

# Membranes Based on Polyimide–Polyaniline Nanocomposites for Pervaporation of Organic Mixtures

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**ABSTRACT:** Polyimide–polyaniline nanocomposites were obtained by mixing poly{[4,4'-bis(4''-N-phenoxy)diphenylsulfone]imide-1,3-bis(3,4-dicarboxyphenoxy)benzene} (PI) and polyaniline (PANI) solutions in *N*-methylpyrrolidone. These solutions were used for the preparation of homogeneous and composite membranes. Uniform distribution of PANI particles in the membranes, resulted from interactions between macromolecules, was confirmed by transmission electron microscopy. Membranes based on PI and PI–PANI were tested in pervaporation of binary organic mixtures: methanol/toluene and methanol/cyclo-

hexane and showed a remarkable selectivity with respect to methanol. In both pervaporation processes, selectivity was improved in PANI-containing membranes. Interactions between membrane polymers and liquid penetrants (methanol, toluene, and cyclohexane) were studied by measurements of surface tension, sorption, and pervaporation parameters. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2175–2182, 2010

**Key words:** membranes; pervaporation; polyimide; polyaniline

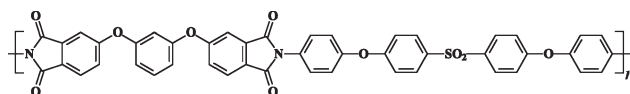
## INTRODUCTION

Diversification of membrane technologies in modern applications, such as separation of chemically aggressive mixtures in electronic industry and development of new energy sources, promotes the search of new membrane materials, both polymeric and composite, with high productivity and selectivity. In this respect, polyaniline (PANI) may be of great practical interest because it exhibits high electroconductivity, being an air stable conjugated polymer that is highly resistant to the most organic and inorganic solvents.<sup>1–3</sup> Studies on transport properties of PANI in membrane processes of gas separation and pervaporation have shown its high selectivity in separation of liquid and gaseous small molecules.<sup>4–8</sup> However, poor mechanical properties and high melting point of PANI restrict the formation of free-standing films for their application as membranes.

To maintain the required mechanical properties, composites of PANI and other polymers are pro-

duced in a variety of fashions. Hybrid nanocomposite membrane has been obtained by *in situ* polymerization of aniline in poly(vinyl alcohol) matrix and used for pervaporation of water/isopropanol mixtures.<sup>9</sup> Laminate composite membranes have been produced by casting polystyrene solution in benzene on PANI film and by evaporation of benzene. These two-layer membranes have been investigated in gas separation.<sup>10</sup> Composite membranes of polyaniline and polyimide (BTDA/ODA) were prepared by casting films from mixed poly(amic acid) and PANI solutions in *N*-methylpyrrolidone (N-MP) and their heating up to 300°C to convert poly(amic acid) to polyimide.<sup>11</sup> These membranes exhibit an improved gas transport properties and selectivity in separation of water/acetic acid mixtures. Aromatic polyimides and their composites are promising materials for polymer membranes.<sup>12–14</sup>

In this work, PANI was introduced in the matrix of aromatic polyimide poly{[4,4'-bis(4''-N-phenoxy)diphenylsulfone]imide-1,3-bis(3,4-dicarboxyphenoxy)benzene} (PI)



duced in membrane processes of gas separation<sup>15</sup> and pervaporation.<sup>16</sup>

An enhanced chain flexibility of this PI because of the presence of bridge groups between phenylene

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cycles in its structure makes it soluble in, for example, aprotic amide solvents (*N,N*-dimethylformamide, *N,N*-dimethylacetamide, and *N*-methylpyrrolidone). The PI is also thermoplastic, exhibiting melt flow properties at temperatures below the onset of its thermal destruction. These properties of the PI make it possible to form membranes from its solutions and to prepare thermostable polyimide bindings and highly heat-resistant composite materials.<sup>17</sup>

In this article, from the solutions of the PI and PANI composites in N-MP, free-standing polymer films were prepared and their membrane properties were investigated. The membranes were characterized by thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and surface tension measurements. Transport properties of membranes were studied in pervaporation and swelling (sorption) experiments. Pervaporations of two organic mixtures, methanol/toluene and methanol/cyclohexane, were investigated in the wide range of methanol content (10–90 wt %) in the feed at 50°C.

## EXPERIMENTAL

### Materials

Monomers for the PI synthesis (dianhydride of 3,3',4,4'-(1,3-diphenoxybenzene) tetracarboxylic acid and 4,4'-bis(4''-aminophenoxy)diphenylsulfone) and N-MP were purified as described elsewhere.<sup>18</sup>

Synthesis of poly[[4,4'-bis(4''-*N*-phenoxy)diphenylsulfone]imide-1,3-bis(3,4-dicarboxyphenoxy)benzene]

The PI was obtained by polycondensation of dianhydride of 3,3',4,4'-(1,3-diphenoxybenzene) tetracarboxylic acid and 4,4'-bis(4''-aminophenoxy)diphenylsulfone in a N-MP solution and by subsequent cyclodehydration of the formed poly(amic acid) in the same solution at 180–190°C. Water formed in the cyclodehydration process was distilled off from the reaction solution as toluene–water azeotropic mixture, obtaining 15–20% solution of the PI in N-MP.

### Synthesis of polyaniline

Powder PANI in its emeraldine base form was synthesized by chemical oxidative polymerization of aniline hydrochloride by ammonium peroxydisulfate and the following treatment of the obtained product by 1M solution of ammonium hydroxide. The reduced viscosity of 0.1 wt % PANI solution (N-MP, 22°C) was 0.3 dL/g.

### PI–PANI composition preparation

A total of 3 wt % PANI solution in N-MP was intensely stirred for 2 h, sonified for 40 min, and fil-

tered off. To prepare polymer compositions, PANI and PI solutions in N-MP were mixed in the appropriate amounts.

### Membranes

Homogeneous PI and PI–PANI membranes (dense films ~20–40 μm thick) were obtained by casting 5 wt % polymer solution in N-MP onto a glass plate and by drying in vacuum at 50°C up to the constant weight.

Composite (PI + 6 wt % PANI)/PPO membranes were prepared by casting a 3% solution of the mixture (PI + 6 wt % PANI) in N-MP on the surface of a poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) support with pores protected by decane from the penetration of the polymer solution. Excess solution was poured off, and the membrane was dried up to the constant weight.<sup>15</sup>

PPO porous support was prepared from an 8% PPO solution in the chloroform/butanol (85 : 15 wt %) mixed solvent. A 350-μm-thick layer cast onto a glass plate was subsequently immersed into ethanol and then into decane.

### Thermogravimetric analysis

TGA was performed in airflow (50 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate 10°C min<sup>-1</sup> with a Perkin Elmer TGA 7 Thermogravimetric Analyzer.

### Transmission electron microscopy

Microphotographs of a transversal cut of composite PI–PANI films were taken on the transmission electron microscope Zeiss 922 Omega.

### Contact angle measurements

Contact angles of liquids on homogeneous membrane surfaces were measured by the Wilhelmy plate technique, using the KRUSS installation. In the Wilhelmy plate technique, the advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) angles are calculated from the force exerted as the sample is immersed or withdrawn from a liquid.<sup>19</sup> A computer controls the stage velocity and movements and provides the software required for calculations.

Liquids under study were water with surface tension  $\sigma = 72.4$  mN/m, methanol with  $\sigma = 22.6$  mN/m, and toluene with  $\sigma = 28.4$  mN/m.

Based on measured data, surface tension  $\sigma_s$  of membranes was calculated. As the liquids have different polarity, we cannot use a simple method such as critical surface tension. Instead, the approach explained in Ref. 20 was used. The interfacial

parameter should be split into two components

$$\sigma_s = \sigma_s^d + \sigma_s^p, \quad (1)$$

where the superscript *d* (resp. *p*) indicates dispersion (resp. polar) term. Measured contact angles  $\theta$  for three above liquids gave an overdetermined set of equations

$$(\cos \theta + 1) \cdot \sigma_l = 2 \cdot \left( \sqrt{\sigma_l^d \cdot \sigma_s^d} + \sqrt{\sigma_l^p \cdot \sigma_s^p} \right) \quad (2)$$

which solution gave the two required components. Surface tension components of liquids (indicated by subscript *l*) were found in Ref. 21.

### Swelling experiments

Homogeneous membrane samples of known weight were immersed in a liquid at 20°C. After 1 h they were removed and weighted when superfluous liquid was wiped. This procedure was repeated until the weight of swollen films became constant. Then, the kinetics of desorption (liquid evaporation) was measured by weighing the sample every 10 min until the weight of dry films became constant. Equilibrium swelling of polymer membrane,  $\Delta W$  (%), was calculated by the equation

$$\Delta W = \frac{m_s - m_d}{m_d}, \quad (3)$$

where  $m_s$  is the weight of a swollen membrane and  $m_d$  is the weight of a dry membrane.

To determine the polymer–solvent interaction parameter, the polymer volume fraction in swollen samples,  $\phi_2$ , was calculated as

$$\phi_2 = \frac{1}{1 + \rho_2/\rho_1 \cdot \Delta W}, \quad (4)$$

where  $\rho_1$  and  $\rho_2$  are solvent and polymer densities ( $\text{g}/\text{cm}^3$ ), respectively.

Then, the equation of Flory-Huggins theory<sup>22</sup> was used:

$$\ln a_1 = \ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2. \quad (5)$$

The interaction parameter,  $\chi$ , was calculated in the ideal solvent approximation ( $a_1 = 1$ , i.e.,  $\ln a_1 = 0$ ) by the following formula:<sup>23</sup>

$$\chi = \frac{-[\ln(1 - \phi_2) + \phi_2]}{\phi_2^2}. \quad (6)$$

Flory-Huggins interaction parameter directly characterizes the solubility of a polymer in a given liquid.

If the interaction between the polymer and the penetrant increases, the amount of penetrant inside the polymer also increases and  $\chi$  decreases. In contrast, with decreasing affinity between the polymer and the penetrant,  $\chi$  increases. Therefore, a lower value of  $\chi$  implies higher sorption.

The diffusion coefficients,  $D$  ( $\text{cm}^2/\text{s}$ ), of penetrants into a polymer membrane were determined from the derivatives of the desorption kinetic curves taken at the initial time moment:<sup>24</sup>

$$D = \frac{\pi}{16} (\tan \gamma)^2, \quad (7)$$

where  $\tan \gamma$  is the tangent of the initial slope of the desorption kinetic curves.

### Pervaporation

Pervaporation properties were measured using a laboratory cell having an effective membrane area of 14.8  $\text{cm}^2$  at 50°C with stirring. Downstream pressure below  $10^{-1}$  mmHg was maintained. The permeate was collected into a liquid nitrogen cooled trap, weighed, and then analyzed by refractometry and gas chromatography. Methanol, toluene, and cyclohexane were used as mixture components.

Membrane permeation flux,  $J$  ( $\text{kg}/\text{m}^2\text{h}$ ), was determined as an amount of liquid transported through the unit area of the membrane per time unit.

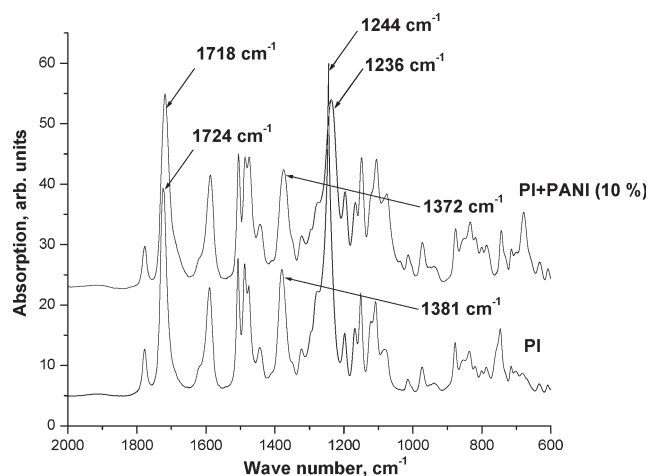
The selectivity or the separation factor,  $\alpha$ , was defined by the equation

$$\alpha = \frac{y_i/y_j}{x_i/x_j}, \quad (8)$$

where  $y_i$  and  $y_j$  are the weight fractions of components *i* and *j* in the permeate and  $x_i$  and  $x_j$  are the weight fractions of components *i* and *j* in the feed.



**Figure 1** TEM micrograph of the cross section of a composite PI film containing 3 wt % of PANI.



**Figure 2** FTIR spectra of pure PI and composite PI + PANI (10%) films.

## RESULTS AND DISCUSSION

Stable uniform free-standing nanocomposite PI-PANI films were obtained. At the PANI content below 10 wt %, these films possess good mechanical properties ( $E = 2.0\text{--}2.4$  GPa,  $\sigma_p = 55\text{--}60$  MPa,  $\varepsilon_p = 8\div 10\%$ ), making possible their use as pervaporation homogeneous membranes for separation of organic liquid mixtures.

To investigate the distribution of PANI along the normal to the film surface, transversal cross sections of the films were prepared and studied by TEM (Fig. 1). This method is widely used for visualization of nano- and microparticles distributed in polymeric matrices and, in particular, for PI-PANI mixtures.<sup>25</sup>

As seen from Figure 1, the distribution of PANI microparticles within the PI matrix is rather uniform, provided the content of PANI is not very high (up to 6 wt %). This is also confirmed by the fact that the PI-PANI composites, containing PANI doped with camphorsulfonic acid, have the conductivities  $\sim 10^{-2}$  S/cm at the percolation threshold of  $\sim 1\text{--}2$  wt % of PANI. Obviously, such a uniform distribution of PANI in the solution of PI-PANI mixtures and composite films, cast from these solutions, is due to interactions between PI and PANI macromolecules,<sup>26</sup> being donor-acceptor (between  $\pi$ -donor PANI aromatic rings and  $\pi$ -acceptor PI imide cycles) and/or H-bonding (between amino groups of PANI and carbonyl groups of PI) in nature.<sup>27,28</sup>

In Figure 2, Fourier transform infrared (FTIR) spectra of pure PI and PI-PANI (10%) composite films are presented. A shift of  $6\text{ cm}^{-1}$  to lower vibration frequencies is noticeable for the imide C=O stretching vibration band in the composite ( $1718\text{ cm}^{-1}$ ) with respect to that in pure PI ( $1724\text{ cm}^{-1}$ ). This shift is attributable to hydrogen bond formation between carbonyl groups of PI and amine groups of PANI, leading to a slight weakening of the imide C=O bonds. Simultaneously, lower frequency shifts of  $\sim 8\text{ cm}^{-1}$  are observed for the bands at  $1381$  and  $1244\text{ cm}^{-1}$ , which are assigned to imide C-N stretching vibrations and aromatic cycle vibrations, respectively, pointing to a possible involvement of phenyl groups of PANI into interactions with the PI matrix.

The emphasis of this work is on experimental studies of the interaction of PI-PANI composites with methanol, toluene, and cyclohexane by characterization of surface tension, sorption, and pervaporation parameters. Some physical properties of the liquids under study are shown in Table I.

### Surface tension

Contact angles of liquids are the most widespread characteristics of the solid surface. Contact angles of water, methanol, and toluene on surfaces of membranes based on PI-PANI composites are listed in Table II. Based on the measured data, surface energy of solid was calculated. As the liquids have different polarity, separately polar  $\sigma^p$  and dispersion  $\sigma^d$  interactions had to be evaluated.<sup>20</sup>

Contact angle of water on PI surface equals to  $87.4^\circ$ . PANI additives cause the increase of this contact angle. A simple approach would indicate decrease of surface energy of the solid. However, as we can see in the Table II, in fact only polar interaction decreases. In contrary, dispersion interaction increases with PANI addition. The contact angle of toluene, a hydrophobic liquid, decreases on the surfaces containing PANI. This fact suggests the trend of enhancing hydrophobic properties in PI-PANI composites, when compared with those of pure PI films, and correlates with the behavior of water and methanol drops on the membrane surfaces.

Behavior of methanol is given not only by surface energetics but also by the fact that methanol sorption

**TABLE I**  
Properties of Penetrants, 25°C

Penetrant	MW	Density (g/cm <sup>3</sup> )	Molar volume (cm <sup>3</sup> /mol)	Viscosity (mPa s)	Solubility parameter (J/cm <sup>3</sup> ) <sup>1/2</sup>
Methanol	32.0	0.792	40.4	0.55	29.7
Toluene	92.1	0.867	107.1	0.54	18.2
Cyclohexane	84.2	0.779	109.4	0.89	16.7



TABLE II  
Contact Angles (°) Measured at 20°C

Membrane	Water		Methanol		Toluene		Surface tension (mJ/m <sup>2</sup> )	
	$\theta_a$	$\theta_r$	$\theta_a$	$\theta_r$	$\theta_a$	$\theta_r$	$\sigma_s^d$	$\sigma_s^p$
PI	87.4	56.1	7.5	0.0	35.8	34.7	19.7	5.0
PI + 3% PANI	89.2	61.9	13.2	0.0	31.1	30.1	24.0	2.8
PI + 6% PANI	90.5	65.7	19.0	0.0	17.9	17.7	24.3	2.5

is rather rapid. Advancing contact angle  $\theta_a$  of methanol is the smallest and increases in PI-PANI composites. Receding contact angle  $\theta_r$  was found 0 for all samples, that is, membranes withdrawn from methanol remain uniformly wet by it for several minutes.

### Sorption

Swelling experiments make it possible to study the kinetics of sorption and desorption of methanol, toluene, and cyclohexane in membranes based on PI and its composites. It should be noted that only data on desorption from swollen membranes were used for calculations and analysis in this work. This is due to the fact that PI forms strong complexes with N-MP and, therefore, PI-based membranes contained a considerable amount of N-MP even after their drying in vacuum at 50°C. According to the TG analysis (Fig. 3), there is a noticeable weight loss ( $\Delta m$ ) of 8–9 wt % at N-MP boiling point for all membranes. Hence, during the swelling membrane films in liquid sorbates (methanol and toluene) N-MP was gradually washed out and substituted by the sorbate, making the sorption kinetic curves anomalous in shape.

Table III presents the equilibrium swelling and Flory-Huggins parameter values for methanol, toluene, and cyclohexane. The values of equilibrium

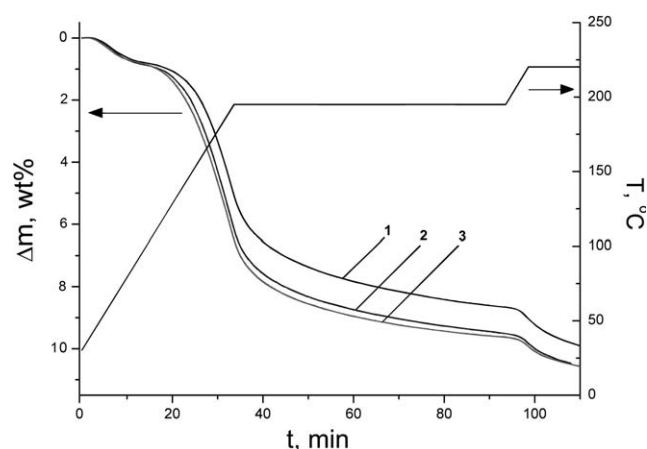


Figure 3 TG curves of (1) PI, (2) PI + 3 wt % PANI, and (3) PI + 6 wt % PANI. Jogged line is heating rate of samples.

swelling for both methanol and toluene decrease upon inclusion of rigid PANI centers into the PI matrix, which leads to increasing  $\chi$ , i.e., decreasing the affinity of the liquids to the polymer. Equilibrium swelling in both cases (methanol and toluene) changes in the opposite way with respect to  $\chi$ .

It is important to emphasize the absence of cyclohexane sorption by both pure PI and composite PI-PANI films. Thus, these membranes should be effective in separating liquid mixtures, containing cyclohexane.

Swelling kinetics is controlled by the diffusion of penetrant molecules between polymer chains. The data on desorption of methanol and toluene from swollen membranes of pure PI and its composites, containing 3 and 6 wt % PANI, are shown in the kinetics curves as a function of  $M_t$  on the square root of reduced time  $t^{1/2}/l$  (where  $l$  is the thickness of dry membrane sample,  $M_t$  is the weight loss at time  $t$ ) (Figs. 4 and 5). Desorption of methanol occurs more rapidly than that of toluene. In the initial stage of the desorption of both liquids, the weight loss occurs very rapidly, giving linear regions in the plots, then desorption slows down, and finally ceases. Linear regions in the initial stage of desorption were used for the calculations of diffusion coefficients (Table IV).

As seen from Table IV, diffusion coefficients of methanol are higher than that of toluene for all membranes. Diffusion coefficients of methanol in PI membrane increase after inclusion of 3 and 6 wt % PANI. On the contrary, diffusion coefficients,  $D$ , of toluene decrease upon inclusion of PANI into the PI matrix. As a result of these opposite changes, the  $D$  values for methanol and toluene in PI + 6 wt % PANI composite membranes differ by an order of magnitude, whereas these values are similar for pure PI membranes. This fact may be of practical importance for pervaporation.

### Pervaporation of methanol/toluene mixture

Pervaporation of organic mixtures with azeotropic points is a complex process for which membranes with both selective properties and chemical resistance to penetrants are required. The components of PI-PANI composites are stable in methanol and

**TABLE III**  
Equilibrium Swelling and Flory-Huggins Parameters

Membrane	Methanol		Toluene		Cyclohexane, $\Delta W$ (%)
	$\Delta W$ (%)	$\chi$	$\Delta W$ (%)	$\chi$	
PI	12.5	1.35	7.7	1.71	0
PI + 3% PANI	11.1	1.42	7.4	1.73	0
PI + 6% PANI	10.6	1.44	6.9	1.78	0

toluene, so it is appropriate to study the separation of this mixture that is characterized by the azeotropic point (69 wt % of methanol and 31 wt % of toluene at 20°C, 760 mmHg). According to Vrevsky low, the azeotropic point position on a liquid-vapor diagram varies with pressure and temperature.<sup>29</sup> Therefore, the pervaporation experiments were carried out in the concentration range of 30–90 wt % of methanol in the feed that involve possible azeotropic mixture in the pervaporation conditions (50°C and 10<sup>-1</sup> mmHg).

Figures 5 and 6 show the results of methanol/toluene mixture pervaporation using homogeneous membranes based on pure PI and its composite containing 6 wt % PANI. For all feed compositions, permeate was enriched with methanol, that is, all membranes are selective with respect to methanol.

Figure 6 shows the dependence of specific permeation flux,  $J \cdot l$ , on the methanol content in the feed. The total permeation flux,  $J$ , is inversely proportional to homogeneous membrane thickness,  $l$ , which varied from 20 to 40  $\mu\text{m}$ , and permselectivity strongly depends on it.<sup>13,30</sup> Therefore, the product  $J \cdot l$  was used for comparing the permeability of homogeneous membranes with different thickness. It is seen from Figure 6 that membrane specific flux increases with the methanol concentration in the feed. The inclusion of PANI into the PI membrane decreases the flux of penetrant through the membrane, which

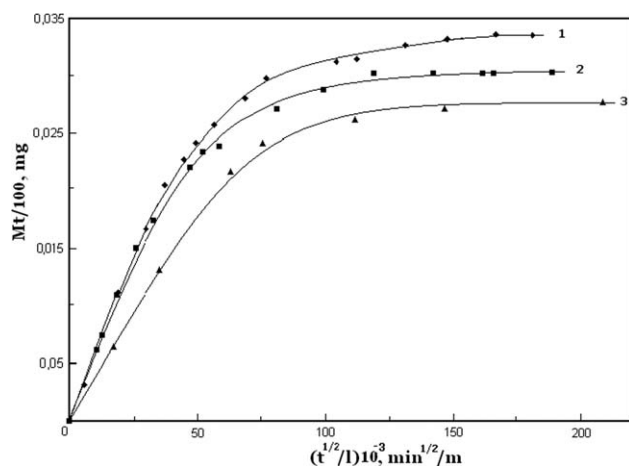
becomes slightly lower than that through the pure PI membrane. This is due to the decrease in the sorption ability of membranes for both mixture components with the increase in polymer-solvent interaction parameter values for PI-PANI composites (Table III).

As seen from Figure 7, the membrane selectivity decreases with the increase of the methanol content in the feed. It is important to stress that the inclusion of PANI into the PI matrix increases the selectivity of the composite membrane when compared with that of the pure PI membrane in pervaporation of methanol-toluene mixture. This positive effect may be due to the increase of the diffusion coefficient for methanol and decrease of that for toluene in PI-PANI composites (Table IV).

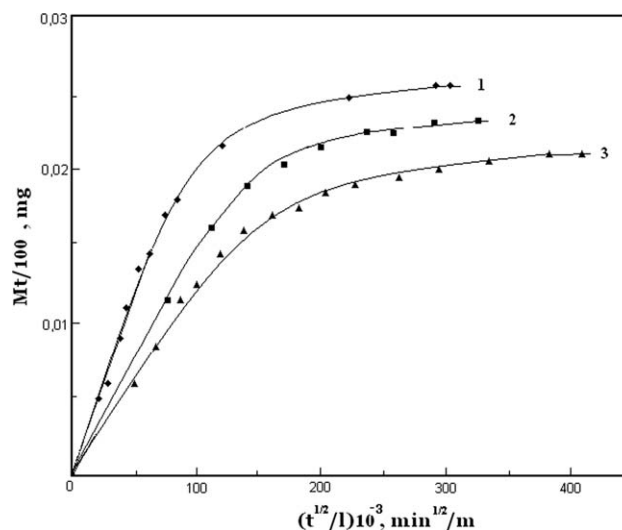
#### Pervaporation of methanol/cyclohexane mixture

Two types of membranes were used for studying pervaporation of methanol/cyclohexane mixture, namely, homogeneous membranes (25–40  $\mu\text{m}$  thick) and composite membranes, consisting of the selective layer made of PI + 6 wt % PANI (3–5  $\mu\text{m}$  thick) supported by a porous membrane made of PPO.

The methanol/cyclohexane mixture is often used as a model of the methanol/methyl-*t*-butyl ether



**Figure 4** Kinetic curves of methanol desorption from membranes (1) PI, (2) PI + 3 wt % PANI, and (3) PI + 6 wt % PANI.



**Figure 5** Kinetic curves of toluene desorption from membranes (1) PI, (2) PI + 3 wt % PANI, and (3) PI + 6 wt % PANI.

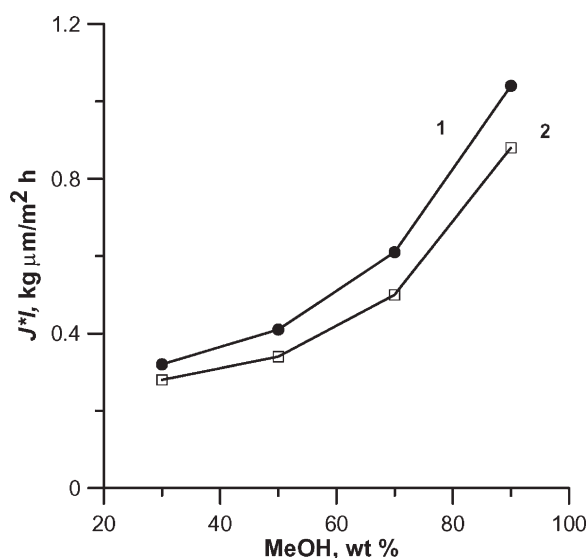
**TABLE IV**  
Diffusion Coefficients

Membrane	$D \cdot 10^9$ (cm <sup>2</sup> /s)	
	Methanol	Toluene
PI	2.0	1.5
PI + 3% PANI	6.8	1.0
PI + 6% PANI	8.5	0.8

(MTBE) mixture. MTBE finds its application as an antiknock additive to gasoline. The positive result in the pervaporation of methanol/cyclohexane mixtures can be used in MTBE purification from impurities after its synthesis where methanol is used as one of the reagents.<sup>16,31</sup>

Studies on pervaporation of methanol/cyclohexane mixtures, containing small amount of methanol, are of current importance. Table V shows transport properties of homogeneous membranes in pervaporation of pure methanol and the 10 wt % methanol + 90 wt % cyclohexane mixture. PANI additives to the PI membranes increase the specific flux ( $J \cdot l$ ) in pervaporation of both pure methanol and its mixture with cyclohexane. The selectivity in separation of the mixture is very high because of that cyclohexane is inert with respect to the PI (Table III). It should be noted that the inclusion of PANI into the PI matrix helped to improve the selectivity in methanol elimination.

It is known that the flux through sufficiently thick homogeneous membranes is low, and this is why composite membranes are used to increase the productivity of membrane processes. The present data also demonstrate low flux values through homoge-



**Figure 6** The dependence of specific permeation flux,  $J \cdot l$ , on the methanol content in the feed for the pervaporation of methanol/toluene mixture through (1) PI and (2) PI + 6 wt % PANI homogeneous membranes.

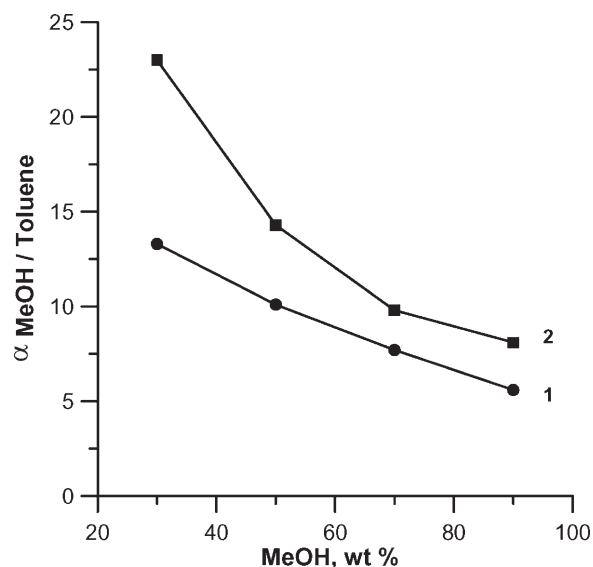
neous membranes based on the PI and its composition with PANI (Table V). Therefore, pervaporation of the methanol/cyclohexane mixture in a wide range of feed content was studied by using the (PI + 6 wt % PANI)/PPO composite membrane. Figure 8 shows the dependence of flux and selectivity on the methanol content in the feed.

The permeate is enriched with methanol in the entire range of feed content, selectivity is rather high, especially in the region of low methanol content in the feed. The employment of composite membranes results in a considerable increase in productivity of membranes and improves their mechanical properties.

## CONCLUSIONS

Membranes based on PI-PANI composites were tested for their possible application in organic mixture separation by pervaporation. The interaction of PI-PANI composites with liquids used in the pervaporation (methanol, toluene, and cyclohexane) was studied by the measurements of contact angles and sorption properties.

Contact angles of water and methanol on membrane surfaces increase, whereas contact angle of toluene decreases, with increasing PANI content in the composite. It is evidenced that membrane surfaces became more hydrophobic because of the inclusion of PANI into the PI matrix. The values of equilibrium swelling or sorption for both methanol and toluene decrease upon inclusion of rigid PANI centers into the PI matrix, which leads to increasing Flory-



**Figure 7** The dependence of selectivity on the methanol content in the feed for the pervaporation of methanol/toluene mixture through (1) PI and (2) PI + 6 wt % PANI homogeneous membranes.

TABLE V  
Transport Properties of Homogeneous Membranes

Membrane	$l$ ( $\mu\text{m}$ )	Methanol		10% methanol + 90% cyclohexane		Selectivity
		Flux ( $\text{kg}/\text{m}^2 \text{ h}$ )	$J \cdot l$ ( $\text{kg } \mu\text{m}/\text{m}^2 \text{ h}$ )	Flux ( $\text{kg}/\text{m}^2 \text{ h}$ )	$J \cdot l$ ( $\text{kg } \mu\text{m}/\text{m}^2 \text{ h}$ )	
PI	25	0.099	2.48	0.046	1.15	1800
PI + 6%PANI	40	0.085	3.40	0.046	1.84	2300

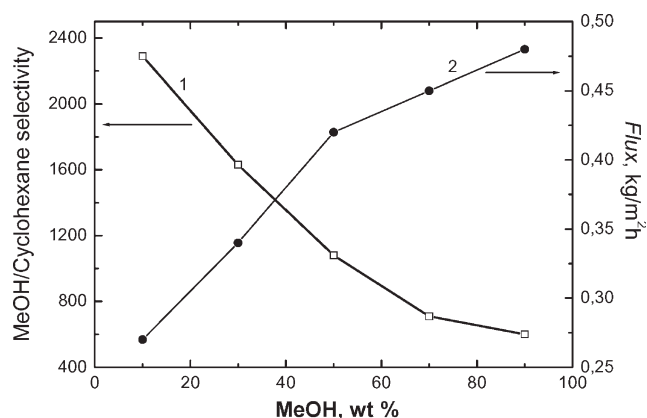


Figure 8 The dependence of selectivity (1) and flux (2) on the methanol content in the feed in pervaporation of the methanol/cyclohexane mixture by the composite (PI + 6 wt % PANI)/PPO membrane.

Huggins interaction parameters  $\chi$ , i.e., decreasing the affinity of the liquids to the polymer.

Membranes based on PI-PANI composites are selective with respect to methanol in pervaporation of binary organic mixtures methanol/toluene and methanol/cyclohexane. In pervaporation of methanol/toluene mixture, flux of penetrants is slightly lower but selectivity is higher in composites containing 6 wt % PANI than that in PI membranes. These membranes exhibit especially high efficiency in the pervaporation of 10 wt % methanol/cyclohexane mixture, selectivity is equal to 2300, and the flux is about 1.5 times higher than that through the pure PI membrane. The employment of composite (PI + 6 wt % PANI)/PPO membranes results in a considerable increase in productivity of membranes and improves their mechanical properties.

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