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Pervaporation membranes based on composites of polyimide with polyaniline or its copolymer

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ABSTRACT

Sorption and pervaporation properties of homogeneous membranes based on composites containing polyaniline (PANI) and copolymer of aniline with anthranilic acid (coPANI) involved in matrix of aromatic polyimide (PI) were investigated for binary organic mixtures with azeotropic points. It was established that PI membrane exhibited the highest selectivity to methanol during separation of methanol/toluene mixture due to the higher degree of equilibrium sorption and lower Flory-Huggins polymer-solvent interaction parameter with respect to methanol as compared with PI/PANI composites. Addition of coPANI in PI matrix leads to increasing of hydrophilic properties and consequently equilibrium sorption of water during separation of water/isopropanol mixture. PI/coPANI exhibits higher transport properties (flux and selectivity) as compared with that of PI membrane.

Keywords: Membranes; Aromatic polyimide; Polyaniline; Sorption; Diffusion; Pervaporation

1. Introduction

Pervaporation is the perspective soft trend of membrane technology that possesses such advantages as nonreactivity, low power consumption and high effectiveness. Pervaporation also allows separating organic and water-organic mixtures which are hardly divisible. If membrane shows selective sorption or selective molecular diffusion to one of mixture components it can be effective for separation. Thus development and investigation of new promising pervaporation materials is the primary task.

From this point of view composites comprising polyaniline (PANI) are of a great practical interest. PANI is the commonly used polyconjugative material possessing a row of unique properties. Stability in air and resistance to aggressive organic and inorganic media makes it attractive for using as the membrane material [1–3]. An analyses of literature data indicated that during gas separation PANI is selective in separation of small molecules [4–8]. Pervaporation properties of PANI membranes doped by poly acrylic acid (PAAc) were investigated in separation of water/isopropanol mixture [9]. All membranes are selective with respect to water. Due the doping effect, the hydrophilic properties of PANI/PAAc membranes increase with the PAAc content. It results in increase of

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equilibrium sorption, selectivity, and permeability of PANI/PAAc membranes as compared with PANI membrane. Nanocomposite membranes containing doped PANI nanoparticles dispersed in PVA matrix have been also used in pervaporation of water/isopropanol mixture [10]. The membrane swelling increased slightly, but systematically with increasing amount of PANI in the matrix. Membranes could exhibit an increased selectivity to water compared to the pure PVA membrane and reduced water flux.

In the present work transport properties of composites containing PANI or copolymer aniline with antranilic acid (coPANI) involved in matrix of aromatic polyimide were investigated in the case of separating azeotropic mixtures. Aromatic polyimide – poly[4,4′-bis-(4″N-phenoxy) diphenylsulfone] imide-1,3-bis(3,4-dicarboxy-phenoxy)benzene] (PI) was used as matrix polymer. Polyimides are the class of thermoplastic polymers possessing excellent mechanical properties and already it was proved to be the diffusion material [11,12]. Transport properties of these composites were determined by sorption and pervaporation studies for two mixtures: methanol/toluene and water/isopropanol.

2. Experimental

2.1. Materials

Poly[4,4′bis(4″-N-phenoxy)diphenylsulfone]imide-1,3-bis(3,4-dicarboxyphenoxy) benzene] (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.

Polyaniline (PANI) in its emeraldine base form was synthesized by chemical oxidative polymerization of aniline by ammonium peroxydisulfate in the medium of 1 M solution of hydrochloric acid and the following treatment of the obtained product by 1 M solution of ammonium hydroxide.

Copolymer of aniline and antranilic acid (coPANI) was synthesized by chemical oxidative polymerization of aniline and antranilic acid using the same synthesis method as for PANI with the increasing the time of synthesis from 7 to 30 h.

PI/PANI and PI/coPANI composites were prepared by mixing solutions of polymer components in N-MP in the appropriate amounts. These solutions were intensely stirred for 2 h, sonified for 40 min and filtered off.

2.2. Membranes

Homogeneous membranes ($\sim$20–40 μm thick) were obtained by casting of polymer solutions in N-MP on a glass plate and following drying in vacuum at 50°C up to the constant weight.

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed in airflow (50 $\mathrm{cm^3\ min^{-1}}$) at a heating rate 10°C·per min with a Perkin Emler TGA 7 Thermogravimetric Analyzer.

2.4. Swelling experiments

Sorption tests were performed by immersing the samples in Petri dish with liquid under study at 20 ± 0.5°C. At appropriate time intervals the samples were taken out, dried with a filter paper and weighed. The procedure was repeated until equilibrium weight was reached, i.e. no further weight gain was observed. Then the swollen samples were taken out from solvent and placed in ambient condition of desorption, i.e. in the controlled environment containing molecular sieve absorber (zeolite).

The weight change of sample m_0 was calculated by the following equation:

$$\Delta m = [(m - m_0)/m_0] \cdot 100 \tag{1}$$

where m_0 is an initial weight of sample, m is a weight of swollen samples at the moment t.

N-MP using as a solvent in preparation of polymer solutions was not removed completely from the samples after drying at vacuum at 50°C. Therefore the weight lost of samples was observed during the sorption experiments caused by removing of N-MP. Amount of the solvent Δm_b (%) washed out from membrane during sorption experiment was expressed as:

$$\Delta m_\mathrm{b} = [(m_0 - m_\mathrm{c})/m_0]100 \tag{2}$$

where m_c is a weight of sample after its drying at atmospheric pressure and 20°C when sorption test is finished.

Degree of sorption S (g/100 g polymer) was calculated taking into account amount of Δm_b *and* Δm [13]:

$$S = \Delta m + |\Delta m_b| \tag{3}$$

Thermodynamic polymer-solvent interaction parameter, χ_1, expressing affinity between the polymer and the penetrant, was defined using the equation of Flory-Huggins theory [14]:

$$\ln a_1 = [\ln(1-\varphi_2) + \varphi_2 + \chi\varphi_2^2] \tag{4}$$

where a_1 denotes a penetrant activity, φ_2 is a penetrant volume fraction in a swollen polymer sample expressed as:

$$\varphi_2 = \frac{1}{1+\frac{\rho_2}{\rho_1}\Delta s} \tag{5}$$

where ρ_1, ρ_2 are the density of penetrant and polymer consequently, Δs is amount of penetrant sorbed by polymer (g/g).

For a liquid penetrant $a_1 = 1$, and χ_1 was calculated by the following equation [15]:

$$\chi_1 = \frac{-[\ln(1-\varphi_2) + \varphi_2]}{\varphi_2^2} \tag{6}$$

The desorption curves of M_t/M_∞ was plotted as a function of $t^{1/2}/l$ (where M_t is weight loss of swollen sample at the moment t, M_∞ is equilibrium amount of penetrant sorbed by samples; l is a thickness of sample). The diffusion coefficients, D (cm^2/s), of penetrants into a polymer membrane were determined from the desorption kinetic curves at the initial time moment [16]:

$$D = \frac{\pi}{16}(tg\gamma)^2 \tag{7}$$

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

2.5. Pervaporation

Pervaporation properties were measured using a laboratory cell having an effective membrane area of 14.8 cm^2. The experiments were carried out with stirring feed mixtures at constant temperature 50°C. Downstream pressure below 10^{-1} mm Hg was maintained. The permeate was collected in cold traps by condensation in liquid nitrogen. The permeate was analyzed by refractometry using reflactometer IFR – 454B2M and gas chromatography using chromatograph Chromatec crystal 5000.2.

Membrane permeation flux, J (kg/m^2 h), was determined as an amount of liquid transported through unit of the membrane area and per time unit. Because J is inversely proportional to membrane thickness, l, which varied from 20 to 40 μm, permselectivity strongly depends on it. Therefore the product $J{\cdot}l$, so called specific permeation flux, was used for comparing the permeability of membranes with different thickness just as in [17].

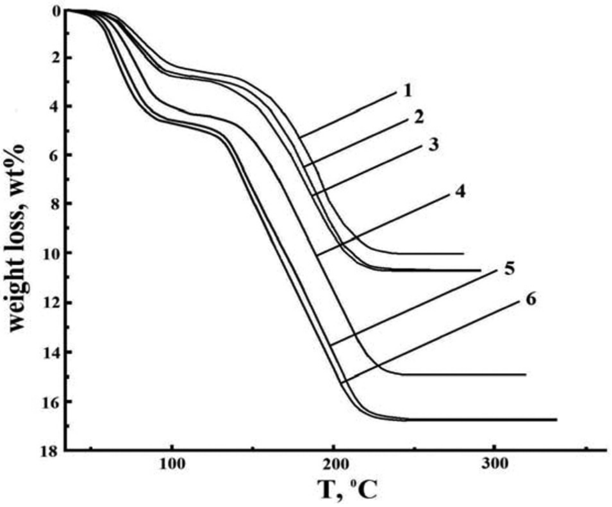

Fig. 1. TG curves of (1) PI, (2) PI/PANI (3 wt%), (3) PI/PANI (6 wt%), (4) PI/coPANI (5 wt%), (5) PI/coPANI (10 wt%),(6) PI/coPANI (15 wt%).

The selectivity or the separation factor, α, was defined by the equation [18]:

$$\alpha = \frac{y_i/y_j}{x_i/x_j} \tag{8}$$

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.

3. Result and discussion

PI/PANI and PI/coPANI composites were obtained by mixing polymer solutions in N-MP and used for homogeneous membrane preparation by solvent evaporation. It should be noted that polymers composed these membranes form strong complexes with N-MP that was not removed after careful drying in vacuum at 50°C and as a result the substantial amount of solvent retained in membranes. The residual solvent acts as a plasticizer in membrane material. The amount of solvent retained in membranes was estimated by TG analysis. Fig. 1 shows weight loss of membrane samples as a function of temperature. The weight loss was due to removing of moisture (up to 150°C) and residual N-MP (near the boiling temperature of N-MP). The weight loss caused by removing of residual N-MP was greater for PI/PANI as compared with PI membrane (9–11%). Amount of N-MP

Table 1
Properties of penetrants

Penetrant	MW	Density, g/cm^3	Molar volume, cm^3/mol	Viscosity, m·Pa·s	Dipole moment, debye
Methanol	32.0	0.792	40.4	0.55	1.69
Toluene	92.1	0.860	107.1	0.54	0.01
Water	18.0	0.997	11.4	$1.01 \cdot 10^{-9}$	1.84
Isopropanol	60.1	0.786	45.2	2.40	1.70

(15–17%) removed from PI/coPANI during TG analysis was greater than that from PI and PI/PANI membranes. This fact is connected with peculiarities of composite preparation. TGA data correlation with the sorption parameters was shown below.

Transport properties of homogeneous membranes prepared from PI and its composites were studied at pervaporation of mixtures with azeotropic points. Pervaporation of methanol/toluene mixture was processed using membranes from PI/PANI composite. PI/coPANI membranes being more hydrophilic as compare with PI/PANY were studied in separation of water/isopropanol mixture. Some physical properties of all penetrants under study are listed in Table 1.

3.1. Transport properties of PI/PANI membranes

The methanol/toluene mixture separation is an actual task for petroleum refining industry in the case of toluene obtaining from gasoline. Toluene is extracted from gasoline by methanol mixed with ethylene glycol, after that the important problem becomes toluene purification from methanol because of toluene forms azeotropic mixtures with methanol.

3.1.1. Sorption test

Membrane sorption properties were studied by immersion method. Due to the presence of solvent in the membrane sample, at first, two processes take place after the sample immersion in sorbat (methanol, toluene). They are N-MP washing out and exchange of N-MP with sorbat. These processes affect sorption parameters that are listed in Table 2. Therefore to calculate sorption degree, $\triangle m_b$ that is a relative amount of solvent (N-MP) removed from membranes during experiment was taken into account.

According to Table 2 methanol being the polar liquid washes out more amounts of N-MP then toluene and the membrane weight decreases after sorption and drying. Probably this fact is connected with strong specific interaction of methanol with PI chains and rearrangement of polymer structure that leads to release of large amount of solvent.

Compared to PI membrane, PI/PANI sorbs methanol and toluene in lesser extend. In the case of the methanol this is apparently connected to a change in the character of membrane surface, namely with the increase of the hydrophobic properties upon PANI addition. The determinative factors of toluene sorption are its molecular size and the structural peculiarities of the obtained polymer composites preventing sorption of large toluene molecules.

All objects studied in the present work sorb methanol better than toluene. Therefore, the Flory-Huggins interaction parameter χ_1 calculated using sorption data for all membranes is higher for toluene as compared to methanol. This indicates the higher affinity of PI and PI/PANI membranes to methanol.

Fig. 2 shows curves of desorption kinetics of methanol and toluene: sorbed amount vs. time. These curves were used for calculation of the effective diffusion coefficients. For all types of membranes, effective diffusion coefficients of methanol are higher than the corresponding values for toluene (Table 3). Furthermore, upon PANI addition into PI matrix the increase of methanol diffusion coefficient is observed. On the contrary, the effective diffusion

Table 2
Data of sorption measurements for methanol and toluene

	Δm_b, %		S, g/100 g polymer		χ_1	
Membrane	Methanol	Toluene	Methanol	Toluene	Methanol	Toluene
PI	14.5	3.0	12.5	7.7	1.35	1.71
PI/PANI (3%)	14.3	2.8	11.1	7.4	1.42	1.73
PI/PANI (6%)	14.2	2.6	10.6	6.9	1.44	1.78

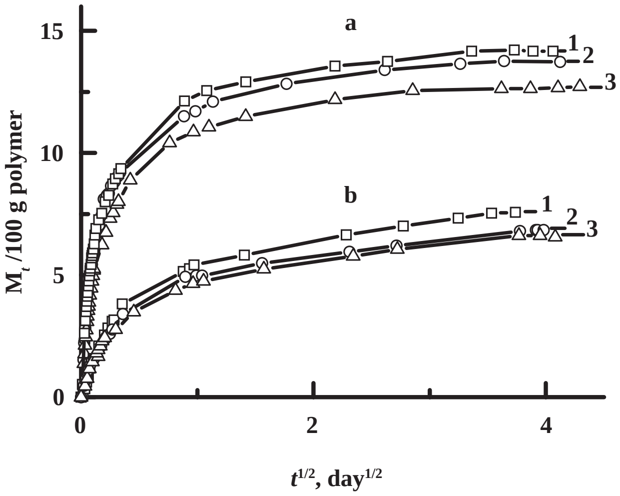

Fig. 2. Curves of desorption kinetics of (a) methanol and (b) toluene for (1) PI, (2) PI/PANI (3 wt%), (3) PI/PANI (6 wt%) membranes.

coefficients of toluene decrease for PI/PANI composites compared with PI membrane. Probably disposition to aggregation and formation of PANI agglomerates prevents diffusion of large volume toluene molecules through composites. So diffusion coefficients of methanol differ approximately one order of magnitude from that of toluene for PI/PANI (6 wt%) membrane. The same magnitudes were obtained for PI membrane. This fact is a great important for the pervaporation process.

3.1.2. Pervaporation of methanol/toluene mixture

The mixture under study is characterized by the azeotropic content 69 wt% methanol and 31 wt% toluene at 20°C and 760 mm Hg. According to Vrevsky low the azeotropic point position on a liquid–vapor diagram varies with pressure and temperature [19]. Therefore, the pervaporation experiments were carried out in the concentration range 30–90 wt% methanol in the feed that involves possible azeotropic mixture at the pervaporation conditions 50°C and 10^{-1} mm Hg.

Table 3
Effective diffusion coefficients of solvents

Membrane	$D\cdot10^{13}$, m^2/s	
	Methanol	Toluene
PI	2.0	1.5
PI/PANI (3%)	6.8	1.0
PI/PANI (6%)	8.5	0.8

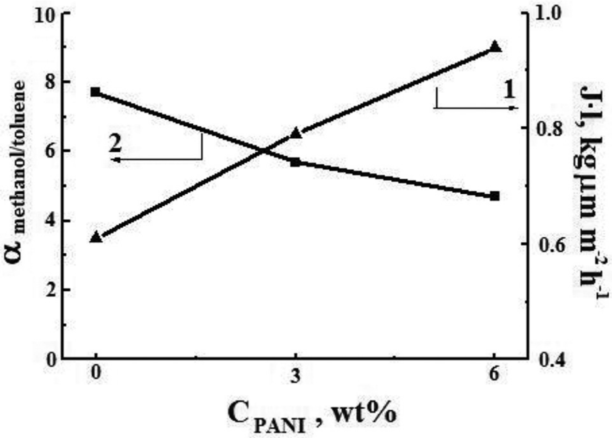

Fig. 3. The dependence of (1) flux, *J·l*, and (2) selectivity, α, on the PANI content in membranes for the pervaporation of methanol/toluene azeotropic mixture.

Fig. 3 shows transport properties of membranes containing 0, 3 and 6 wt% PANI during separation of azeotropic mixture.

During pervaporation all studied membranes were selective relative to methanol that was caused by higher sorption–diffusion characteristics for methanol than that for toluene. At separation of azeotropic mixtures the addition of PANI in PI matrix increases permeability but decreases selectivity of separation. It is also in agreement with data of sorption experiment. Table 2 shows that inclusion of PANI in PI matrix decreases degree of equilibrium sorption and values of the Flory-Huggins interaction parameter χ_1. Furthermore, effective diffusion coefficients of methanol increase in this case (Table 3).

3.2. Transport properties of PI/co PANI membranes

The coPANI filler contained carboxyl substitutes in phenyl cycle that should be impact hydrophilic properties to the membrane. So PI/coPANI composites were reasonable to use for separation of water/alcohol mixtures.

Isopropanol is obtained by hydration of propen and commonly used in industry [20]. During synthesis the isopropanol solution containing up to 10 wt% water is formed. This aqueous–alcoholic system is characterized by azeotropic content 12 wt% water and 88 wt% isopropanol. Therefore pervaporation is used for dehydration as the cheap method of effective separation of aqueous alcohol system without adding special chemical reagents [21].

3.2.1. Sorption test

To determine sorption parameters of PI/coPANI membranes in water/isopropanol system, $\triangle m_b$ that is

Table 4
Data of sorption measurement for water and isopropanol

	Δm_b, %		S, g/100 g polymer		χ_1	
Membrane	Water	Isopropanol	Water	Isopropanol	Water	Isopropanol
PI/coPANI (5%)	1.8	1	2.7	0.2	2.6	4.8
PI/coPANI (5%)	2.3	0.8	3.0	0.4	2.5	4.2
PI/coPANI (10%)	3.6	1.3	4.0	0.5	2.3	3.7
PI/coPANI (15%)	7.4	1.9	7.6	0.6	1.7	3.6

relative amount of N-MP removed from membranes during experiment was also take into account as in the case of PI/PANI composite. Polar liquids such as isopropanol and water washed out significant amount of N-MP.

According to Table 4 the degree of sorption both water and isopropanol increases after coPANI addition in PI matrix. However membranes under study sorb water to a grater extend than isopropanol. Therefore the Flory-Huggins interaction parameter χ_1 calculated for all membrane types is higher for isopropanol than that for water. This fact indicates on great affinity of PI and PI/coPANI to water.

Study of desorption kinetics of isopropanol were not made because of the lowest sorption of this liquid. As to water the dependence of diffusion capability of liquids molecules on coPANI content in membranes was studied (Fig. 4). According to obtained data the coPANI inclusion in polymer matrix leads to faster diffusion of penetrates molecules. It should be noted that increasing of water concentration in feed mixture leads to increasing the diffusion coefficient for all membranes. This fact is connected with the structure peculiarities of membranes.

3.2.2. *Pervaporation of water/isopropanol mixture*

Aqueous–alcoholic mixture separation is one of the most used pervaporation application. The effect of coPANI addition on pervaporation properties was studied using PI and PI/coPANI (5 wt%) membranes in the range of water concentration in feed up to 30 wt% water including possible azeotropic content. Fig. 5 shows the dependence of selectivity on water concentration in feed. For all feed content permeate is enriched by water, i.e. our membranes are selective with respect to water. Enhanced selectivity of PI/coPANI (5 wt%) can be explained by arising hydrophilic interaction between water and macromolecules and also increasing sorption–diffusion parameters compared with PI membrane (Table 4).

Fig. 6 shows the dependence of permeability on water concentration in feed. Inclusion of coPANI filler leads to the increase of penetrant flux through PI/coPANI membranes. This fact is a result from structural disordering of polymer matrix after coPANI addition that is reflected in the increase of diffusion coefficients of water in PI/coPANI composites compared with PI membrane (Fig. 4).

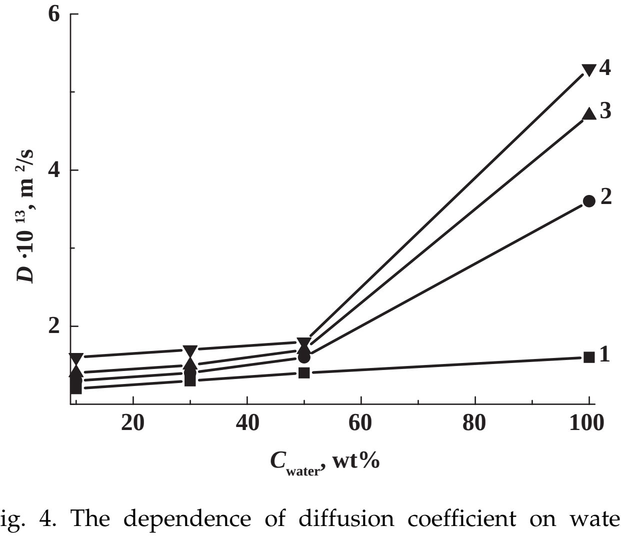

Fig. 4. The dependence of diffusion coefficient on water content in feed for (1) PI, (2) PI/coPANI (5 wt%), (3) PI/coPANI (10 wt%), (4) PI/coPANI (15 wt%).

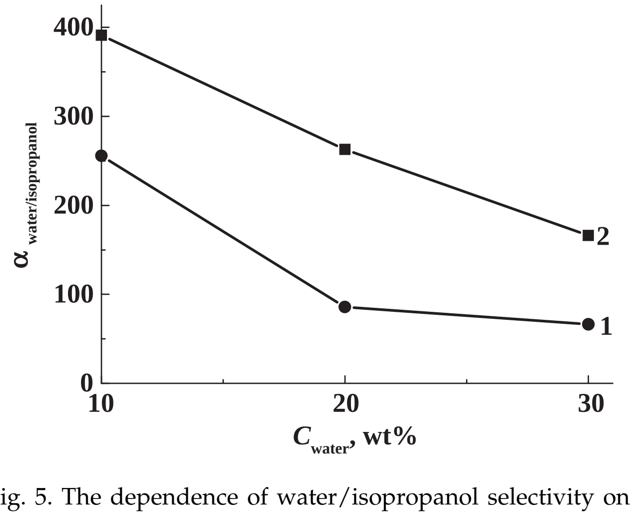

Fig. 5. The dependence of water/isopropanol selectivity on the water content in the feed for (1) PI and (2) PI/coPANI (5 wt%) membranes.

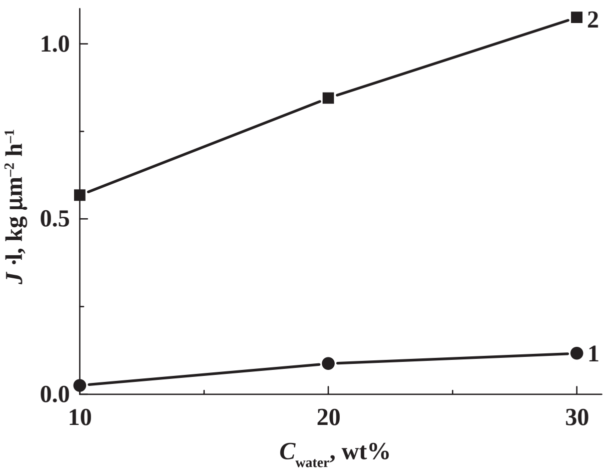

Fig. 6. The dependence of flux, *J·l*, on the water content in the feed for (1) PI and (2) PI/coPANI (5 wt%) membranes in the pervaporation of water/isopropanol mixture.

4. Conclusion

Membranes based on composites of polyimide with polyaniline or its copolymer are effective at separation of azeotropic mixtures by pervaporation, namely PI/PANI in the case of methanol/toluene mixture and PI/coPANI in the case of isopropanol/water mixture.

PI/PANI composites are selective with respect to methanol in pervaporation of methanol/toluene mixture that is related to the higher values of diffusion coefficients and sorption degree for methanol compared with analogical parameters for toluene. An increase of PANI content in composite leads to the growth of Flory-Huggins parameters both methanol and toluene; as a result the selectivity of membranes decreases but their permeability increases at pervaporation.

PI/coPANI composites are selective to water during pervaporation of isopropanol/water mixtures. Addition of coPANI facilitates selectivity and permeability of membranes that is connected with the increase of sorption–diffusion characteristics of PI/coPANI.

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List of symbols

S	degree of equilibrium sorption, g/100 g polymer
m_0	initial weight of sample, g
m_c	constant weight of sample after its drying when sorption test is finished, g
$\triangle m_b$	amount of the solvent washed out from membrane during sorption experiment, %
χ_1	polymer-solvent interaction parameter of Flory-Huggins
ϕ_2	volume fraction of solvent in a swollen polymer sample
D	diffusion coefficients, cm^2/s
t	time, s
M_t	amount of penetrant sorbed by membrane samples at time t, g
l	thickness of dry membrane sample, μm
tan γ	tangent of the initial slope of the desorption kinetic curves
$J \cdot l$	specific permeation flux, kg mm^{-2} h^{-1}
α	selectivity or the separation factor
y_i, y_j	weight fractions of components i and j in the permeate
x_i, x_j	weight fractions of components i and j in the feed

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