Study on Polybenzoxazinone Membrane in Pervaporation Processes

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ABSTRACT: Poly(benz-3,1-oxazinone-4) was prepared by thermal cyclization of its hydrolytically stable precursor polyamic acid. Both polymer and its precursor were investigated as membrane materials. Thermogravimetric analysis and contact angle measurements were carried out for characterization of peculiarity of membrane compositions and analysis of membrane surface. Pervaporation of water–isopropanol mixture was studied in the wide range of feed composition. To interpret the pervaporation transport properties of the membranes, swelling experiments were performed, kinetic curves of sorption and desorption were plotted, and basic sorption and diffusion parameters were analyzed. It was established that poly(benz-3,1-oxazinone-4) membrane is extremely effective in dehydration of water–isopropanol mixture and shows high separation factor. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 4024–4031, 2013

INTRODUCTION

The membrane processes have now well established applications in many industrial processes. One of the most actual industrial tasks—an effective separation of liquid mixtures especially azeotropic, isomer, and thermally nonstable mixtures—can be solved by pervaporation.[1–8]

In pervaporation, the feed mixture is placed in contact with the upstream side of the membrane, while the vapor permeate is removed from the downstream side under the vacuum application. Chemical potential gradient across the membrane acts as the driving force of molecular transport. Pervaporation is a more energy saving, environmentally safe, and clean technology of liquid mixture separation as compared with the existing techniques such as distillation, rectification, ect.[9,10]

Dehydration of alcohols is the main application of pervaporation because of the alcohols are miscible with water in all proportions but form an azeotropic mixtures. Isopropanol is widely used as a cleaning agent in modern chemical semiconductor and electronic industries, thus the recycling of isopropanol solutions is essential from an environmental and economical point of view. Isopropanol forms an azeotrope at 12.5 wt % of water and this fact causes problems in terms of its recovery by distillation.[11]

The efficiency of pervaporation separation considerably depends on the choice of membrane and individual properties of materi-

als.[9,12,13] Therefore, the development of novel membranes with the high performance is the primary task. Polymers of heteroaromatic structure are a promising membrane materials due to their unique range of physicochemical properties. Their high thermal stability, mechanical strength, resistance to aggressive media, and peculiarity of morphology (high structure order, glass temperature, and fixed free volume) determine their application as membrane materials. It is well known that polymers of heteroaromatic structure such as polyimide, polyetherimide, polyamidimide are widely used for alcohol dehydration. Membranes based on polyetherimides are effective in pervaporation of water–isopropanol mixture. Polyamide, polyimide, polybenzimidazole, and modified copolyimide P84 have been used for separation water–alcohol mixtures such as water–ethanol, water–isopropanol, and water–buthanol.[14–26] Precursors of polybenzoxazinoneimides as a thin selective layer of composite membrane on porous polyphenylene oxide support have been studied in separation of aqueous solution of organic liquids (ethanol, isopropanol, acetone, and ethyl acetate) and organic–organic mixture (methanol–cyclohexane).[27] Nevertheless only the detailed investigation of structure peculiarity and individual properties of developed membranes promotes the foundation of materials with an optimal separation factor and flux for industrial applications.

The effectiveness of liquid separation by pervaporation considerably depends on the choice of membrane and individual properties of materials[1–3]; therefore, the development of novel
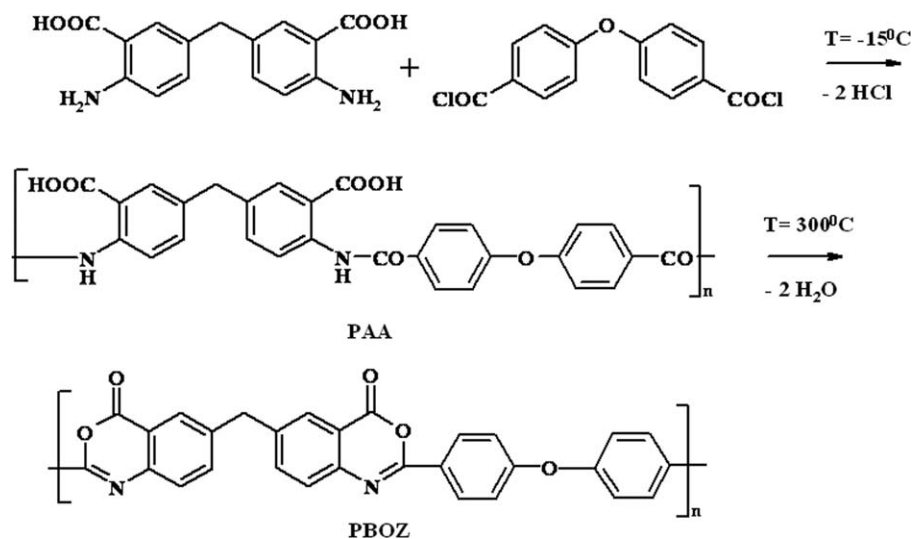
Scheme 1. Synthesis of PAA and PBOZ.

membranes with the high performance is the primary purpose. Polyheteroarylenes are one of the most actual polymer classes in membrane technology due to unique range of physicochemical properties. Their high thermostability, mechanical strength, resistance to aggressive media and peculiarity of morphology (high structure order, glass temperature, and fixed free volume) determine their application as membrane materials. It is well known that polymers with heteroaromatic structure such as polyimide, polyetherimide, polyamidimide are widely used for dehydration of water-alcohol mixtures, which separation has an industrial importance. Membranes based on polyetherimides are effective in pervaporation of water–isopropanol mixture, polyamide, polyimide, polybenzimidazole, and modified copolyimide P84 are used for separation water–alcohol mixtures such as water–ethanol, water–isopropanol, and water–buthanol.[4–16] Precursors of polybenzoxazinoneimides as a thin selective layer of composite membrane on porous polyphenylene oxide support were studied in separation of aqueous solution of organic liquids (ethanol, isopropanol, acetone, and ethyl acetate) and organic–organic mixture (water–cyclohexane).[17] Nevertheless the peculiarity of structure and individual properties of developed membranes is unable to ensure an optimal separation factor and flux for industrial applications.

In the present work, a novel polymer of heteroaromatic structure–poly(benz-3,1-oxazinone-4) (PBOZ) was synthesized by thermal rearrangement of its precursor—poly[(methylene-bis-anthranilamide) 4,4′-diphenyloxidicarboxylic acid] (PAA). Membranes based on PBOZ and its precursor were prepared and characterized by various techniques such as contact angle measurement, thermogravimetric analysis, and pervaporation. The differences between properties of PBOZ and PAA membranes were discussed. Special attention was given to analyze the transport properties of membranes under study. The flux (J), separation factor (α), and pervaporation separation index (PSI) were determined in pervaporation of water–isopropanol mixture. To interpret the performance of membranes the swelling experiments were carried out.

EXPERIMENTAL

Materials and Polymer Synthesis

N-methylpyrrolidone (NMP), isopropanol were of chemically pure (CP) grade, they were purchased from Vekton Company (Russia) and used without further purification.

The PBOZ was obtained by two stage process (Scheme 1). At the first stage its precursor PAA was synthesized by low-temperature polycondensation according to a procedure.[28] PAA was synthesized in a flask equipped with a stirrer where 1 mmol of methylene-*bis*-(anthranilic acid) and 7.5 mL of NMP were stirred until methylene-*bis*-(anthranilic acid) had completely dissolved. Then, the solution was cooled using an ice-salt bath and 4,4′-oxydibenzoic acid dichloroanhydride was added. The PAA solution was used for the film preparation directly after synthesis without any purification.

At the second stage, the PAA was rearranged to PBOZ by intramolecular thermal dehydration and cyclization at 300°C.

Membrane Preparation

PAA membranes (30–40 μm thick) were obtained by casting a PAA solution in NMP on a glass plate followed by evaporation of the solvent at 80°C in air. Films fixed on the glass plate were dried to a constant weight at 80°C in vacuum for 10 days.

PBOZ membranes (20–30 μm thick) were obtained by a heating of PAA films fixed on the glass plate as a result of solid-state reaction demonstrated in Scheme 1. 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 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.

Contact Angle Measurements

Contact angles (Θ) of liquids on homogeneous membrane surfaces were measured by the Wilhelmy plate technique, using the KRUSS installation. In the Wilhelmy plate technique, the advancing (θ_a) and receding (θ_r) angles are calculated from the force exerted as the sample is immersed or withdrawn from a

liquid. Water ($\sigma = 72.2$ mn/m) and isopropanol ($\sigma = 23.0$ mn/m) were liquids under the study.

Thermal Gravimetric Analysis

The thermal gravimetric (TG) measurements in air atmosphere were conducted using ~ 14 and ~ 7.3 mg of PAA and PBOZ samples contained in a platinum crucible under a heating rate of $10°C$/min. The TG 209 F3 Iris thermo-microbalance (Netzsch) was used to carry out these tests.

Pervaporation

The pervaporation experiment was carried out on a laboratory cell with an effective membrane area of 14.8 cm^2 at 50°C with stirring. Downstream pressure below 10^{-2} mm Hg was maintained. The feed was water–isopropanol mixture. The permeate was collected into a liquid nitrogen cooled trap, weighed, and analyzed. The composition of permeate was determined using chromatograph «Chromatec–Crystal 5000.2» (Chromatec Company, Russia) with thermal conductivity detector and refractometer «IFR–454B2M» (KOMF Company, Russia).

From the pervaporation experiments, total permeation flux (J), separation factor (α), PSI were calculated. The separation factor was determined using the following equations:

$$\alpha_{water/isopropanol} = \left(Y_{water} / Y_{isopropanol} \right) / \left(X_{water} / X_{isopropanol} \right) \quad (1)$$

where X_{water} and $X_{isopropanol}$ are weight fraction of water and isopropanol in feed, Y_{water} and $Y_{isopropanol}$ are weight fraction of water and isopropanol in permeate.

Total permeation flux (J) was determined as amount of liquid penetrated through membrane area per time unit:

$$J = \frac{Q}{A \cdot t} \quad (2)$$

where Q is the total weight of the permeate collected at time t, A is the effective surface area of the membrane.

To compare flux of membranes with different thickness (l) varied from 20 to 40 μm, the values of normalized flux (J_n) were used. J_n is the flux through membrane with 20 μm thick calculated as:

$$J_n = J \cdot l / 20 \quad (3)$$

Membrane efficiency was estimated through the PSI[29] that was calculated by equation:

$$PSI = J_n \left(\alpha_{water/isopropanol} - 1 \right) \quad (4)$$

Swelling Experiment

Swelling experiments were performed by immersing of membrane samples into an individual liquid (water or isopropanol) under atmospheric pressure at 20°C. The weight change was determined gravimetrically with the error $\pm 10^{-4}$ g. The experiment was continued until equilibrium was attained. The kinetic curves of sorption were plotted. The degree of sorption (S) was

calculated from the weight difference between the wet membrane (M_{wet}) at equilibrium and the weight of dry sample (M_{dry}) as shown in eq. (5):

$$S = \frac{M_{wet} - M_{dry}}{M_{dry}} \quad (5)$$

Diffusion in nonporous membranes is regarded as the process by which penetrant is moved from one bulk liquid phase to polymer film as results of random molecular motion. It is assumed that membrane is in the stationary state and the analysis of experimental data is based on solving of Fick's laws.[30–32] In the case of one-dimensional diffusion, when diffusion coefficient is independent of concentration at the initial time, the amount of sorbs/desorbs substance (M_t) at the moment (t) was calculated by equation:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (6)$$

where M_∞ is equilibrium amount of sorbs/desorbs substance determined as difference between the weight of swollen membrane and the weight of membrane dried to constant weight.

The effective diffusion coefficient (D) was calculated by the equation:

$$D = \frac{\pi}{16} \left(\tan \beta \right)^2 \quad (7)$$

where $\tan \beta$ is tangent of the initial linear slope of the desorption kinetic curves in coordinates of M_t/M_∞ vs. $t^{1/2}/l$.[33–35]

RESULTS AND DISCUSSION

TG Analysis

The heteroaromatic amorphous polymers are characterized of nonequilibrium structure. Therefore, some complications can appear during membrane properties investigation and interpretation of experimental results. It was already noted that membranes prepared by solvent evaporation from polymer solutions in chloroform or amide solvents (NMP, dimethylformamide, etc.) contain a substantial amount of residual solvent that is bounded with macromolecules by donor–acceptor bonds.[36,37] The residual solvent availability in solid films can be caused some variations of macromolecular structure that influence on the functional properties of membranes. To estimate the amount of low-molecular weight admixtures in the PAA and PBOZ membranes, TG analysis was carried out (Figure 1).

The TG and DTG curves of PAA membrane [Figure 1(a,b), curves 1] show two regions of substantial weight loss at the heating up to 350°C. The first process at the region up to 110°C reflects the removal of water ($\sim 2\%$) absorbed by the membrane during its storage at room conditions. The large decrease of the PAA specimen weight ($\sim 27\%$) was registered in the range 130–350°C. This weight loss is caused by two parallel processes: the removal of water that arises as the coproduct of the PAA thermal curing, and the removal of residual solvent
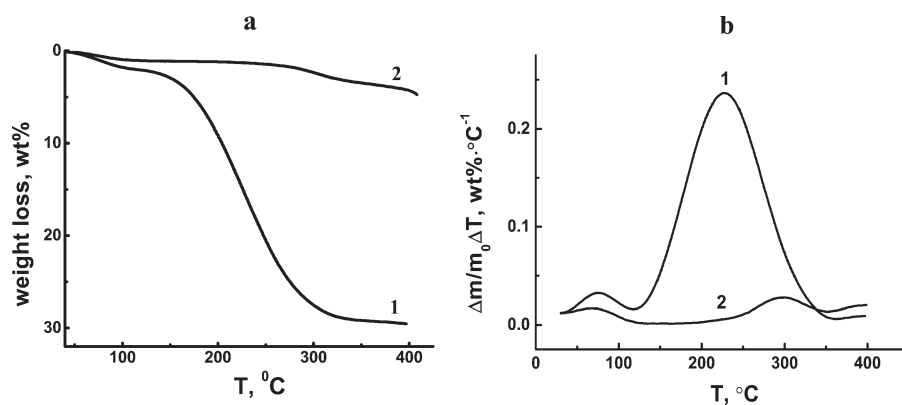
Figure 1. (a) TG and (b) DTG curves of (1) PAA and (2) PBOZ films.

NMP. The amount of water produced at PAA dehydration can be calculated from the appropriate reaction (Scheme 1). It is equal to 7.1%. Therefore, the concentration of residual solvent in membrane is equal to ~20%.

The TG and DTG curves of PBOZ membrane [Figure 1(a,b), curves 2] show that the total weight loss at heating up to 350°C is equal to ~3%. The weight loss due to the removal of absorbed moisture was about 1% (the region up to 110°C). In the range 200–350°C the elimination of residual solvent from the PBOZ film proceeds. It was already reported that NMP cannot be totally removed from membranes produced by the solution technology.[37–39] The amount of bound solvent in the PBOZ membrane can be estimated using TG data. It is equal to 2% that is only one tenth of the total NMP amount in the PAA membrane before heating (see TGA data for PAA membrane). The onset of thermal destruction of PBOZ films was registered at 385–390°C.

Pervaporation

In pervaporation, molecular transport proceed due to the concentration gradient that exists between feed and permeate side the membrane; this process is generally explained by the solution-diffusion mechanism.[40] According to this principle, initially, permeating molecules dissolve in the membrane and then diffuse out as a consequence of the concentration gradient. However, the overall separation can be explained on the basis of physical nature of the liquids, their affinity towards membrane as well as the morphology of the membrane. Some properties of liquids composed water–isopropanol mixture for pervaporation are presented in Table I.

Dehydration of isopropanol is an actual task because of the products of isopropanol synthesis contain water admixture and

isopropanol forms an azeotrope at 12.5 wt % of water. Separation of the azeotropic mixture by distillation is possible only by adding a third component such as benzene or toluene, which are hazardous liquids. In pervaporation separation, the membrane acts as a third phase to break the azeotrope, and the process become energy saving.

The pervaporation of water–isopropanol mixture was studied over a wide range of feed composition. It was shown that PBOZ and PAA membranes are mainly permeable to water. Figure 2 demonstrates comparison of pervaporation results with vapor-liquid equilibrium (VLE) data for the water–isopropanol system. The curve trend of the permeate-feed concentration dependence for pervaporation differs essentially from VLE diagram. The pervaporation curves are located above the VLE curves throughout the feed composition. The data confirm that pervaporation is more effective process of separating this mixture as compared to conventional distillation.

It was established that separation factor of PBOZ membrane is considerably higher than that of PAA membrane (Figure 3). Thus, in separation of mixture containing 10 wt % water, the values of separation factor are equal to 9000 for PBOZ membrane and 140 for PAA membrane.

Figure 4 shows the dependence of membranes flux on water content in feed. Flux of PAA membrane is better than that of PBOZ membrane. Thus, in separation of mixture containing 10 wt% water the difference in flux is from 3 g/m^2 h for PBOZ membrane to 60 g/m^2 h for PAA membrane.

The overall separation performance of the membranes in the separation of aqueous isopropanol can be characterized by the PSI, as shown in Figure 5. The PBOZ membrane exhibits a higher PSI than that for PAA membrane in separation of water–

Table I. Physical Properties of Liquids Under Study

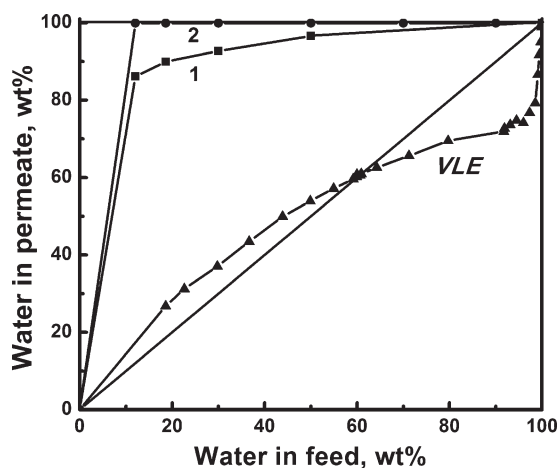| Liquid	Molecular weight (g/mol)	Density (25°C) (g/cm^3)	Kinetic diameter (Å)	Viscosity (20°C), (mPa s)	Hildebrand solubility parameter (J/cm^3)$^{1/2}$	$T_{boiling}$ (°C)
Water	18.0	0.997	2.9	1.0	49.6	100
Isopropanol	60.1	0.786	4.7	2.4	23.9	84.2

Figure 2. Vapor–liquid equilibrium curve (VLE) and dependence of water concentration in permeate on water concentration in feed for the pervaporation of water–isopropanol mixture through (1) PAA and (2) PBOZ membranes.

isopropanol mixture due to extremely high selectivity of PBOZ membrane.

To interpret a transport mechanism, it is necessary to study the interaction of membrane polymers and components of separating mixture. Affinity of liquids to membrane materials and diffusion ability of penetrant, which determine transport properties of membranes in pervaporation were estimated by sorption experiments.[13]

Sorption Study
Sorption tests were made by immersing of PAA and PBOZ membrane samples into an individual liquids (water or isopropanol). The amount of liquid sorbed by membrane provides essential information about the affinity of alcohol and water towards the membrane material. Figure 6(a,b) shows sorption kinetic curves. They were plotted as a function of a time dependence of the amount of sorbate (Δm) divided by the weight of dry membrane (m_0). There are three curves on the figure because PBOZ membrane does not sorb isopropanol. Curve of water sorption in the PBOZ membrane has standard shape [Figure 6(b)] with the linear part of the membrane
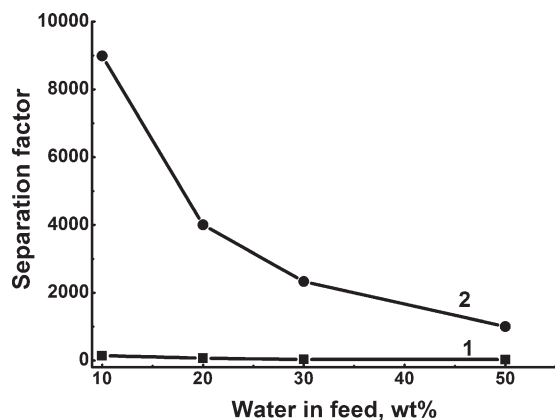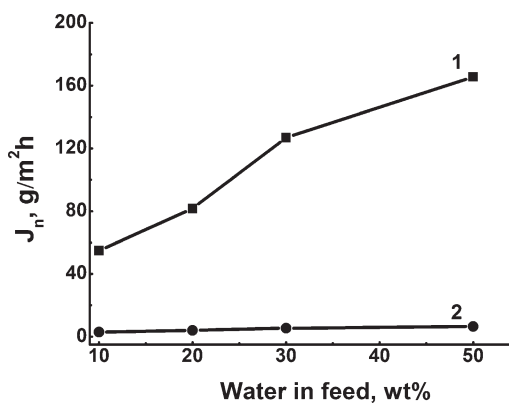
Figure 4. Dependence of flux on water content in feed in pervaporation of water–isopropanol mixture using (1) PAA and (2) PBOZ membranes.

weight increasing at the initial time that corresponded to the Fick's law.

Kinetic curves of water and isopropanol sorption in PAA membrane have an unusual shape. Curve of water sorption in PAA membrane passes through a maximum [Figure 6(a), curve 1]. Because of water sorption the weight of sample is rising sharply in the beginning of experiment but then it declines. Such behavior can be associated with the polymer realignment and washing out of the residual solvent.[41] Data of TG analysis indicates on the possibility of the last process that is washing out of the residual solvent NMP from PAA membrane.

There is two-step kinetics in the case of isopropanol sorption in PAA membrane [Figure 6(a), curve 2]. The first sorption step is rapid and completed by establishment of an intermediate quasi-equilibrium state. The second step is characterized by slow increase of the membrane weight in isopropanol and it is more long-continued as compared with the first stage. Such two-step kinetics can be also explained by rearrangement of polymer chains followed by washing out of the residual solvent.

Figure 7 shows the kinetic curves of desorption as the amount of liquid ($\Delta m'$) that was removal from PBOZ and PAA membranes up to the achievement of dry membrane weight (m_0). All curves have standard shape: the curves are linear in the
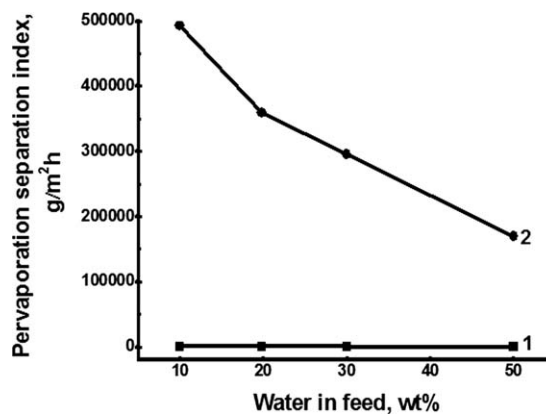

Figure 3. Dependence of water–isopropanol separation factor on water content in feed for (1) PAA and (2) PBOZ membranes.

Figure 5. Dependence of the pervaporation separation index on water content in feed by using (1) PAA and (2) PBOZ membranes.
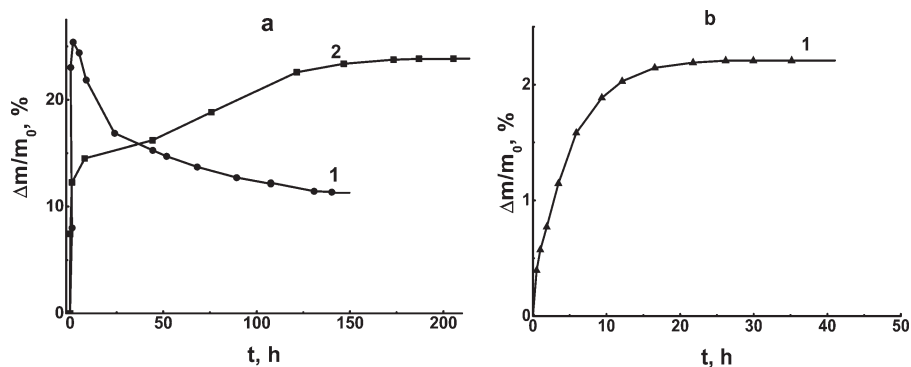
Figure 6. Kinetic curves of sorption for PAA (a) and PBOZ (b) membranes in (1) water and (2) isopropanol.
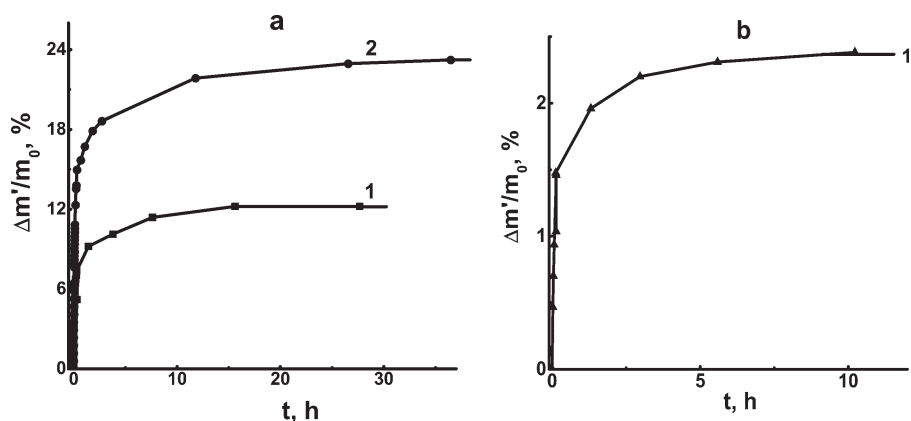

Figure 7. Kinetic curves of desorption for PAA (a) and PBOZ (b) membranes of (1) water and (2) isopropanol.

initial stage, and then become concave to the abscise axis up to a limiting value. In all cases, kinetics of desorption have linier type at the initial time and can be considered as followed by Fick's law. Therefore, desorption curves can be used for determination of diffusion coefficients of water and isopropanol that are listed in Table II.

The data of Table II gives some explanation of membrane mass transport through polymer membranes. PAA membrane has high sorption activity to both liquids; however, the sorption of isopropanol is significantly better in comparison with water sorption. The diffusion rate of small water molecules in PAA membranes is better than diffusion rate of isopropanol.

In the case of PBOZ membrane the sorption of water is small but the diffusion coefficient of water is rather great. High values of effective diffusion coefficients of water for both membranes are the result of the process of membrane formation by the solvent evaporation from the PAA solution in NMP. The flux of

evaporating solvent from a glassy plate to the surface of the polymer solution should determine the character of macromolecules aggregation in supra-molecular structures and the availability of local areas with lower density. As a result, the nonequilibrium supramolecular polymer structure is formed and channels for mass transfer are generated.[42] It is known that polymer membranes obtained by the heating of their precursor are usually characterized the excessive free volume in structure.[43–45] It was established that transformation of PAA to PBOZ membrane also leads to an increase of fractional free volume as a result of thermal dehydration and cyclization during membrane formation and due to the removal of residual solvent. The excessive free volume of PBOZ film is equal to 3–4% of total volume.[46,47] This fact greatly influences on the high diffusion coefficient of water molecules in PBOZ membrane in comparison with PAA membrane.

High polymer affinity to both water and isopropanol provides high flux and low separation factor of PAA membrane in

Table II. Sorption Degree (S) and Effective Diffusion Coefficients (D) of Water and Isopropanol

	Water		Isopropanol	
Membrane	S (%)	D (m²/min)	S (%)	D (m²/min)
PAA	12.0	1.6×10^{-4}	23.4	1.6×10^{-12}
PBOZ	2.1	2.0×10^{-2}	0	0

Table III. Contact Angles, Degree

	PBOZ		PAA	
Liquid	Θ_a	Θ_r	Θ_a	Θ_r
Water	85.9	43.1	82.2	37.8
Isopropanol	32.5	33.4	23.4	22.4

Table IV. Comparison the Present PV Data with the Literature Results

Membrane	Temperature	Water in feed (wt%)	Flux (g/m²h)	Separation factor	References
PVA/PMMA (95 : 5)	50	10	75	400	10
P84-ckeda-4hr	60	15	1141	242	23
Ultem	60	15	7.0	585	24
Torlon	60	15	6.8	2973	24
Torlon/P84 (9 : 1)	60	15	500	7	25
Crosslinked P84/PES dual-layer	60	15	454	953	48
PBOZ	50	10	3	9000	Present work

PVA, poly(vinylalcohol); PMMA, poly(methylmethacrylate); PES, polyethersulfone; P84, copolyimide; Torlon, polyamide-imide; Ultem, polyetherimide; P84-ckeda-4hr, 4hr ethylene diamine crosslinked P84 membrane.

pervaporation of water–isopropanol mixture. Low water swelling of PBOZ membrane and passivity to isopropanol lead to very high selectivity in water–isopropanol separation and moderate flux of the process.

According to Table II, PBOZ membrane shows the barrier properties to isopropanol and low sorption degree of water. To characterize the membrane surface, contact angles of water, and isopropanol were measured by the Wilhelmy plate technique (Table III). Higher values of contact angles were obtained for PBOZ that indicates on worse moistening of membrane surface by both water and isopropanol in comparison with that of PAA. Low sorption capacity of PBOZ can be explained by more hydrophobic properties of PBOZ membrane surface as compared with PAA membrane.

Comparison of PV Results with Literature

Comparison of transport properties of the present membranes with literature data on pervaporation of water–isopropanol mixture is given in Table IV.

Table IV lists data on separation factor (water–isopropanol) and flux that have been obtained by use of different polymer membranes in published works. It should be mention that flux of PBOZ membrane is moderate, while the selectivity is excellent and significantly higher as compared with the previously published reports. The value of separation factor for present PBOZ membrane is considerably higher than that of the known membranes. However, permeability of the present membrane is lower than those of the published reports. An effort to improve flux is necessary, probably by development of composite membrane or other modes and this will be undertaken in future.

CONCLUSION

PAA and PBOZ membranes were tested in the separation of water–isopropanol mixture. It was shown that both membranes are preferentially permeable to water but PBOZ membrane exhibits considerably higher selectivity than that of PAA membrane. The overall separation performance of the PBOZ membrane in the pervaporation of aqueous isopropanol was characterized by PSI, the values of PSI are extremely high for mixtures containing up to 50 wt % water.

To interpret the transport properties of membranes, the sorption–diffusion parameters were determined due to data of swelling experiments. It was established that the PBOZ membrane does not sorb isopropanol. The barrier properties of PBOZ membrane with respect to isopropanol and high diffusion ability of water molecules in this membrane is hold responsible for high separation performance in pervaporation of water–isopropanol mixture. From these results, it can be concluded that the PBOZ can be recommended as membrane material for dehydration of isopropanol by pervaporation.

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