3).

In this work, the transport properties of membranes prepared from coPA and MPC were investigated in the separation of toluene/methanol mixtures. The process of mass transfer of toluene and methanol molecules through coPA and MPC membranes was studied by conducting pervaporation and sorption experiments.

The pervaporation process of a toluene/methanol mixture was studied for several feed mixture compositions, including the azeotropic point of 31 wt % toluene and 69 wt % methanol. Figure 4 shows the dependence of the toluene concentration in the permeate on the toluene concentration in the feed mixture during pervaporation of a toluene/methanol mixture, 40°C. It was found that for all feed compositions, the both coPA and MPC membranes predominantly pass toluene.

Based on the pervaporation results indicating the preferential selectivity of the studied polymers to toluene, it can be assumed that these membranes are the most cost-effective in separating toluene/methanol mixtures with low toluene content. Table 2 presents the data on the membrane flux and separation factor in the pervaporation of feed mixtures containing toluene in a small amount (10 wt %) and nearly at the azeotropic point (31 wt % toluene). For each feed composition, the flux through MPC membrane is ~2 times that for the coPA membrane. Meanwhile, the separation factor ($\alpha_{Tol/MeOH}$) for the coPA membrane is significantly higher than that of the MPC membrane.

To explain the experimental results, the characteristic properties of the penetrant−membrane system were calculated using the Baker method [36], namely, the permeability and selectivity parameters ($\alpha_{Tol/MeOH}$) normalized by the operating conditions. Figure 5 shows the dependence of the toluene and methanol permeability on the toluene concentration in the feed mixture. The toluene permeability significantly exceeds the methanol permeability for both membranes, and the toluene permeability decreases with an increase in the toluene concentration in the feed, but the permeability of methanol, on the contrary, increases slightly. It is shown that the MPC has an
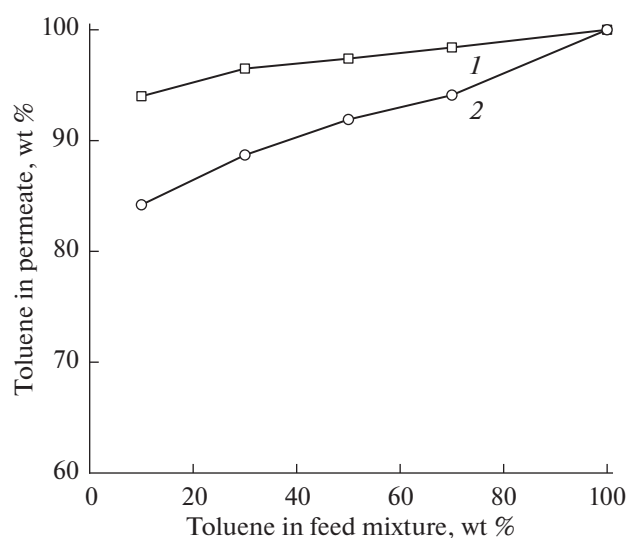

Fig. 4. Dependence of toluene concentration in permeate on toluene concentration in the feed mixture during pervaporation of toluene/methanol mixture using (*1*) coPA and (*2*) MPC membranes, 40°C.

increased permeability of both components of the feed mixture compared to the coPA membrane.

Figure 6 shows the dependence of the selectivity ($\beta_{Tol/MeOH}$) on the toluene content in the feed mixture during pervaporation using the coPA and MPC membranes. Both membranes are indeed selective with respect to toluene; the selectivity of the coPA membrane is higher than that of the MPC.

Figure 7 presents the results of a sorption study on the coPA and MPC membranes in the individual liquids toluene and methanol. The test membranes sorb methanol to a greater extent than toluene; the degree of equilibrium sorption of methanol significantly exceeds that of toluene. The mixture of methanol and toluene is a composition of highly polar and weakly polar liquids. Polar MeOH molecules are small in size and are more quickly sorbed on membrane active sites (=N−H and C=O) capable of hydrogen bonding, thereby forming "*hydrophobic*" channels for the transport of toluene molecules. This fact plays an important role in the pervaporation process.

The set of experimental and calculated data on pervaporation and sorption allows us to suggest the fol-

Table 2. Transport properties of dense nonporous membranes

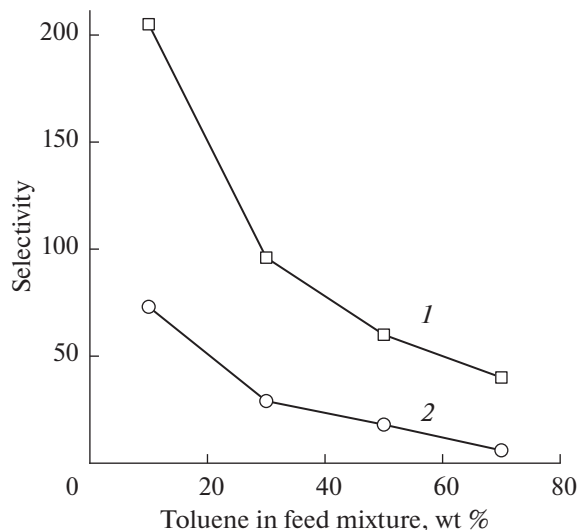| Membrane	Toluene concentration in the feed toluene/methanol mixture			
	10 wt %		31 wt %	
	Flux, g/(m² h)	Separation factor $\alpha_{Tol/MeOH}$	Flux, g/(m² h)	Separation factor $\alpha_{Tol/MeOH}$
coPA	12.4	141	13.5	64
MPC	22.5	48	26.7	18
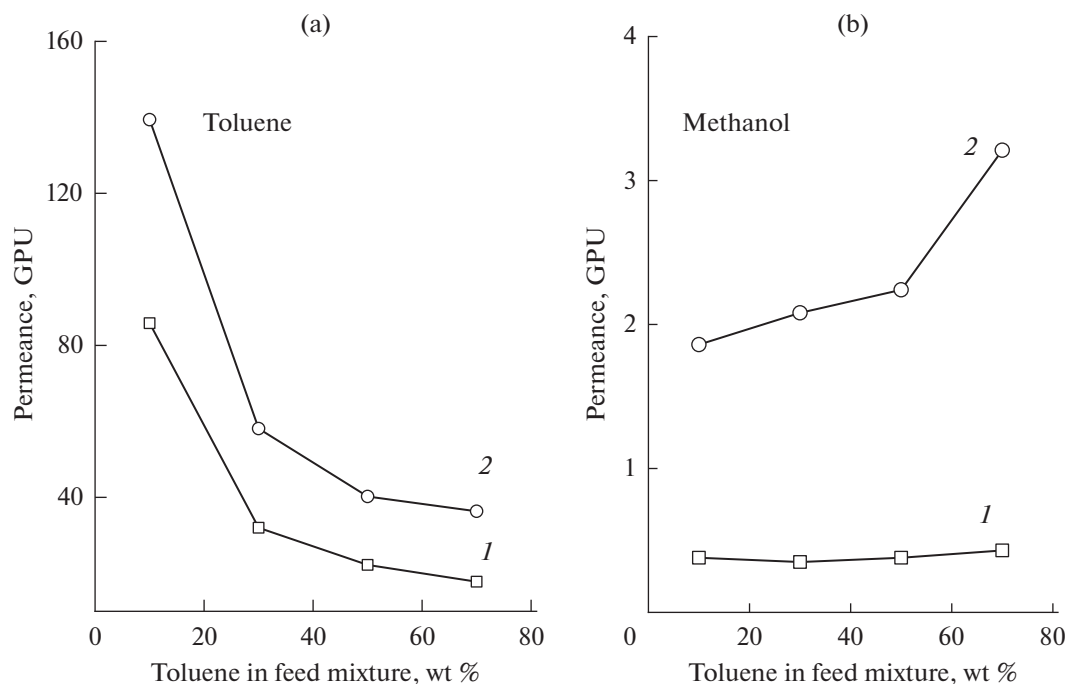
Fig. 5. Dependence of permeability of (a) toluene and (b) methanol on toluene concentration in the feed mixture during pervaporation using (*1*) coPA and (*2*) MPC membranes, 40°C.

lowing mechanism of transport during pervaporation of a toluene/methanol mixture through coPA and MPC membranes. Preferential and active sorption of methanol molecules on the surface and inside the polymer matrix, which is due to the polar nature and the possibility of forming hydrogen bonds between methanol and the membrane polymer, leads to the retention of alcohol molecules inside the membranes

and the formation of special channels with hydrophobic surface groups that facilitate the preferential transport of toluene molecules due to hydrophobic interactions involving methyl and phenyl groups.

When separating the azeotropic toluene−methanol mixture, which contains a smaller amount of toluene (31 : 69 by weight) compared to methanol, the recovery of toluene is an economically more advantageous process compared to the isolation of methanol. New

Fig. 6. Dependence of selectivity ($\beta_{Tol/MeOH}$) on the concentration of toluene in the feed mixture during pervaporation using (*1*) coPA and (*2*) MPC membranes, 40°C.
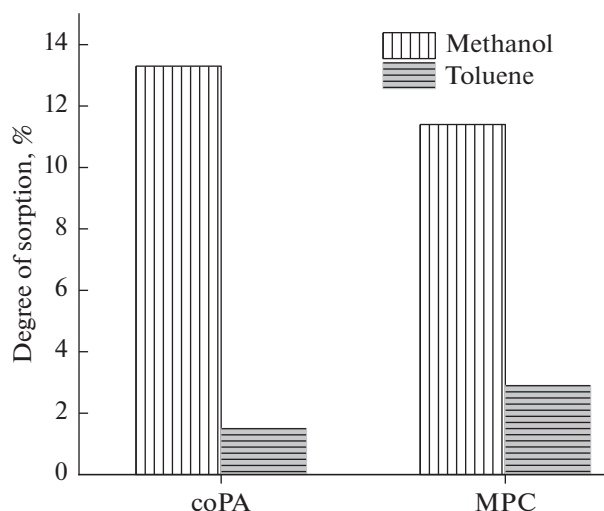
Fig. 7. Degree of equilibrium sorption of methanol and toluene in coPA and MPC membranes.

structures of polyheteroarylenes coPA and MPC seem to be promising materials for toluene-selective membranes.

CONCLUSIONS

New polyheteroarylenes, copolyamide coPA and its metal−polymer complex coPA-Cu^{2+} (MPC), were synthesized and used to fabricate dense nonporous membranes. A comparative study of some physical properties of the membranes showed that the MPC membrane has an increased density and a significantly higher glass transition temperature compared to coPA. The water contact angle of MPC increases compared to coPA, indicating an increase in the hydrophobicity of the MPC membrane. The process of mass transfer of toluene and methanol molecules through coPA and MPC membranes was studied in sorption and pervaporation experiments. During pervaporation of toluene/methanol mixtures, it was found that coPA and MPC membranes are predominantly permeable and selective for toluene for all feed mixture compositions. In separation of the azeotropic mixture, the coPA membrane showed a separation factor ($\alpha_{Tol/MeOH}$) of 64, and the MPC membrane showed a higher permeance of 26.7 g/(m^2 h). To explain the experimental results, the characteristic properties of the penetrant−membrane system were calculated using the Baker method, namely, the permeability and selectivity parameters normalized by operating conditions. It was proven that both membranes are indeed selective with respect to toluene, with the selectivity of the coPA membrane being higher than that of the MPC. The sorption measurements showed that the studied membranes sorb methanol to a greater extent, with the degree of equilibrium sorption of methanol significantly exceeding that of toluene. A transport mechanism is proposed during pervaporation of the toluene/methanol mixture through the coPA and MPC membranes. Preferential and active sorption of methanol molecules on the surface and inside the polymer matrix leads to the formation of transport channels with hydrophobic surface groups, which facilitate the preferential transport of toluene molecules due to hydrophobic interactions involving methyl and phenyl groups.

Comparison of the transport properties of the new membranes with published data on the pervaporation of the azeotropic toluene/methanol mixture showed that the films obtained in this work have a higher selectivity than most known membranes. The proven selectivity of the studied polymers to toluene suggests that these membranes are the most cost-effective in separating toluene/methanol mixtures with low toluene content.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflict of interest.

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