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Preparation and Properties of Organophilic Membranes for Pervaporation of Water-Organics Mixtures

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ABSTRACT

Several dense membranes made of polydimethylsiloxane (PDMS), poly(ether block amide) (PEBA) and ZSM-5-type, zeolite-filled PEBA were prepared by the casting method. Morphology of membranes was determined by using differential scanning calorimetry (DSC) and wide-angle x-ray scattering method (WAXS). The swelling and pervaporation properties of prepared membranes were investigated in the contact with water-methyl t-butyl ether (H_2O-MTBE), water-butyl acetate (H_2O-BuAc), and water-methyl acetate (H_2O-MeAc) mixtures.

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It was found that transport and selectivity properties depended both on the kind of a membrane and the kind of a liquid mixture. PDMS membranes showed the best pervaporation properties. Both the PEBA and zeolite-filled PEBA membranes showed similar selectivity during pervaporation. The presence of zeolite filler in the PEBA membrane enhanced transport of both water and organic component of the separated mixture.

Key Words: Pervaporation; Organophilic membranes; Polydimethylsiloxane; Poly(ether block amide); ZSM-5 type zeolite; Separation of water-organics mixtures.

INTRODUCTION

Pervaporation is a membrane-based process used for the separation of liquid mixtures. In this technique, the liquid feed mixture is in contact with one side of a membrane and permeate in a vapor phase is continuously removed from the other side of membrane into the vacuum or sweeping gas.[1–3] Pervaporation can be applied for the dehydration of organics, for the extraction of organics from aqueous solutions, and/or for the separation of the components of nonaqueous mixtures.[4–18]

Methyl and butyl acetates are examples of esters that can be found in the effluents from chemical and pharmaceutical industries. Methyl t-butyl ether (MTBE) is a gasoline additive that is used to enhance combustion.[19] Recently, MTBE has been detected in lakes, reservoirs, and groundwater used as potable water suppliers.[20,21] The most commonly used technologies for removing VOCs from water, like air stripping or carbon adsorption, generate secondary wastes. The above-mentioned facts, coupled with a growing interest in recycling both for economic and environmental reasons, open new opportunities for membrane technologies, like pervaporation.[7–17]

The efficiency of pervaporation depends strongly on the membrane employed, therefore, the choice of the most performant membrane is very important. Membranes prepared from various hydrophobic polymers are widely used for the extraction of organics from aqueous streams.[22] Different hydrophobic fillers, like active carbon or zeolites, can be also incorporated into the membrane to tailor its selectivity and permeability.[22–26]

In the present work, we studied the swelling and pervaporation properties of membranes made of polydimethylsiloxane (PDMS), poly(ether block amide) (PEBA) and ZSM-5 zeolite-filled PEBA in contact with the following water-organics mixtures: water-methyl t-butyl ether (H_2O-MTBE), water-methyl acetate /H_2O-MeAc/ and water-butyl acetate (H_2O-BuAc).

EXPERIMENTAL

Materials

Zeolite

Zeolites are porous crystalline aluminosilicalites possessing the pore size in the molecular sieving range (i.e., < 1 nm).[27–29] The hydrophobic zeolite used in this investigation was prepared in the Industrial Chemistry Research Institute (Warsaw, Poland) and was designated as a T-15 ZMS-5 type one. The high Si/Al ratio equal to 34.5 presumably makes this zeolite organic selective.

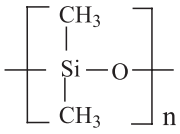
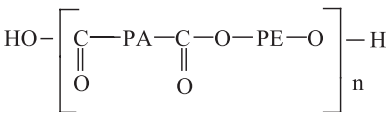
Polymers

The following hydrophobic polymers were chosen for this investigation: polydimethylsiloxane (PDMS), prepared from EL.LR 7660A elastomer and EL.LR 7660B curing agent (Wacker Chemie GmbH, Germany), and poly(ether-block-amide) PEBA-4033 (Elf Atochem, France).

EL.LR 7660A is a vinyl-methyl-polysiloxane ($M_w \approx 40{,}000$) containing a platinum catalyzer. EL.LR 7660B is a hydrogen functional crosslinker.

PEBA block copolymer is a combination of a rigid polyamide (e.g., polyamide-11, polyamide-12, or polyamide-6) and a soft polyether (e.g., polyoxytetramethylene, polyoxyethylene, or polyoxypropylene).[30] Table 1 summarizes the general chemical structure of the materials used.

Table 1. Chemical structure of the materials used.

Material	Chemical structure
T-15 zeolite	$Na_n[Al_nSi_{(96-n)}O_{192}]\cdot 16H_2O$, $n < 27$
Polydimethylsiloxane (PDMS)	
Poly(ether block amide) (PEBA)	

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Membrane Preparation

PDMS Membranes

PDMS membranes were prepared by mixing the two components of EL.LR 7660. Two weight ratios of prepolymer to the curing agent were chosen: 95:5 and 90:10. The mixture of prepolymer and curing agent was cast on a Teflon plate, after the air bubbles were removed. Crosslinking was carried out at 323°K for 24 h. Throughout the test, PDMS were designated if needed, according to the amount of curing agent used: PDMS 5 and PDMS 10.

PEBA Unfilled Membranes

PEBA dense membranes were prepared by casting 10 wt% and/or 15 wt% PEBA-4033 polymer solution onto a glass plate using 0.3, 0.5, and/or 1.5 mm casting knives. A mixture of n-butanol and n-propanol (4:1 by weight) was used as a polymer solvent.[31] The obtained films were dried for 24 h at different temperatures in the range of 293 to 323°K. Where necessary, the PEBA membranes were designated in the following way: PEBA A/B, where A describes the polymer concentration in the polymer solution, and B denotes the temperature of drying.

T-15 Zeolite-Filled PEBA Membranes

T-15 zeolite in the amount of 10 up to 50 wt% of the polymer was added to the 15 wt% polymer solution. After obtaining a homogeneous dispersion by mixing, the solution was cast on a glass plate using different casting knives. Formed membranes were dried at room temperature for 24 h. These membranes were designated as PEBA T-15.

Membrane Morphology

The morphology of membranes was studied by means of differential scanning calorimetry (DSC) and wide-angle x-ray scattering method (WAXS).

Calorimetric Measurements (DSC)

DSC measurements were performed on a PL DSC differential scanning calorimeter (Polymer Laboratories, Epsom, UK) interfaced with a thermal analysis data system, after previous calibration with indium and water. The

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DSC was purged with nitrogen and a subambient temperature was attained with liquid nitrogen. Samples were sealed in aluminium pans and then cooled in the calorimeter down to about 110°K at the rate of 20°K/min and held at that temperature for approximately 5 min before heating to 373°K (PDMS) and 523°K (PEBA), at a rate of 20°K/min. All scans were collected twice to check the reproducibility. The glass transition (T_g) was determined as the midpoint of the change in the heat capacity. Temperature at the maximum of the crystallization exotherm was presumed as the crystallization temperature (T_c). The temperature of the melting endotherm peak was presumed as the melting point (T_m).

Wide-Angle X-Ray Scattering

Wide-angle x-ray scattering (WAXS) measurements were performed by means of HZG-4 x-ray diffractometer employing the symmetrical reflection method of registration. A copper target x-ray tube operated at 30 kV and 30 mA was used as the source of radiation. Monochromatization was carried out by the Ross double-filter method. Diffraction curves were taken from 5° to 40°, with a step of 0.1°.

Swelling Measurements

The sorption capacities of the obtained membranes were measured by immersing the dry membranes either in the pure solvent or in a water–organic solution in a thermostated vessel at 298°K for 24 h. After blotting off any excess solution, the swelled membranes were weighed.

The total liquid uptake S onto a dry membrane was calculated according to the following relation:

$$S = \frac{(m - m_o)}{m_o} \qquad \text{(g of sorbed liquid/g of dry membrane)} \qquad (1)$$

where S = total sorption uptake (swelling degree), m = weight of swollen membrane, and m_o = weight of dry membrane.

Swelling measurements were performed for membranes in contact with pure water, methanol (MeOH), MeAc, BuAc, and MTBE and for membranes in contact with binary water–organic mixtures.

Pervaporation Experiments

Pervaporation experiments were performed using the standard laboratory pervaporation set-up (Figure 1). The permeation rates were determined

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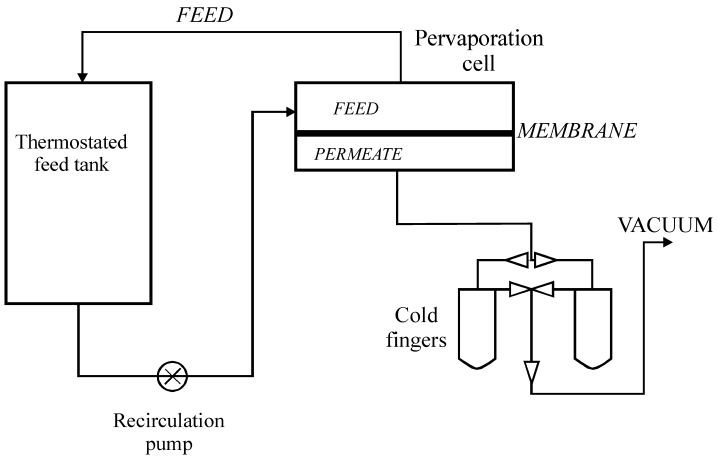


Figure 1. Scheme of the pervaporation setup.

by weighing permeate collected over a given period of time in the permeate trap. Composition of both the feed mixture and permeate were determined by using VARIAN 3300 gas chromatograph. The system was operated at 298°K and at a pressure on the permeate side below 1 hPa.

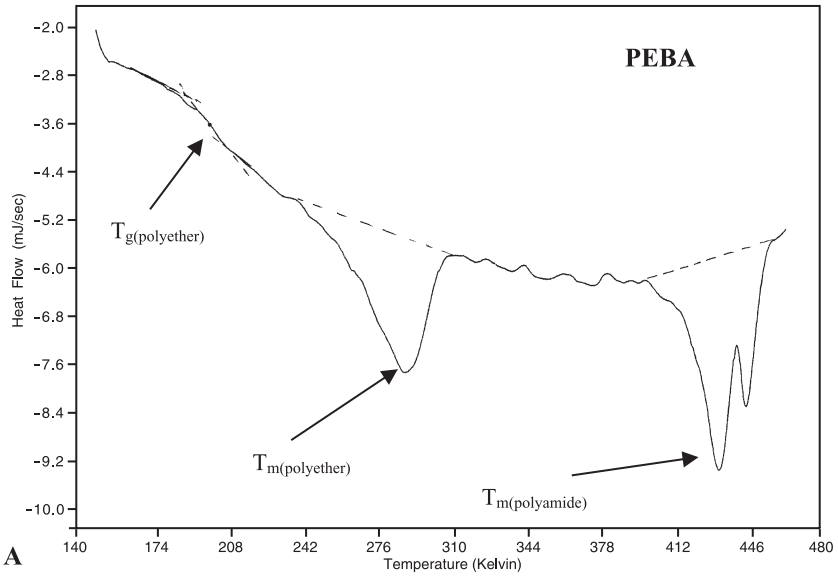
Prior to use, the PEBA and PEBA T-15 membranes underwent conditioning to remove the excess solvents used to dissolve a polymer. The membranes were put into the pervaporation cell and pervaporation of water was proceeded until the constant flux was obtained. The membranes needed around 100 h to produce a constant flux at 298°K and about 30 h at 313°K. In all pervaporation experiments, only samples of conditioned membrane were used.

Because membranes were of different thickness, the normalized fluxes (J_N) were calculated according to the following relation:

$$J_N = Jd \qquad [\mu m\ kg\ m^{-2}\ h^{-1}] \tag{2}$$

where J = permeate flux in kg m^{-2} h^{-1} and d = thickness in μm. J_N expresses the permeate flux in kg of permeate during 1 hour through the membrane of an area of 1 m^2 and of thickness equal to 1 μm.

Pervaporation experiments were performed for membranes in contact with the following binary water–organic mixtures: water–MTBE, water–MeAc, and water–BuAc.



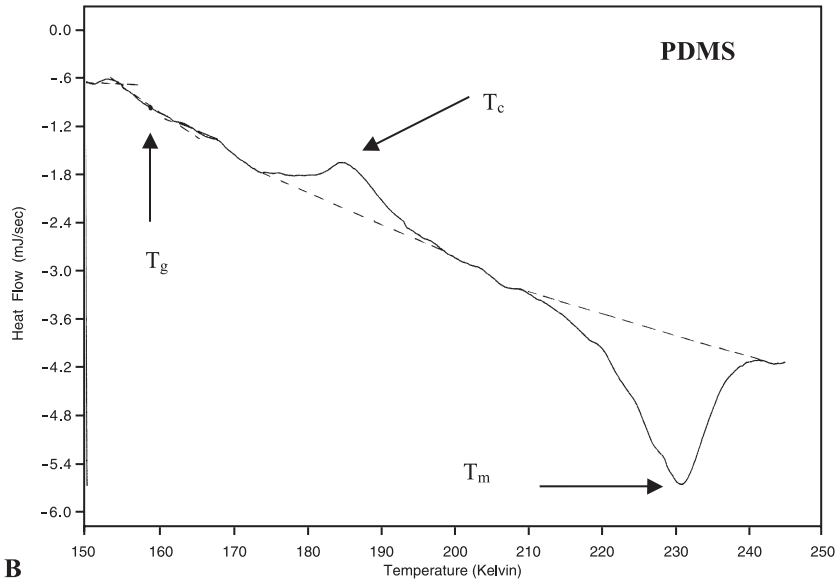


Figure 2. DSC thermograms of the PEBA 15/30 membrane (A) and the PDMS 10 membrane (B).

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RESULTS AND DISCUSSION

Membrane Morphology

The results obtained from DSC scans for the PEBA-type membranes are shown in Figure 2A and Table 2. Table 2 also presents the results found for the pellets of PEBA-4033 polymer. PEBA is a thermoplastic elastomer that consists of rigid polyamide linear blocks and flexible polyether linear blocks.[30] As was stated by means of the DSC method, the membranes were semicrystalline and in the scans, exhibited several thermal events. The main events corresponded to a glass transition of polyether segments, melting of polyether-type crystallites (low temperature endotherm), and melting of polyamide-type crystallites (high temperature endotherm) (see Figure 2A). A number of discrete endothermic peaks were seen on the DSC scans between 280 and 410°K that can be connected with the multiphase characteristics of the material and presence of solvents in the membranes.[32–35] The glass transition temperature corresponding to the polyether blocks in the PEBA membranes varied between 207 and 200°K (see Figure 2A, Table 2). This temperature was about 9 to 16°K lower than the T_g of the PEBA-4033 polymer. The temperature interval, in which the glass transition occurred (ΔT_g), was in the range of 27 to 44°K. It was 3 to 4 times broader than that for the PEBA polymer. However, the observed values of T_g and ΔT_g showed no systematic trend with casting conditions. Moreover, the casting conditions exerted little effect on the melting points of the crystalline phases presented in the membranes. The contents of crystallinities of polyamide and polyether were not determined because the total mass of the corresponding blocks in the starting material was unknown.[30]

Table 3 presents the glass transition temperatures (T_g), crystallization peak temperatures (T_c), and melting peak temperatures (T_m) for the

Table 2. Transition temperatures for PEBA-4033 polymer and PEBA membranes.

Membrane	T_g	ΔT_g	T_m (polyether)** (K)	T_m (polyamide)** (K)
PEBA-4033*	216	11	288	442
PEBA 15/20	207	34	290	437
PEBA 15/30	200	27	290	434
PEBA 15/50	201	39	291	436
PEBA 10/50	203	44	290	437

*Pellets of PEBA polymer.
**The main melting peak.

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Table 3. Transition temperatures and enthalpies for PDMS membranes.

Membrane	T_g (K)	T_c (K)	T_m (K)	ΔH_c (J/g)	ΔH_m (J/g)
PDMS 5	158	183	234	1.2	9.0
PDMS 10	160	185	231	1.0	6.1

crosslinked PDMS-type membranes. In the same table, melting and crystallization enthalpies (ΔH_c and ΔH_m, respectively) are also summarized. The T_g values for the studied PDMS membranes were practically the same (see Table 3). Only small differences in crystallization and melting parameters for the membranes were observed. The trend of the changes depended on the crosslinking density of PDMS. However, the crosslinking degree did not influence the sorption and pervaporation properties of PDMS membranes because these membranes operated at a temperature high above T_g and T_m.

Swelling Experiments

Membrane Swelling in Pure Solvents

Table 4 presents the molar swelling degree of PDMS and unfilled PEBA membranes in contact with pure solvents. The results obtained with the PDMS membrane showed that the swelling degree depended on the polarity of the solvent and followed the order:

$$H_2O < MeOH < MeAc < BuAc < MTBE$$

The swelling degree of the PEBA membrane in water was small, which confirmed the general hydrophobic character of this membrane. However, comparing the swelling degree of the PEBA membrane in the organic

Table 4. Swelling of PDMS and PEBA membranes in contact with pure solvents (T = 298°K).

	Swelling degree (mmol solvent/g dry membrane)				
Membrane	H_2O	MeOH	MeAc	BuAc	MTBE
PDMS 10	0.3	1.1	6.1	9.7	14.6
PEBA 15/50	0.5	12.9	4.2	5.3	3.3

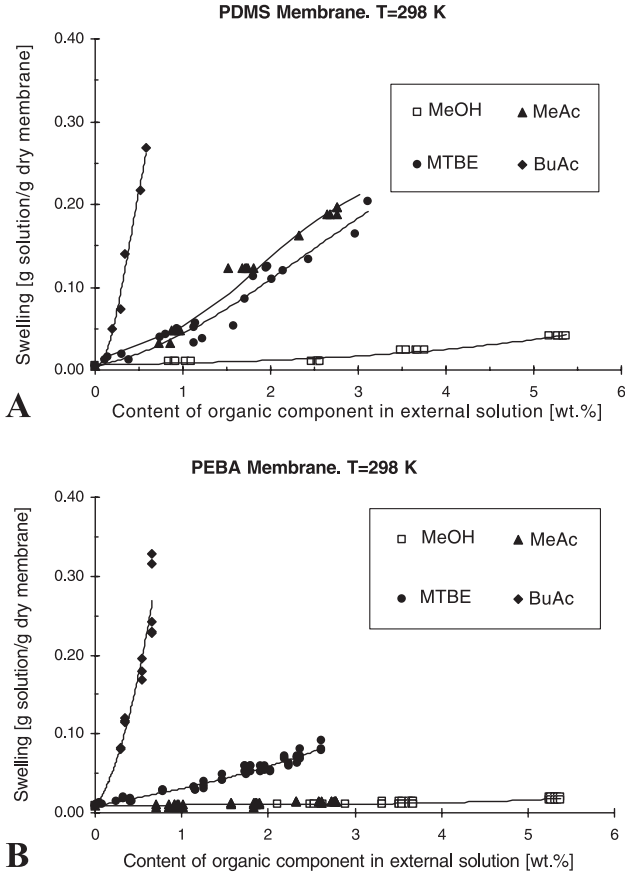


Figure 3. Swelling of the PDMS membrane (A) and the PEBA membrane (B) in the binary water–organics mixtures.

solvents, it was found that both the polyamide and polyether segments played an important role in the resultant swelling properties. Unexpectedly, PEBA showed the highest swelling in contact with pure methanol (12.9 mmol MeOH/g dry membrane). This fact could indicate the strong interactions between polyamide segments and methanol. On the other hand, PEBA swelled only moderately in contact with MTBE (3.3 mmol MTBE/g dry membrane) suggesting that the solubility parameters, δ, for PEBA and MTBE are quite different.[36–38] Unfortunately, neither the exact composition of PEBA polymer nor the solubility parameters δ of MTBE and PEBA were available.

Membrane Swelling in Contact with Water–Organic Mixtures

The sorption capacities of investigated membranes in contact with water–organics binary mixtures are presented in Figure 3. The swelling degree of all prepared membranes increased with increasing the content of organic component in the binary mixtures. The swelling properties of PEBA and PDMS membranes in contact with different binary mixtures (see Figure 3) showed that both membranes swelled the best in contact with the water–BuAc mixture and that the weakest swelling occurred when membranes were in the contact with the water–MeOH mixture. These facts proved the suggestion that swelling properties were dependent both on the polarity of the organic component and on the miscibility of organic solvent with water.

The conditions of membrane formation influenced the swelling properties to a small extent only (Table 5). On the other hand, the T-15 zeolite filling of the PEBA membrane enhanced sorption from the water–MTBE mixture, when compared to the unfilled membrane.

Pervaporation Characteristics of PDMS and PEBA Membranes

The selective properties of PDMS, PEBA, and PEBA T-15 membranes in contact with water–MTBE and water–MeAc mixtures are presented in Figure 4. All investigated membranes were selective toward the organic component of the mixture. The PDMS showed the best selectivity properties among the membranes investigated (see Figure 4A) and this observation corresponded well with the results of swelling experiments. PEBA and zeolite-filled PEBA T-15 membranes showed similar selectivity in contact with the water–MTBE mixture (see Figure 4A). The relations between feed composition of the water–MeAc mixture and the membrane selectivity (see

Table 5. Swelling properties of PDMS and PEBA membranes in contact with aqueous MTBE solutions.

MTBE content in external solution (wt.%)	Swelling (g solution/g dry membrane)				
	PDMS 5	PDMS 10	PEBA 10	PEBA 15	PEBA T-15
1.0	0.046	0.045	0.033	0.029	0.086
2.0	0.098	0.109	0.068	0.058	0.154
3.0	0.173	0.210	0.120	0.099	0.287

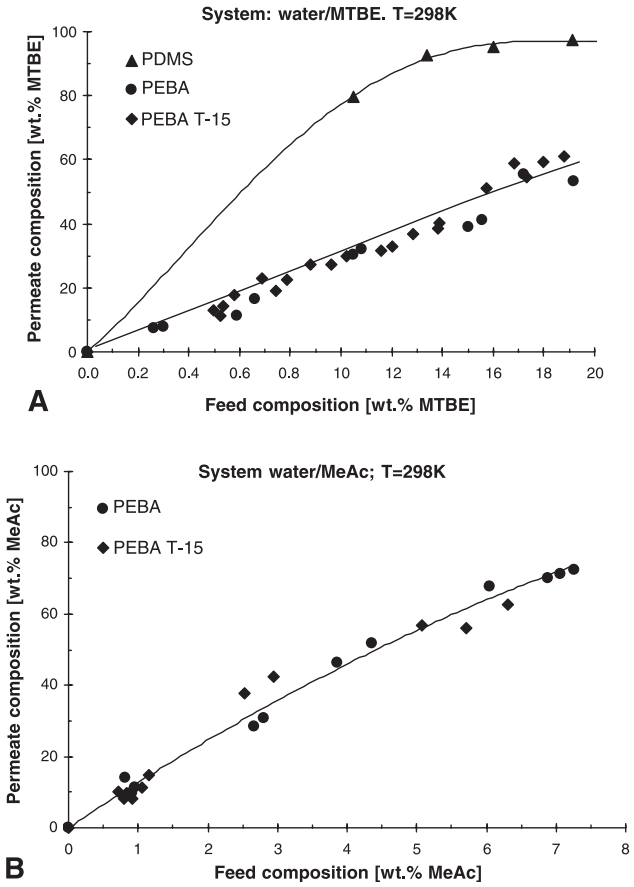
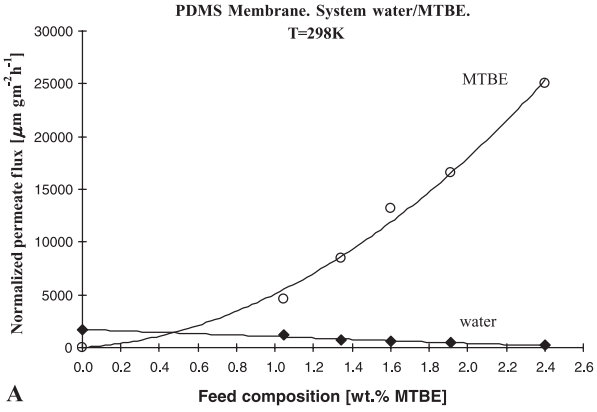
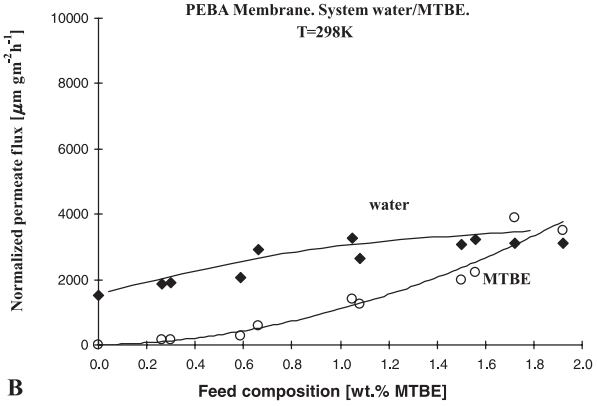


Figure 4. Selective properties of hydrophobic membranes in contact with the binary mixtures. (A) Water–MTBE mixture. (B) Water–MeAc mixture.

Figure 4B) were quite similar to those observed for water–MTBE mixture. The T-15 zeolite filling did not improve the selectivity properties of PEBA T-15 membrane in contact with the water–MeAc mixture.

The transport properties of investigated membranes in contact with water–MTBE mixtures are presented in Figure 5. For all investigated membranes, the permeate flux of MTBE increased with increasing MTBE content in the feed mixture and this relation was of the exponential type. The highest MTBE permeate flux was produced using PDMS membrane in contact with 2 wt% MTBE in water. The normalized permeate flux was 15





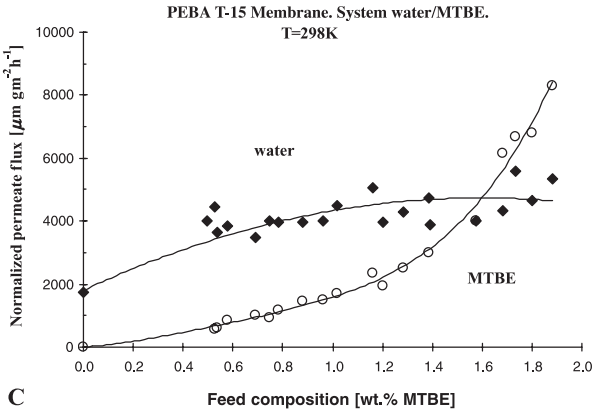


Figure 5. Transport properties of the hydrophobic membranes in contact with the binary water-MTBE mixture. (A) PDMS membrane. (B) PEBA membrane. (C) PEBA T-15 membrane.

(μm kg m^{-2} h^{-1}). The permeate fluxes of MTBE through the PEBA and PEBA T-15 membranes were smaller compared to those through PDMS membrane. The PEBA membrane in contact with 2 wt% MTBE aqueous solution produced an MTBE flux of 3.5 (μm kg m^{-2} h^{-1}), whereas, the PEBA T-15 membrane produced an MTBE flux of 9 (μm kg m^{-2} h^{-1}) in the same conditions.

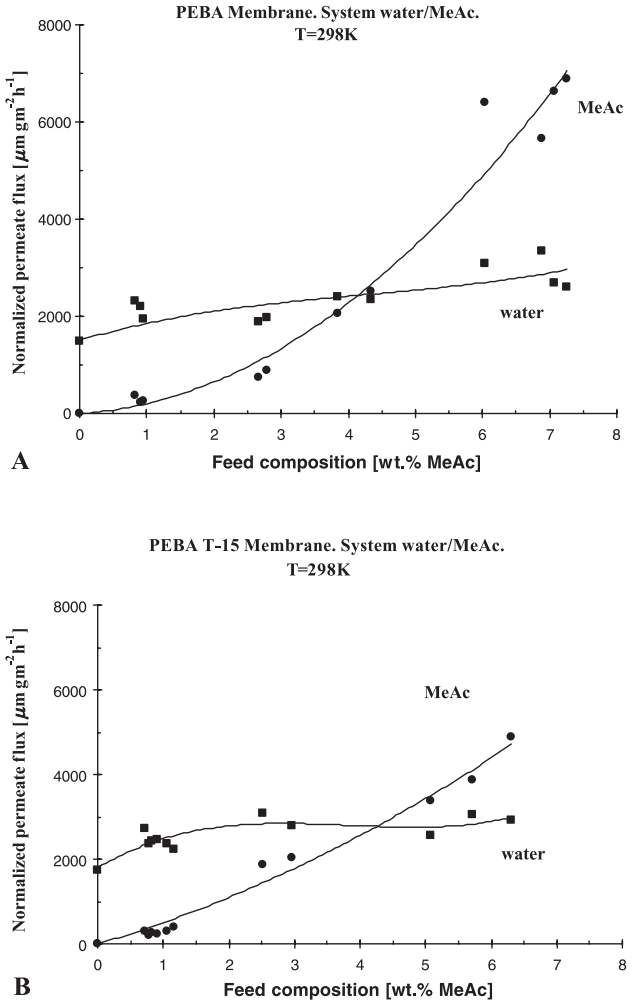


Figure 6. Transport properties of (A) PEBA and (B) PEBA T-15 membrane in contact with binary water–MeAc mixture.

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The concentration dependence of the water flux was different for the PEBA membranes and the PDMS one. For the former ones, the flux of water increased slightly and became practically constant at a feed concentration above 0.8 wt% MTBE (see Figure 5B, C). Such behavior suggests couplings between water and MTBE molecules during transport through PEBA and PEBA T-15 membranes. The water flux through the PDMS membrane was small and decreased monotonically within the investigated concentration range (see Figure 5A), which suggested that water molecules were continuously excluded from this highly hydrophobic membrane with the increasing amount of MTBE transported through the membrane.

In Figure 6, the transport properties of PEBA and PEBA T-15 membranes in contact with the water–MeAc mixture are presented. The relations between feed composition and the transport properties found for this system were quite similar to those observed for the water–MTBE mixture. The T-15 zeolite filling did not improve the selectivity properties of the PEBA T-15 membrane in contact with the water-MeAc mixture (see Figures 4 and 6) but it did improve the transport properties of this membrane.

The transport properties of PEBA and PEBA T-15 membranes in contact with other binary mixtures studied are summarized in Table 6. The flux of water through the PEBA membrane was similar for all investigated mixtures, except for the water–MTBE one. This enhanced water transport suggested strong synergetic effects between water and MTBE molecules. The zeolite filling did not influence the transport properties in the case of the water–MeOH mixture, i.e., in the case where both components of the mixture were relatively polar. On the other hand, if membranes contacted aqueous organic mixtures in which the organic component possessed low polarity, the zeolite filling enhanced both the flux of organic component

Table 6. Normalized molar fluxes through PEBA and PEBA T-15 membranes in contact with water–organic binary mixtures investigated.

System	Feed composition (wt.% organic component)	PEBA		PEBA T-15	
		$J_{organic}$	J_{water}	$J_{organic}$	J_{water}
		(10 μm kg m^{-2} h^{-1})		(10 μm kg m^{-2} h^{-1})	
BuAc/water	0.2	1.3	11	1.8	16
MTBE/water	1.0	1.2	16	1.8	24
MeAc/water	2.0	0.8	11	1.5	15
MeOH/water	2.0	0.2	9	0.2	10

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and the flux of water molecules. The incorporation of the inorganic hydrophobic particles into the polymeric matrix should result in an increase in the diffusion path of all transported species and in an increase of the sorption of the nonpolar component of the mixture (see Table 5). Because the amount of zeolite filling in PEBA T-15 membrane was relatively small (10 wt%), so the tortuosity increase was rather small. However, the swelling increase of both polyamide and polyether segments was substantial enough to increase the transport of small water molecules through the PEBA T-15 membrane.

CONCLUSION

PDMS, PEBA, and zeolite-filled PEBA dense membranes prepared by the casting method showed the hydrophobic character in the contact with different water–organic mixtures. The preparation conditions (i.e., concentration of polymer in the casting solution, and amount of curing agent) influenced the membrane properties to a small extent only. Membranes made of PDMS swelled better compared to membranes made of PEBA polymer. Sorption of organic solvents into PDMS was inversely proportional to the polarity of solvent. In the case of PEBA membranes, the highest sorption occurred in contact with pure methanol, which was caused by the presence of polyamide blocks in the membrane structure. PDMS and PEBA membranes showed similar affinity to organics in contact with water–organic binary mixtures: the highest sorption was found for the water–BuAc system and the lowest for the water–MeOH mixture. Zeolite-filled, PEBA T-15 membrane showed better sorption properties than the unfilled PEBA one, especially in contact with more concentrated water–organic solutions. Both zeolite-filled and unfilled PEBA membranes possessed similar selectivity in contact with water–organic binary mixtures. The pervaporation fluxes were higher through the PEBA T-15 membrane when compared to unfilled PEBA one.

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