Ethanol purification from methanol via pervaporation using polybenzoxazinoneimide membrane☆

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Polybenzoxazinoneimide membrane was prepared in three steps: a dichlorodianhydride (obtained by the reaction of trimellitic anhydride with 4,4′-oxydianiline) was treated with methylene-bis(anthranilic acid). The resulting polyamic acid was dissolved in N-methylpyrrolidone, the solution was cast as a thin film, the solvent was evaporated and the membrane was heated under controlled conditions to convert polyamic acid into polybenzoxazinoneimide. Density, free volume parameters, sorption parameters for methanol and ethanol of the membrane were determined. The membrane was used for the pervaporation of methanol/ethanol mixtures containing 5–20 wt.% methanol which are mixtures modeling bioalcohol. The membrane was preferentially permeated by methanol with high separation factors.

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Contents

1. Introduction

Since the 1980s ethanol was applied in the energy market as a promising alternative energy source, which competes successfully with a

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gasoline. In a number of countries ethanol efficiently employs as automobile fuel; it can be used as independent fuel or as additive (3–25 wt.% ethanol) [1]. The application of ethanol improves the ecological feature of the fuel due to reducing the release of carbon dioxide into the atmosphere. At present the significant amount of the ethanol is produced by the enzymatic fermentation of food containing carbohydrates. Biosynthesis has the environmental and economic advantages. However, the product of fermentation, except the main admixtures such as water and CO_2, contains methanol which can also be derived from biomass [1]. Purification of the ethanol from admixtures is a technically complicated task and involves an energy-intensive separation process to concentrate the diluted streams obtained in the fermentation stage and to overcome the azeotropic behavior of the ethanol–water mixture. It is usually solved by the sequential separation of ethanol from the other components by distillation. However, this technique does not satisfy the requirements of the modern environmentally appropriate, economically and technologically founded processes of separation and purification of liquids. In the recent years the purification of the ethanol from numerous admixtures (mainly water) has been performed by the resource-saving and ecological method of membrane technologies — pervaporation [2–4]. The mechanism of the pervaporation consists of the following steps: selective sorption of liquid molecules on the membrane surface of the feed side, selective diffusion of these molecules through the membrane and desorption from the permeate side of the membrane as a vapor. Pervaporation separation of liquid mixture is caused by dominant membrane permeability for component in the mixture. A wide range of pervaporation membranes has been investigated in the processes of alcohol purification [5–17]. Literature data on the pervaporation of alcohol mixtures are very limited, especially on separation of ethanol/methanol mixture. Bettens et al. and van Veen et al. investigated microporous ceramic membranes that demonstrated the separation factor (methanol/ethanol) of 17.0 and 9.0 at fluxes of 0.270 kg/m^2 h and 0.8 kg/m^2 h respectively in pervaporation of ethanol/methanol (95:5 wt.%) [18,19]. These values of separation factor are low because the microporous structure of ceramic membranes and the poor sorption capacity cannot provide the effective separation.

Membranes based on polymers of heteroaromatic structure are one of the most promising for pervaporation. Some of them have been already studied in separation of aqueous solutions of acids, aldehydes, alcohols and exhibited preferable permeation of water. Such membranes are characterized by the thermal stability, excellent release properties and resistance towards liquids under study.

Xu and co-workers developed a series of membranes based on aromatic polyimides for the ethanol dehydration [20]. All membranes preferably permeated water at 318–348 K. The most selective and low permeable membranes were rigid-chains polyimides. Membranes based on polyamides with less packed structure had low separation efficiency and a high flux. The growth of the pervaporation temperature leads to increasing permeability and to decreasing membrane selectivity.

Fluorinated aromatic polyamides have been investigated in pervaporation of water–alcohol mixtures [21]. It was shown that solubility of ethanol in these membranes was higher than that of water but diffusion of the water molecules was much faster than that of alcohol. As a result, separation factor of water–ethanol mixture (10:90) was equal to 83 and flux was equal to 262 g/m^2 h at 25 °C. Novel copolyimide membranes modified by three different modes of crosslinking: thermally, by diol, or by diamine have been also studied in alcohol dehydration [22]. Membranes based on polybenzoxazinone were studied in pervaporation of water–isopropanol mixture and showed the high separation factor in dehydration of isopropanol [14].

Polymer of heteroaromatic structure which combines the valuable properties of polyimide and polybenzoxazinone, namely polybenzoxazinoneimide, was developed and investigated as gas separation membrane that exhibited high permselective properties [23].

The aim of the present work was to study polybenzoxazinoneimide (PBOI) as a membrane material in separation of alcohol mixtures to solve the unique task — ethanol purification from methanol admixture via pervaporation. PBOI has not been researched as a pervaporation membrane. It should be noted that PBOI precursor — imide-containing polyamic acid (PI-PAA) was studied as a thin selective layer of composite membrane on porous support in separation of aqueous solution of organic liquids (ethanol, isopropanol, acetone, ethyl acetate) and organic–organic mixture (methanol/cyclohexane) [24].

2. Experimental

2.1. Materials

Solvents and reagents were purified and monomers were synthesized as described in [25]. They were trimellitic anhydride (mp = 167 °C), aromatic diamine (bp = 191 °C), thionyl chloride (bp = 75.5 °C), methylene-bis(anthranilic acid) (MBAA) (mp = 239–240 °C), acetic anhydride (bp = 140 °C), pyridine (bp = 115 °C),benzene (bp = 80 °C), trifluoroacetic anhydride (bp = 39.5–40 °C), N,N-dimethylformamide (DMF) (bp = 153 °C). N-methylpyrrolidone (Fluka) was used without additional purification. Methanol and ethanol were purchased from Vekton Co (Russia) and purified by two times rectification. The purity of alcohols was verified chromatographically as 99.99 wt.% (impurity of water was 0.01 wt.%).

2.1.1. Synthesis of dichloroanhydrides of bis(trimellitimidodicarboxylic) acids

A three-neck round-bottom flask equipped with a stirrer, a thermometer, a reflux condenser, and an inlet for argon was charged with aromatic diamine (0.1 mol) and DMF (150 ml). After cooling to 0 °C, trimellitic anhydride (0.2 mol) dissolved in 50 ml of DMF was added. While anhydride was being added, the temperature of the reaction mixture was not higher than 10 °C. After the reaction mixture was stirred for 6 h, acetic anhydride (24 ml) and pyridine (6 ml) were added [26]. The mixture was heated at 150 °C for 5 h and then cooled to room temperature. The precipitate of bis(trimellitimide) was filtered, washed with DMF and acetone, and dried with a lamp and in vacuum at 180 °C for 6 h. A one-neck round-bottom flask equipped with a reflux condenser was charged with bis(trimellitimide) (0.01 mol) and a tenfold excess of thionyl chloride, and some drops of DMF were added. After the mixture was heated for 7 h, it was cooled. The formed crystals were filtered, washed with toluene, and dried in vacuum at 80 °C for 6 h. Dichloroanhydrides were formed according to the Scheme 1a.

2.1.2. Synthesis of imide-containing polyamic acid (PI-PAA)

A flask equipped with a stirrer was charged with MBAA (0.01 mol) and N-methylpyrrolidone (20 ml), and the mixture was stirred until MBAA completely dissolved. Then, the solution was cooled to 0 °C using a water bath. Dichloroanhydride (0.01 mol) was added to a cooled solution. After the suspension was stirred at 0 °C for 15 min, propylene oxide (0.3 ml) was added, the cooling was stopped, and the mixture was stirred at room temperature for 5 h. The scheme of formation of imide-containing poly(amic acid)s is outlined in the Scheme 1b.

The PI-PAA solution was used for the film preparation directly after synthesis without any purification.

2.2. Membranes preparation

Dense PI-PAA films (~20–30 μm thick) were obtained by casting the 10 wt.% PI-PAA solution in N-methylpyrrolidone on a glass plate followed by evaporation of the solvent at 80 °C in the air for 5 days. Membranes were dried to a constant weight at 80 °C in vacuum for 10 days.

Dense PBOI membranes (~20 μm thick) were obtained by heating PI-PAA membranes as a result of the solid-state reaction (Scheme 1b). The heating was carried out by a stepwise mode: 120 °C for 30 min; 140 °C for 20 min; 160 °C for 20 min; 180 °C for 20 min; 200 °C for

a

b

PI-PAA
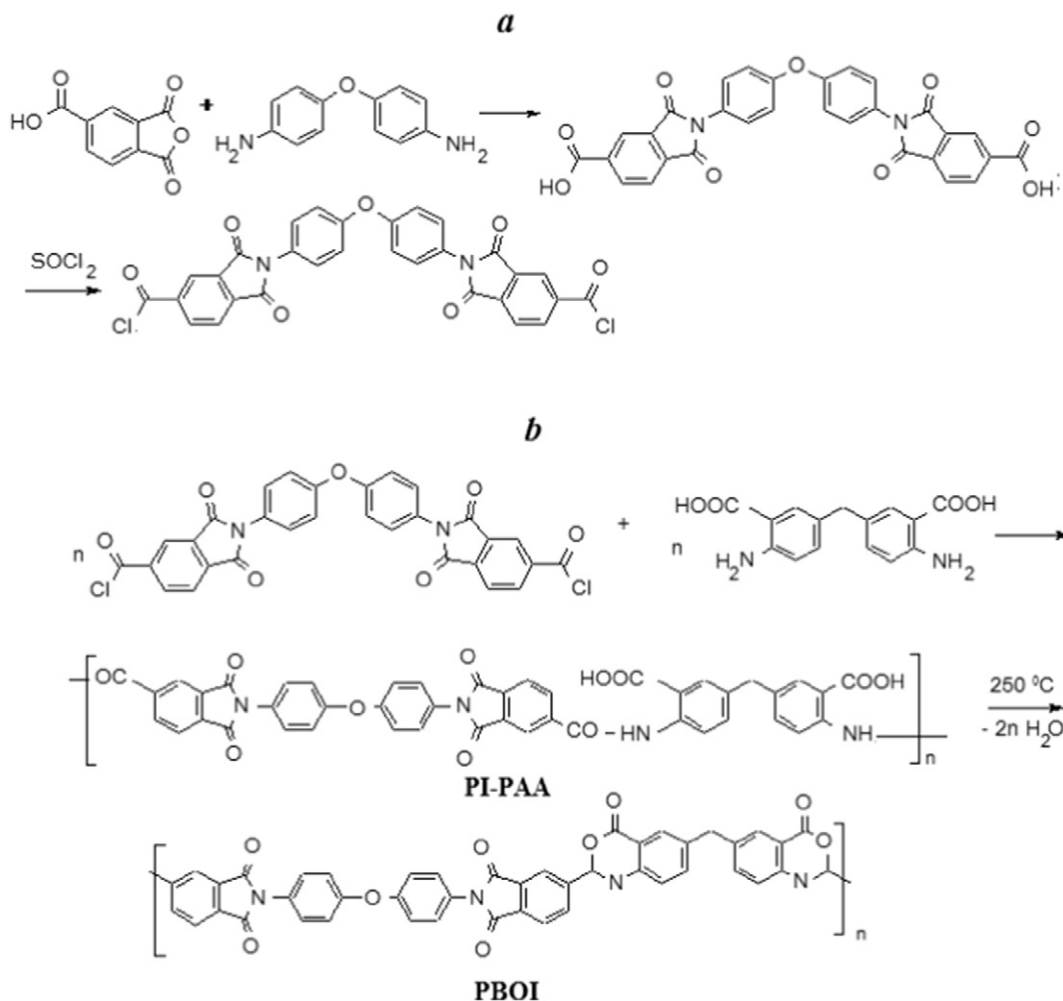
PBOI

Scheme 1. Synthesis of PBOI.

20 min; 250 °C for 30 min; 300 °C for 30 min in the electrical furnace "SNOL 7.2/1100, Lithuania" in an argon atmosphere.

FTIR spectra of PBOI films were recorded in the range of 450–4000 cm^{-1} on a Shimadzu FTIR-8400S spectrophotometer. The spectrum showed absorptions at 1760 (CO) and 1250 cm^{-1} (C–O–C) benzoxazinone ring, 1780 (CO) and 1308 (C–N) imide ring; the data confirm PBOI structure (composition).

The thermal characterization was carried out by standard technique using modified derivatograph "C" (MOM, Hungary). Thermal stability characterizes the polymer durability against destruction and determines the upper exploitation temperature of a polymer product. Thermal stability parameters are temperatures (τ_1, τ_5, and τ_{10}) at which the sample weight reduces in 1, 5, and 10 wt.%, respectively, due to destruction. The PBOI values of $\tau_1 = 398$, $\tau_5 = 455$, and $\tau_{10} = 492$ °C indicate on high thermal stability of PBOI membranes.

2.3. Density and free-volume parameters determination

The film density ρ was estimated using the flotation method with a laboratory-made measurement unit. The mixture of toluene and carbon tetrachloride (volume ratio 4:1) was used to equilibrate the specimens at 20 °C.

The fixed volume of liquid mixture which was in equilibrium with specimen was collected in the pycnometer and weighed. The density ρ was determined as:

$$\rho = \frac{m_l - m_p}{V_P} \tag{1}$$

where m_l — the weight of the liquids mixture, m_p — the weight of the pycnometer, V_P — volume of pycnometer.

Fractional free-volume *FFV* of the polymer film was calculated by the following equation [27]:

$$FFV = (V_0 - 1.3 \cdot V_w)/V_0 \tag{2}$$

where $V_0 = 1/\rho$ is the polymer specific volume and V_w is the van der Waals volume of the repeat unit calculated by Bondi's method [28]. The molecular packing coefficient k was calculated as ratio of the experimental value of polymer film density ρ and theoretical value ρ_{theor} of Van-der-Waals density of the tightly packed polymer [29]:

$$k = \frac{\rho}{\rho_{theor}} = \frac{\rho \cdot V_w}{M} \tag{3}$$

where M is the molecular weight of the polymer repeat unit.

2.4. Sorption study

Sorption experiments were performed by immersion of samples into a solvent contained tubes (methanol or ethanol) which were placed in the thermostat at 20 °C. The weight change was determined gravimetrically with the error $\pm 10^{-4}$ g. At the appropriate time intervals the samples were taken out, dried with a filter paper and weighed. The experiment was continued until equilibrium was attained. The kinetic curves of sorption were plotted. The sorption equilibrium degree S_w was calculated as the ratio of the difference between the weight of

Table 1
Physical properties of PBOI membrane.

Membrane	T_g [26], °C	Density, g/cm^3	Fractional free volume, FFV	Molecular packing coefficient	Solubility parameter, δ, (J/cm^3)$^{1/2}$
PBOI	271	1.42	0.08	0.71	28.2

swollen membranes m_{wet} at equilibrium and the weight of dry sample m_0 to the weight of dry sample m_0 [30]:

$$S_w = \frac{m_{wet} - m_0}{m_0}. \tag{4}$$

After completion of sorption experiments, the solvent desorption was carried out by exposing the samples to the air atmosphere and temperature 20 °C in the controlled environment of the exsiccator containing molecular sieve absorber (zeolites). The change of the sample weight as a function of time was recorded until equilibrium has been reached. Kinetics curves of desorption allows determination of the diffusion coefficient D by the equation [30,31]:

$$D = \frac{\pi}{16} (\tan\beta)^2 \tag{5}$$

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

In pervaporation the mass transfer largely depends on the interaction between the polymer membrane and the separating components of the mixture. Therefore, for each liquid the thermodynamic interaction parameter for system polymer-solvent χ_1 was determined using the Flory–Huggins equation [30,32]:

$$\ln a_1 = \left[\ln(1-\varphi_2) + \left(1 - \frac{1}{Z}\right)\varphi_2 + \chi_1 \varphi_2^2 \right] \tag{6}$$

where a_1 is the activity coefficient of the penetrant, Z is the number of segments of the polymer chain, φ_2 is the volume fraction of polymer in the swollen membrane that was determined by the equation:

$$\varphi_2 = \frac{1}{1 + \frac{\rho_2}{\rho_1} \cdot \Delta s} \tag{7}$$

ρ_1 and ρ_2 are density of the solvent and polymer, respectively, Δs is portion of solvent in the swollen membrane, g/g polymer.

For individual liquids $a_1 = 1$, thus the interaction parameter χ_1 was calculated as:

$$\chi_1 = \frac{-[\ln(1-\varphi_2) + \varphi_2]}{\varphi_2^2}. \tag{8}$$

2.5. Pervaporation

The pervaporation experiment was carried out using the laboratory cells with an effective membrane area of 14.8 cm^2 at 20, 50 and 70 °C with stirring. Downstream pressure below 10^{-3} kPa was maintained. The feed was methanol/ethanol mixture. The permeate was collected into a liquid nitrogen cooled trap, weighed and analyzed. The composition of permeate was determined using gas chromatograph «Chromatec–

Crystal 5000.2» (Chromatec Company, Russia) with thermal conductivity detector.

From the pervaporation experiments, total flux J and separation factor β were calculated. The separation factor β was determined by the following equation:

$$\beta = \frac{X_{\text{Methanol}} / X_{\text{Ethanol}}}{Y_{\text{Methanol}} / Y_{\text{Ethanol}}} \tag{9}$$

where Y_{Methanol} and Y_{Ethanol} are weight fraction of methanol and ethanol in the feed, X_{Methanol} and X_{Ethanol} are weight fraction of methanol and ethanol in permeate.

Total permeation flux J was defined by the equation:

$$J = \frac{m}{t \cdot S} \tag{10}$$

where m is the weight of liquid penetrated through membrane area per time t and S is the effective surface area of the membrane. The fluxes were determined with the error within $\pm 10^{-2}$ g/m^2 h.

To compare flux of membranes with different thickness l varied from 20 to 30 μm, the values of normalized total flux J_n were used. J_n is the flux through membrane with 20 μm thick calculated as:
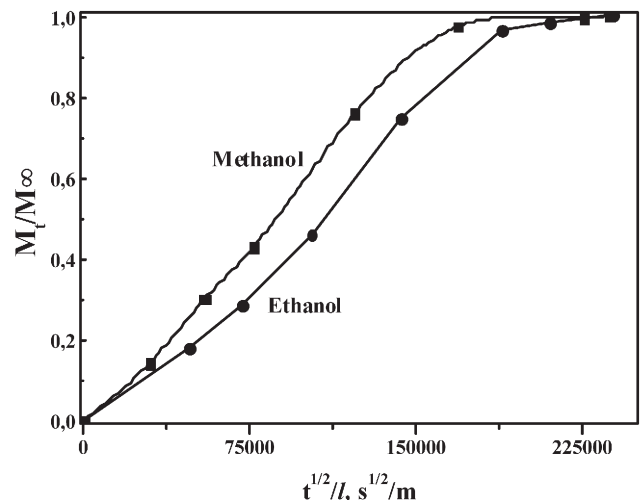
$$J_n = \frac{J \cdot l}{20}. \tag{11}$$

Data on the normalized total flux and the concentration of a component in permeate c_i was used for calculating individual fluxes of methanol and ethanol J_i as follows:

$$J_i = c_i \cdot J_n. \tag{12}$$

For the evaluation of intrinsic properties of penetrant–membrane system, permeability and selectivity were calculated [33]. Membrane permeability P_i is a component flux normalized for membrane thickness and driving force was found as:

$$P_i = j_i \frac{l}{p_{i0} - p_{il}} \tag{13}$$

Table 2
Physical properties of penetrants at 25 °C.

Liquid	T_b, °C	Density, g/cm^3	Molar volume, cm^3/mol	Viscosity, mPa·s	Solubility parameter, δ, (J/cm^3)$^{1/2}$
Methanol	64.7	0.792	40.4	0.547	29.7
Ethanol	78.37	0.789	58.3	1.096	26.0

Fig. 1. Kinetic curves of methanol and ethanol desorption from swollen PBOI membrane.

where j_i is a flux of component i, cm^3 (STP)/cm^2 s, and p_{i0} and p_{il} are the partial pressures of component i on both sides of the membrane (0 stands for the surface on the feed side and l — for the surface on the permeate side). Permeability was calculated in Barrers (1 Barrer = $1 \cdot 10^{-10}$ (cm^3 (STP)·cm/cm^2 s·cm Hg)). In this study, p_{il} is assumed to be negligible since the high vacuum was applied in the permeate side of the membrane.

Membrane selectivity $\alpha_{\text{Methanol/Ethanol}}$ was defined as the ratio of the permeabilities:

$$\alpha_{\text{Methanol/Ethanol}} = \frac{P_{\text{Methanol}}}{P_{\text{Ethanol}}}. \tag{14}$$

3. Results and discussion

3.1. Physical properties

Combination of imide and oxazinone fragments in the PBOI main chain leads to good mechanical parameters of the membrane, resistance to many solvents, and thermal stability up to 400 °C [20]. Data on some physical properties of the PBOI membrane are presented in Table 1.

The membrane density was estimated by the flotation method and was used for calculating the fraction free volume. *FFV* of a polymer membrane depends mainly on the chain rigidity and strength of an interaction between macromolecules. As a rule, *FFV* was about $0.1 \div 0.19$ for polyimides [34]. In the case of PBOI membrane, the value of *FFV* was equal to 0.08 that indicates on very close-packed structure of macromolecules in the membrane. Molecular packing coefficient of PBOI was equal to 0.71. It is higher than the average value of molecular packing coefficient for fully amorphous polymers (around 0.68) [29]. PBOI exhibited high glass transition temperature and so the polymer should be in a glassy state during the pervaporation at high temperature [26].

PBOI solubility parameter δ was defined as the square root of the cohesive energy density which corresponded to the energy of vaporization ΔE_v per molar volume V_w [35]:
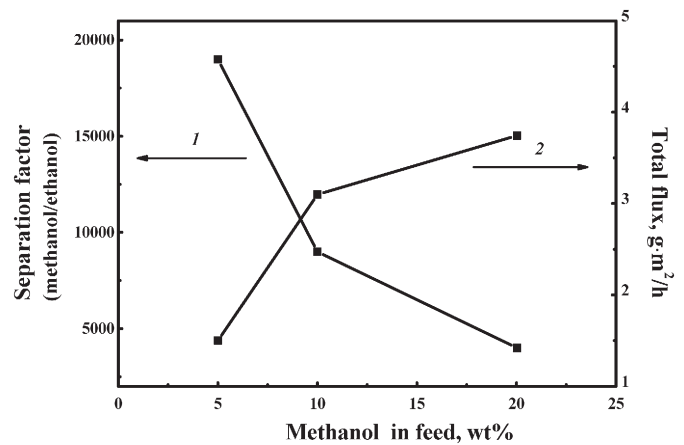
$$\delta = (\Delta E_v / V_w)^{1/2}. \tag{15}$$

Data on PBOI solubility parameter δ can be used to predict solubility of the polymer in different liquids. According to the solubility theory [35], the less difference in solubility parameters of polymer and liquid $|\Delta\delta|$ leads to the better solubility of this liquid in the polymer. Table 2 lists solubility parameters and other physical properties of liquids under study. The small difference between the solubility parameters of methanol and PBOI compared with the difference of these parameters for ethanol indicates on a better interaction of the membrane material with methanol.

3.2. Transport properties

The mechanism of pervaporation involves selective solution of solvent molecules on the skin layer of the membrane, evaporation of molecules, selective diffusion through the membrane and desorption from the permeate side of the membrane. Thus special attention was given to investigation of sorption and transport parameters.

Fig. 2. Dependence of (1) separation factor and (2) total flux on methanol concentration in the feed, 20 °C.

3.2.1. Sorption study

Sorption experiments enable to study the kinetics of sorption and desorption processes of methanol and ethanol in the membrane. They were carried out by the immersing of PBOI samples into individual liquids (methanol or ethanol). Kinetics of sorption is controlled by the diffusion of penetrant molecules between the polymer chains.
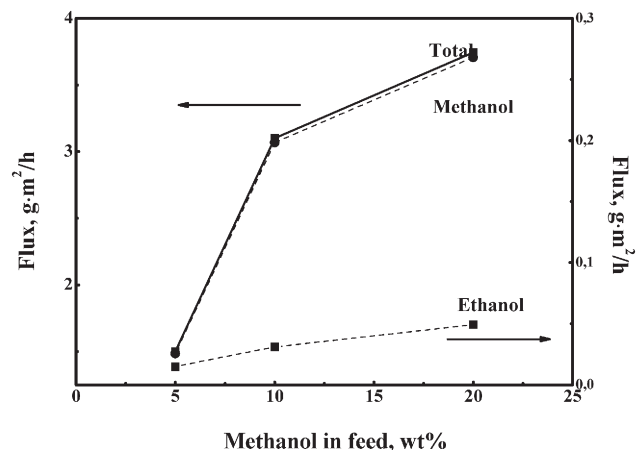
The data on desorption of methanol and ethanol from swollen membrane are presented as kinetics curves in Fig. 1. The kinetics curves are given in suitable coordinates for determination of diffusion coefficients. In the case of one-dimensional diffusion, when diffusion coefficient, D, is independent on concentration at the initial time ($M_t/M_\infty < 0.6$), according to Fick's second law, the amount of sorbs/desorbs substance per time t, M_t, was calculated by the equation [30,31]:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left(\frac{Dt}{\pi} \right)^{1/2}, \tag{16}$$

where M_∞ is the equilibrium amount of desorbed substance.

Desorption of methanol occurs more rapidly than that of ethanol. Linear regions in the initial stage of desorption were used for the calculations of diffusion coefficients. As seen from Table 3, diffusion coefficients of methanol are 3 times higher than those of ethanol. This fact seems to be important in separation of methanol/ethanol mixture via pervaporation.

Table 3 lists data on the equilibrium sorption degree and Flory–Huggins parameter χ_1 of polymer–liquid interaction for PBOI–methanol

Table 3
Data on sorption degree, diffusion coefficient and interaction parameter χ for PBOI membrane.

Liquid	Sorption degree, %	Flory–Huggins parameter χ_1	Diffusion coefficient, m^2/s
Methanol	4.3	2.0	$20 \cdot 10^{-13}$
Ethanol	1.8	2.7	$7 \cdot 10^{-13}$

Fig. 3. Dependence of the total flux and fluxes of individual components on methanol concentration in the feed, 20 °C.
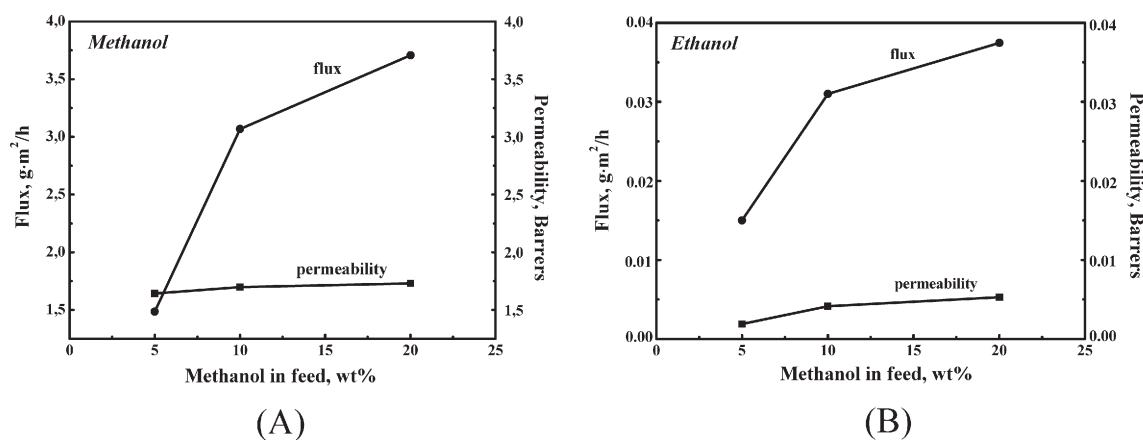
Fig. 4. The dependence of the flux and permeability on the methanol concentration in the feed for methanol (A) and ethanol (B) in pervaporation of methanol/ethanol mixture, 20 °C.

and PBOI–ethanol systems. The sorption degree of methanol is more than two times higher than that of ethanol. The lower value χ_1 in the case of methanol in contrast to ethanol indicates the better polymer affinity to methanol as compared with ethanol that is in agreement with the previous data. Table 3 provides data that the methanol molecules can diffuse through the polymer matrix faster than the ethanol molecules due to the smaller size. Thus, the methanol sorbed and penetrated through PBOI membrane better in comparison with the other alcohol. This fact plays an important role in separation of methanol/ethanol mixture by pervaporation.

3.2.2. Pervaporation of methanol/ethanol mixture

PBOI membrane was studied in the pervaporation of methanol/ethanol mixture over the concentration range from 5 to 20 wt.% methanol in the feed at 20 °C. The membrane was more permeable for methanol than for ethanol. Methanol concentration in the permeate was 99.9 wt.% over all range of feed composition (the traces of water in permeate were around 0.01 wt.%).

Fig. 2 shows the separation factor and the total permeation flux of the membrane vs. the methanol concentration in the feed. The separation factor (methanol/ethanol) decreases while total flux increases with the growth of methanol concentration in the feed. The dominate permeability of methanol in pervaporation can be explain the fact that the membrane preferably sorbs methanol molecules. Also due to dense structure of the membrane the smaller methanol molecules diffuse more easily through the polymer matrix as comparison ethanol. Thus ethanol flux is negligible. With growth of the methanol concentration in the feed, high sorption of permeants leads to decreasing density

of the swollen membrane and increasing the fraction free volume in the membrane structure. In this case diffusion ability of liquid molecules through the membrane increases. Thus, curve 2 (Fig. 2) demonstrates the increase of the total flux with growth of methanol concentration in the feed.

To interpret the transport of methanol/ethanol mixture through the membrane, fluxes of individual components were isolated from the total flux. Fig. 3 shows that total flux is mainly determined by the methanol flux through the membrane due to high sorption and diffusion parameters of methanol. Contribution of ethanol flux is extremely low.

The high separation effectiveness of PBOI membrane in pervaporation of methanol/ethanol mixture is connected with the fact that the vapor pressure of methanol (11.8 kPa) is higher than that of ethanol (5.9 kPa) [36]. If the effect of driving forces (also the vapor pressure, the volatilization, etc.) is removed, the effect of the membrane itself can be seen from the parameters of permeability and selectivity. Therefore, using Baker et al. approach [33], the permeability of methanol and ethanol and the selectivity, $\alpha_{\text{Methanol/Ethanol}}$, were calculated for PBOI membrane. Figs. 4 and 5 show the normalized properties in comparison with ordinary data on flux and separation factor.

Fig. 4A shows the increase of methanol flux and permeability with growth of methanol concentration in the feed. The upper position of flux curve is mostly due to contribution of methanol vapor pressure. The lower position of permeability curve indicates on removing the effect of driving forces. Fig. 4B demonstrates the same trend for ethanol flux and permeability as in the case of methanol. The significant difference is in the magnitudes of flux and permeability, they are much higher in the case of methanol as compared with ethanol.
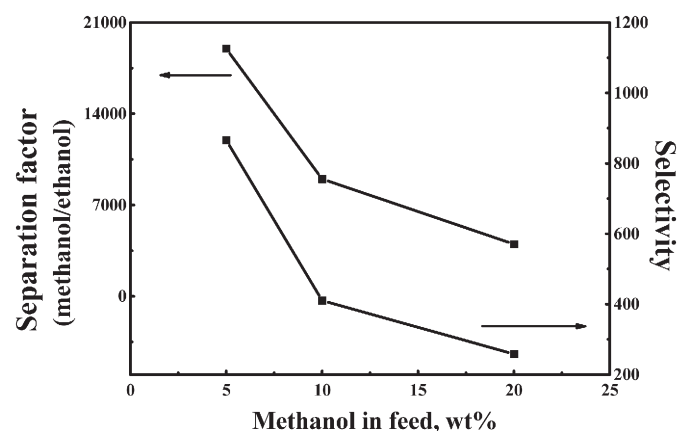

Fig. 5. The dependence of separation factor and selectivity (methanol/ethanol) on the methanol concentration in the feed, 20 °C.
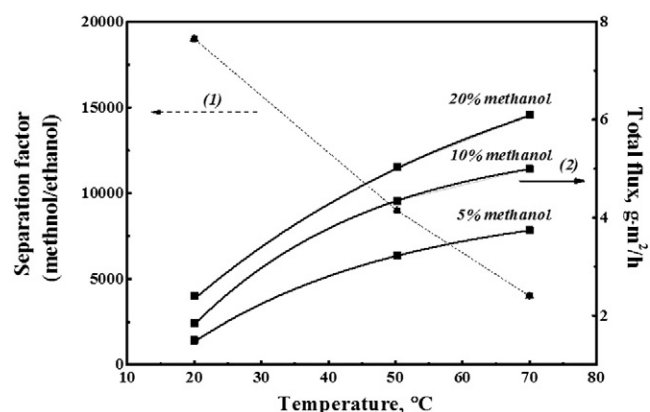

Fig. 6. The dependence of separation factor (1) and total flux (2) on temperature in pervaporation of methanol/ethanol mixture of different composition.
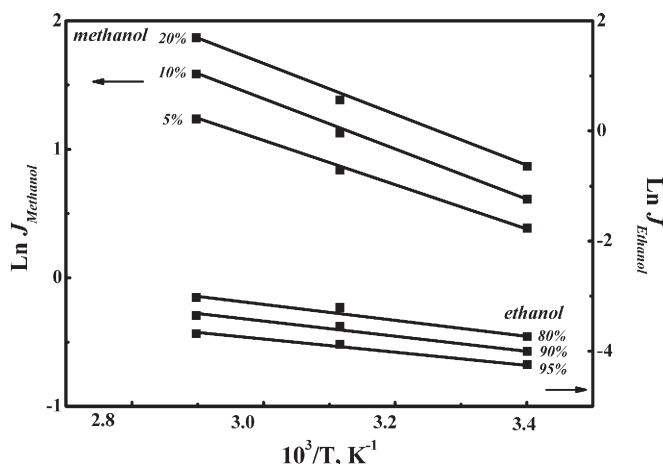
Fig. 7. The logarithmic dependence of individual fluxes on temperature in pervaporation of methanol/ethanol mixture of different composition.

The PBOI membrane selectivity indicates also on its affinity towards methanol. Fig. 5 shows decrease of both separation factor and selectivity with growth of methanol concentration in the feed. The PBOI membrane exhibited lower value of selectivity as compared with separation factor. The highest selectivity and separation factor were achieved in pervaporation of mixture containing 5 wt.% methanol.

Thus, it was established that way of change in flux matches with that in permeability as well as way of change in separation factor matches with that in selectivity. Consequently, the individual properties of PBOI membrane were in concordance with data obtained in the real pervaporation process. This fact determines high permselectivity and perspective application of PBOI membrane in pervaporation of methanol/ethanol mixture [37].

3.3. Effect of temperature in pervaporation

The effect of operating temperature on the pervaporation performance was studied for the feed containing 5, 10, and 20 wt.% methanol at 20, 50, and 70 °C. Fig. 6 shows the dependences of separation factor and the total flux on the operating temperature. The separation factor decreases when the operating temperature increases. The permeation rate increases with temperature growth from 20 to 70 °C for all feed compositions. When the thermal energy increases, the motion of the polymer chain segments intensifies and the free volume of the membrane increases consequently which leads to increase of the total flux.

Fig. 7 shows the logarithmic dependence of the individual fluxes on the inverse temperature in pervaporation of the three compositions of methanol/ethanol mixtures (5:95), (10:90), and (20:80) wt.%. The linear type of curves gives an opportunity to estimate the activation energies of individual components permeation using the Arrhenius type equation [38–41]:

$$\ln J_i = J_0 \exp\left(-\frac{E_{Pi}}{RT}\right) \tag{17}$$

Table 4
Activation energy of methanol and ethanol permeation.

Feed composition, wt.%		Activation energy of permeation, E_{Pi}, kJ/mol	
Methanol	Ethanol	Methanol	Ethanol
5	95	14.5	17.0
10	90	14.0	15.0
20	80	12.5	13.5

where J_i is the flux of individual component in pervaporation, J_0 is a pre-exponential factor, E_{Pi} is the activation energy of individual component permeation, R is the universal gas constant and T is the absolute temperature. When the temperature increases, vapor pressure in the feed compartment also increases, but the vapor pressure in the product compartment does not change. This leads to an increase of driving force with the temperature.

Table 4 lists data on the activation energy of methanol and ethanol permeation in pervaporation using PBOI membrane. The activation energy of methanol permeation is lower than that of ethanol. This fact confirmed that membrane exhibited higher separation efficiency to methanol. The growth of methanol concentration in feed leads to E_{Pi} decrease. The feed containing 20 wt.% methanol shows the lowest E_{Pi} and the feed containing 5 wt.% methanol has the highest one among the feed compositions under study. The system with high E_P needs more energy for permeation.

Table 4 gives ability to E_{Pi} of individual components. The values of E_P methanol are lower than those of ethanol in all cases. This fact confirmed that methanol transport through the membrane needs lower energy for permeation and PBOI membrane exhibits higher separation efficiency towards methanol.

Finally, it should be noted that separation properties of PBOI membrane exceed that of ceramic membranes [18,19] in pervaporation of ethanol/methanol (95:5 wt.%) mixture; separation factor of PBOI is equal to 18,000 against 17 for ceramic membrane. Flux through PBOI membrane is lower than that of ceramic membrane (0.0015 against 0.270 kg/m² h), but this problem can be solved by formation of composite membrane with thin PBOI layer on a porous support.

4. Conclusions

The physicochemical and transport properties of thermally resistant and mechanically strong PBOI membrane were investigated to estimate its possible application in the purification of ethanol from methanol admixture by pervaporation. Values of density, fraction free volume and molecular packing coefficient indicate very close-packed structure of PBOI molecules in the membrane. Mass transport of methanol and ethanol through PBOI membrane was studied in sorption and pervaporation tests. It was established that sorption degree and diffusion coefficients of methanol are higher than that of ethanol.

In pervaporation of methanol/ethanol mixture over the concentration range from 5 to 20 wt.% methanol in the feed, the PBOI membrane was preferably permeated by methanol with high separation factor. Total flux through the membrane is mainly determined by the methanol flux due to its high sorption and diffusion parameters; contribution of ethanol flux is extremely low. Study on driving forces normalized properties (permeability and selectivity) showed high permselectivity of PBOI membrane in pervaporation of methanol/ethanol mixture.

The activation energy of methanol and ethanol permeation through PBOI membrane was calculated by Arrhenius type equation using data on pervaporation at 20, 50, and 70 °C. It was shown that the molecules of methanol overcome lower energy barrier as compared with ethanol at permeation through the membrane and so the flux of methanol is dominating in pervaporation. PBOI membrane is highly effective in the separation of methanol/ethanol mixtures and can be proposed for purification of ethanol as a biofuel. In pervaporation of ethanol/methanol (95:5 wt.%) mixture the separation factor of the PBOI membrane is equal to 18000, low value of the total flux (1.5 g/m² h) can be overcame by formation of composite membrane with thin PBOI layer on a porous support.

Abbreviations

PI-PAA	imide-containing polyamic acid
PBOI	polybenzoxazinoneimide
STP	standard temperature and pressure

List of symbols

α	membrane selectivity
β	separation factor
δ	solubility parameter, J/cm^3
ρ	density, g/cm^3
τ	thermal stability parameters are temperatures, °C
φ_2	volume fraction of polymer
χ_1	interaction parameter for system polymer-solvent
a_1	activity coefficient
D	diffusion coefficient, cm^3/s
E_P	activation energy, kJ
ΔE_v	energy of vaporization, J/cm^3
FFV	fractional free-volume
J	permeation flux, g/m^2 h
l	thickness, μm
M	molecular weight of the polymer repeat unit, g/cm^3
M_t	amount of sorbs/desorbs substance per time, g
M_∞	equilibrium amount of desorbed substance, g
m	weight of liquid penetrated through membrane, g
m_0	weight of dry sample, g
m_l	weight of the liquids mixture, g
m_p	weight of the pycnometer, g
m_{wet}	weight of swollen membranes, g
P_i	membrane permeability, barrer
p	partial pressures of component, kPa
R	universal gas constant, J/mol·K
S_w	sorption degree, %
S	surface area of the membrane, m^2
T	absolute temperature, K
T_b	boiling temperature, °C
T_g	glass temperature, °C
t	time, h
$\tan\beta$	tangent of the initial linear slope of M_t/M_∞ vs·t
V_0	polymer specific volume, cm^3/g
V_P	volume of pycnometer, cm^3
V_w	van der Waals volume, cm^3/g
X	weight fraction of the component in permeate, wt.%
Y	weight fraction of the component in the feed, wt.%

Acknowledgments

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