

Pervaporation Membranes Based on Imide-Containing Poly(amic acid) and Poly(phenylene oxide)

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ABSTRACT: Three imide-containing poly(amic acids) were synthesized and used for homogeneous and composite membrane preparation. The transport properties of composite membranes consisting of an imide-containing poly(amic acid) top layer on an asymmetric porous poly(phenylene oxide) support were studied in the pervaporation of aqueous solutions of organic liquids (ethanol, isopropanol, acetone, and ethylacetate) and organic/organic mixtures (ethylacetate/ethanol, methanol/cyclohexane). For most of the aqueous/organic mixtures, the composite membranes exhibited dehydration properties. Dilute aqueous solutions of ethylacetate were an exception. In these solutions, the com-

posite membranes exhibited organophilic properties, high permeability, and selectivity with respect to ethylacetate. In the pervaporation of methanol/cyclohexane mixtures, methanol was removed with very high selectivity. To account for specific features of pervaporation on the composite membranes, the sorption and transport properties of homogeneous membranes prepared from polymers comprising the composite membrane [imide-containing poly(amic acids) and poly(phenylene oxide)] were studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2361–2368, 2003

Key words: composites; membranes

INTRODUCTION

Membrane technology has recently been used for the purification, concentration, and fractionation of gas and liquid mixtures. The range of commercial membranes is limited. Therefore, the development of new polymers for membranes with high performance and selectivity is of scientific and practical significance. Aromatic polyimides have many valuable physicochemical properties and improved chemical and thermal stability, which are important for their use in gas separation and ultrafiltration and microfiltration.^{1–3} The specific chemical structure of polyimides profoundly affects liquid mixture separation by pervaporation (PV). For this reason, polyimide derivatives with a considerable amount of functional groups are used in PV.^{4–6} Polyimide–poly(amic acids) or imide-containing poly(amic acids) (PI–PAAs) containing imide rings, carboxyl and isomeric amic acid groups in elementary units were studied in this work.

In PV, a liquid is sorbed on the membrane surface, diffused through the membrane, and then desorbed and removed from the other membrane side in the form of vapor with a low partial pressure; this is achieved by evacuation.^{7–9} PV transport through a

nonporous membrane may be described in terms of a solution–diffusion mechanism by the equation

$$P = S \times D$$

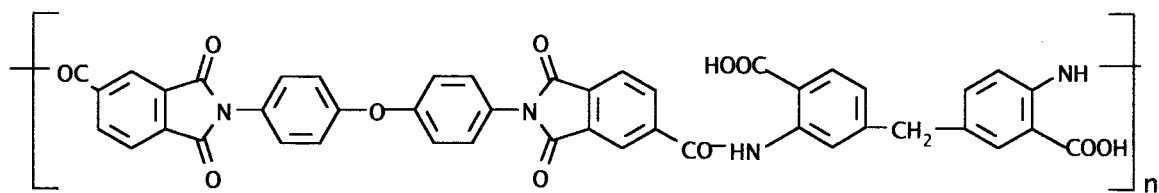
where P is permeation, S is sorption, and D is diffusion. Sorption is a thermodynamic parameter and a measure of the penetrate amount sorbed by the membrane in equilibrium conditions. Diffusion is a kinetic parameter and a characteristic of mass-transfer rate through the membrane. The permselectivity of an organic liquid mixture in PV is mainly due to a higher sorption for one component of the mixture than for the other component. However, excessive sorption for one component causes considerable membrane swelling and results in a loss of selectivity and mechanical strength. Therefore, membrane design should meet certain requirements with respect to the chemical structure of polymers contained in the membrane and the mode of their combination in layers or blends. Composite membranes containing two or several layers are generally used for separation by the solution–diffusion mechanism.^{10–12}

In this study, three PI–PAAs with different structures (Scheme 1) were synthesized and were used for preparation of composite membranes consisting of a PI–PAA top layer on an asymmetric porous support from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Their sorption and transport properties were studied for aqueous/organic and organic/organic mixtures in PV. Similar properties were also studied for homogeneous membranes prepared from PI–PAA and PPO.

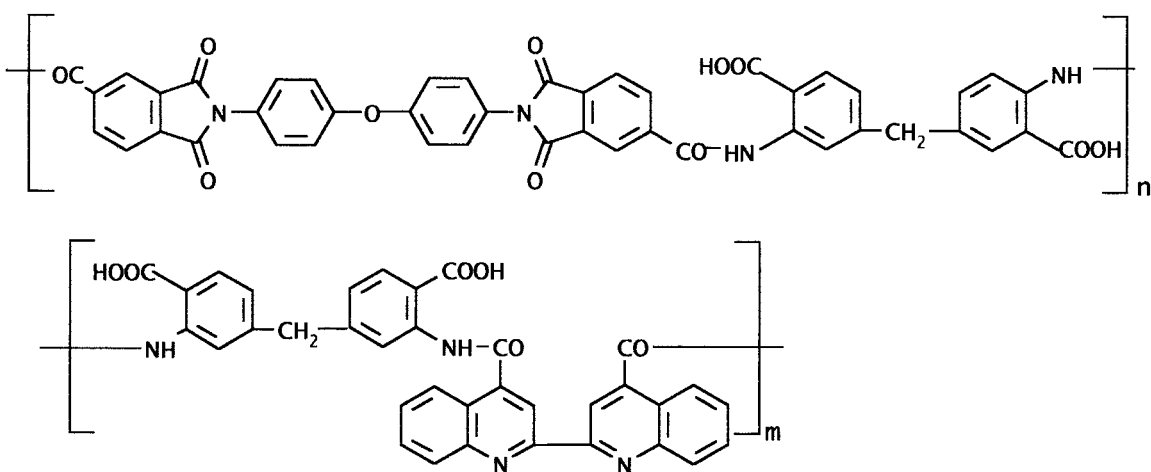
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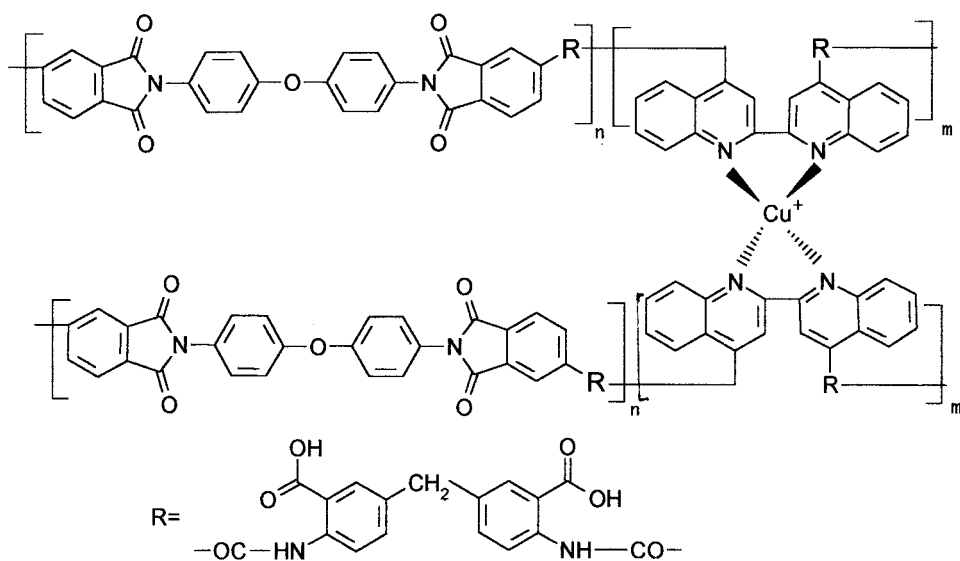
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PI-PAA-1



PI-PAA-2



$$n:m = 80:20$$
PI-PAA-2-Cu⁺

Scheme 1

EXPERIMENTAL

Materials

Monomer and solvent purification and PI-PAA synthesis were carried out by techniques described in ref. 13. Methylenebis(anthranilic acid) was used without additional purification. Thionyl chloride was distilled, and the fraction at 75.5°C was taken off. *N*-Methylpyrrolidone (NMP) was dried over calcium hydride and distilled (boiling point = 78°C at 10 mmHg).

The synthesis of 2,2'-biquinoline-4,4'-dicarboxylic acid was achieved by the Pfitzinger reaction with isatin and acetone.¹⁴

Synthesis of dichloroanhydride of 2,2'-biquinoline-4,4'-dicarboxylic acid

A single-necked round-bottom flask equipped with a reflux condenser was charged with 2,2'-biquinoline-4,4'-dicarboxylic acid (0.016 mol) and thionyl chloride (250 mL). After it was boiled for 4.5 h, the mixture was cooled. The resulting crystals were filtered, washed with toluene, and dried. The yield was 93%. The synthesized dichloroanhydride melted at 251–252°C.

The syntheses of *N,N'*-diphenyl oxidebis(trimellitimido) acid and its dichloroanhydride were described in ref. 13.

Synthesis of imide-containing poly(amic acids)

A two-necked flask equipped with a stirrer was charged with methylenebis(anthranilic acid) (0.002 mol) and NMP (6.5 mL), and the mixture was stirred until the acid was completely dissolved. The solution was cooled to -15°C. The dichloroanhydride of 2,2'-biquinoline-4,4'-dicarboxylic acid (0.0004 mol) and the dichloroanhydride of *N,N'*-diphenyl oxidebis(trimellitimido) acid (0.0016 mol) were added to the solution. After the suspension was stirred at -15°C for 50 min, the cooling was stopped, and propylene oxide (0.05 mL) was added. The mixture was stirred at room temperature for 4–5 h.

A polymer-metal complex (PI-PAA-2-Cu⁺) was obtained by the addition of PI-PAA-2 dissolved in NMP to an equimolar amount of cuprous chloride dissolved in NMP. The complex formation was carried out in a flask with a stirrer for a few minutes at room temperature. The solution of PI-PAA-2-Cu⁺ had an intense violet color.

PPO is a commercially available material.

Membranes

PI-PAA/PPO composite membranes were prepared by the casting of a 2–7% PI-PAA solution in NMP on the surface of a PPO support with pores protected by decane from the penetration of the polymer solution.

Excess solution was poured off, and the membrane was dried to a constant weight.¹⁵

An asymmetric membrane or a PPO support was prepared from an 8% PPO solution in a chloroform butanol solvent (85:15 wt %). A 350 μm thick layer cast on a glass plate was subsequently immersed into ethanol and then into decane.

Homogeneous PPO membranes (100–120 μm thick) were obtained by casting a 5 wt % PPO solution in chloroform on cellophane and drying at 25°C.

Homogeneous PI-PAA membranes (~20 μm thick) were obtained by casting a 2–7 wt % PI-PAA solution in NMP on a glass plate and drying at 80°C.

Methods of investigation

PV properties were measured on a laboratory cell with an effective membrane area of 14.8 cm² at constant temperature of 50°C with stirring. Downstream pressure below 30 Pa was maintained. The permeate was collected in a liquid nitrogen trap, weighed, and then analyzed with the aid of a refractometer. Ethylacetate (EA), methanol, ethanol, isopropanol, cyclohexane (CH), and water were used as mixture components.

Membrane permeation flux [Q (kg/m² h)] was determined as the amount of liquid transported through unit of the membrane area and per time unit.

The selectivity or the separation factor (α) was defined by the equation

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

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.

The degree of equilibrium swelling, or sorption [S (g of liquid/100 g of dry polymer)], was determined at 20°C and calculated by the equation

$$S = \frac{W_s - W_d}{W_d}$$

where W_s is the weight of a swollen membrane and W_d is the weight of a dry membrane.

RESULTS AND DISCUSSION

PI-PAA belongs to the poly(amic acids) class and are used as prepolymers of polybenzoxazinoneimides. Aromatic polyimides are known to exhibit high mechanical properties and thermal and chemical stability¹⁶ and find their application as membranes.¹ However, traditional poly(amic acids), which are prepolymers in processing polyimides membranes, are hydrolytically unstable; therefore, their molecular weight rapidly drops during storage.¹⁷ Another group

of polyheteroarylenes, poly(benz-3, 1-oxazinone-4s), are characterized by lower physicochemical properties, but their prepolymers exhibit markedly higher hydrolytic stability.¹⁸ A novel polymer type, polybenzoxazinoneimides, which combine the valuable properties of polyimides and polybenzoxazinones, was developed in our previous work.¹³ Prepolymers of polybenzoxazinones, imide-containing poly(amic acids) exhibiting good physicochemical properties, are thermally stable up to 180°C and are hydrolytically stable (which is more important). Figure 1 shows that the reduced viscosity of the PI-PAA-1 solution did not change during storage at room temperature for 4 months. The hydrolytic stability of PI-PAA-containing imides and amic acids groups in each elementary unit made it possible for us to apply these polymers for PV membranes.

In this study, imide-containing polyamic acids with different structures were studied. They were the PI-PAA-1 homopolymer, the PI-PAA-2 copolymer, and the PI-PAA-2-Cu⁺ complex. The last polymer-metal complex was obtained by the insertion of 2,2'-biquinoline units in the polymer backbone chain.

PV of aqueous/organic mixtures through the composite PI-PAA/PPO membrane

One of the problems that may be solved by PV is the separation of aqueous/organic mixtures.^{19–22} The direction of selective mass transfer in the PV of aqueous/organic mixtures depends on the balance of the hydrophilic and hydrophobic properties of the membrane polymer. Most membranes based on aromatic polyimides exhibit dehydration properties.^{23,24}

Table I lists the PV properties of the PI-PAA-1/PPO composite membrane for aqueous solutions containing 10% different organic liquids. The composite membrane as a whole displayed the expected dehydration properties and ensured the predominant water mass transfer from mixtures with ethanol, isopropanol, and acetone (with the exception of the EA aqueous solution). High permeability and selectivity

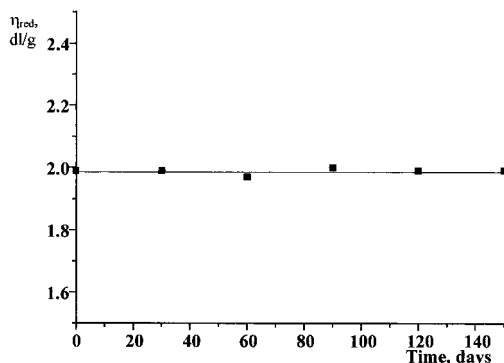


Figure 1 Reduced viscosity of PI-PAA-1 solution versus storage time at room temperature.

TABLE I
PV of Aqueous Solutions Containing 10 wt % Organic Liquids Through the PI-PAA-1/PPO Composite Membrane at 50°C

Organic liquid	Permeate content (wt %)		Flux ₂ (kg/m ² h)	α _{H₂O}
	Organic liquid	H ₂ O		
Acetone	4.5	95.5	0.22	2.4
Ethanol	4.0	96.0	0.51	2.7
Isopropanol	0.1	99.9	0.20	111
EA	99	1.0	1.0	891 ^(EA/H₂O)

with respect to EA was established for a 10% EA aqueous solution.

To determine the reason for the abnormal selectivity of the PI-PAA-1/PPO composite membrane with respect to EA, homogeneous membranes from polymers comprising a composite membrane were prepared, and their sorption and mass-transfer properties for individual liquids and their mixtures were studied (Tables II and III). These properties of homogeneous membranes need to be compared to estimate the contribution of composite membrane components in selective mass transfer. According to the literature data,^{12,25,26} the directions of selective mass transfer through the top layer and the support polymers for some types of composite membranes in the PV of a certain mixture can differ. Therefore, the support polymer contribution to the total selectivity of a composite membrane may be positive, negative, or neutral with respect to the separation aim. In the third case only, the total selectivity of a composite membrane is entirely determined by the selectivity of the top-layer polymer.

To study the influence of the chemical structure of the top-layer polymer on composite membrane properties, the sorption and transport properties of homogeneous membranes prepared from imide-containing poly(amic acids), PI-PAA-1, PI-PAA-2, and PI-PAA-2-Cu⁺, were compared.

Properties of homogeneous membranes

Table II lists the degree of equilibrium swelling or sorption and the specific permeation flux (Ql) of individual liquids through homogeneous membranes based on all of the studied polymers. The total permeation flux was inversely proportional to film thickness (l), which ranged from 20 to 100 μm, and permselectivity strongly depended on it. Therefore, the specific permeation flux value was used to compare the permeability of homogeneous membranes with different thicknesses, just as in ref. 4.

Chemical structure variation in imide-containing poly(amic acids), which ranged from the PI-PAA-1 homopolymer to the PI-PAA-2 copolymer to the PI-

TABLE II
Sorption and Permeability of Homogeneous Membranes for Individual Liquids

Polymer	Water		Ethanol		EA	
	S	Ql (kg μm/m ² h)	S	Ql (kg μm/m ² h)	S	Ql (kg μm/m ² h)
PI-PAA-1	4.7	1.66	5.7	1.14	8.5	0.180
PI-PAA-2	5.6	1.78	7.1	1.19	9.8	0.191
PI-PAA-2-Cu ⁺	6.8	1.96	7.7	1.24	11.0	0.196
PPO	0.1	0.2	14.0	1.96	34.0	16.8

PAA-2-Cu⁺ complex, led to increasing sorption and permeation of individual liquids. We suggest that enhanced sorption was determined by the presence of biquinoline rings in the PI-PAA-2 and PI-PAA-2-Cu⁺ structures.

The data in Table II on the sorption and permeation properties of individual liquids were used for the comparative analysis of PI-PAA and PPO membranes. The order of the sorption value increase was identical for PI-PAA and PPO: water < ethanol < ethylacetate. At the same time, the sorption values for the PPO membranes differed greatly: 0.1 < 14 < 34. This determined the abnormally high permeability of PPO to EA. In contrast, for the PI-PAA-1 membrane, the sorption values of water, ethanol, and ethylacetate were close to each other: 4.7 < 5.7 < 8.5. Therefore, the transport properties of PI-PAA membranes were determined by the diffusion factor, depending on the molecular size of the penetrate. Because the kinetic diameter of the penetrate molecules decreased in the following order, EA > ethanol > water, PI-PAA membranes were more permeable to water than to EA molecules. Hence, a considerable difference in the permeability of PPO and PI-PAA membranes for individual liquids was determined by the difference in the principal mass-transfer constituents. These constituents were the thermodynamic or sorption factor for PPO and the kinetic or diffusion factor for PI-PAA.

When the feed composition is considered, the data in Table III on the sorption and PV properties of the homogeneous PI-PAA and PPO membranes for aqueous solutions of ethanol and ethylacetate were in agreement with those in Table II. The PPO membrane

exhibited high permeability and selectivity in the separation of the EA/water mixture ($\alpha_{EA} = 1116$) and was almost nonselective in that of the ethanol/water mixture. On the other hand, all of the PI-PAA membranes exhibited dehydration properties for the ethanol/water mixture ($\alpha_{H_2O} = 11$) and were nonselective in the PV of the EA/water mixture. The sorption and specific permeation flux values in the PV of mixtures (Table III) were intermediate between those of individual substances (Table II) for all types of homogeneous membranes.

The high selectivity and permeability of PPO for removing EA from its dilute aqueous solutions in the PV process were the most interesting transport properties of the previously discussed homogeneous membranes.

Another attractive and predictable property was the increased selectivity of PI-PAA in the separation of concentrated ethanol/aqueous solutions. It was established that selectivity increased to 55 in the PV of a 90 wt % ethanol aqueous solution with the PI-PAA-1 membrane. The manifestation of dehydration properties by all of the PI-PAA membranes in the PV of an ethanol/water mixture agreed with the literature data¹⁹ on the mechanism of the preferential mass transfer of water molecules, which involves their interaction with polymer functional groups. The preferential transport of water molecules through PI-PAA membranes was due to the presence of imide rings and amic acid groups in the polymer and also resulted from the smaller kinetic diameter of water molecules compared to that of ethanol molecules. Furthermore, the PI-PAA-2-Cu⁺ permeability could increase be-

TABLE III
Sorption and PV Properties of Homogeneous Membranes for the Water/Organic Mixture

Polymer	10% Ethanol + water					10% EA + water				
	S	Ql (kg μm m ² h)	Permeate content (wt %)		α_{H_2O}	S	Ql (kg μm m ² h)	Permeate content (wt %)		α_{H_2O}
			EtOH	H ₂ O				EA	H ₂ O	
PI-PAA-1	4.8	1.75	0.2	99.8	11	7.9	3.6	8	92	1.2
PI-PAA-2	6.8	2.10	0.2	99.8	11	9.3	3.9	8	92	1.2
PI-PAA-2-Cu ⁺	7.2	2.41	0.2	99.8	11	9.8	4.2	10	90	1.0
PPO	5.4	1.68	8.0	92.0	1.2	1.0	15.0	99.2	0.8	1116 (EA/H ₂ O)

cause of the ion–dipole interaction between Cu^+ cations and water molecules.

The selective properties of the PI–PAA membranes were retained in the PV of dilute ethanol/aqueous solutions. This indicated that the degree of PI–PAA plastification by the more permeable component (water) was low.

Properties of composite membranes

PV of the EA/water mixture

According to the data in Table II, the sorption properties and permeability level of homogeneous PI–PAA and PPO membranes with respect to water, EA, and their mixtures differed markedly. This result became the basis for a more careful study of the transport properties of the composite membranes based on these polymers for the PV of dilute EA/aqueous solution. The formation of a thin PI–PAA top layer on the skin-layer surface of the PPO support yielded a PI–PAA/PPO composite membrane. The skin layer (free of pores) of the PPO support participated in diffusion mass transfer through the composite membrane and thus provided a contribution to composite membrane total selectivity and to the PI–PAA top layer.

Figure 2 shows the dependence of flux and permeate content on EA concentration in the feed for three types of PI–PAA/PPO composite membranes. The PI–PAA-1, PI–PAA-2, and PI–PAA-2- Cu^+ imide-containing poly(amic acids) were used as top-layer polymers. All of the membranes were characterized by a high level of selectivity to EA in the studied feed content range (≤ 10 wt % EA). The composite membranes exhibited improved permeability in the case of PI–PAA-2- Cu^+ top layer [Fig. 2(a)] and a higher level of EA removal in the case of PI–PAA-1 top layer [Fig. 2(b)].

To estimate the contribution of each layer to the selective properties of the PI–PAA/PPO composite membrane, the transport properties of the composite membranes (Fig. 2) were compared with the sorption and mass-transfer properties of the homogeneous membranes (Tables II and III). This comparison led us to the conclusion that the PPO contribution was the principal factor. The skin-layer (free of pores) surface of the PPO support was the lowest boundary of the diffusion mass-transfer zone in the composite membrane and exhibited very high thermodynamic affinity to EA. At the same time, the data in Table II show that the PI–PAA top layer did not participate in selective mass transfer through the composite membrane. Therefore, selectivity values for the composite PI–PAA/PPO and homogeneous PPO membranes were close for the separation of mixtures with the same composition. The composite membranes exhibited high permeability because the thickness of the PI–

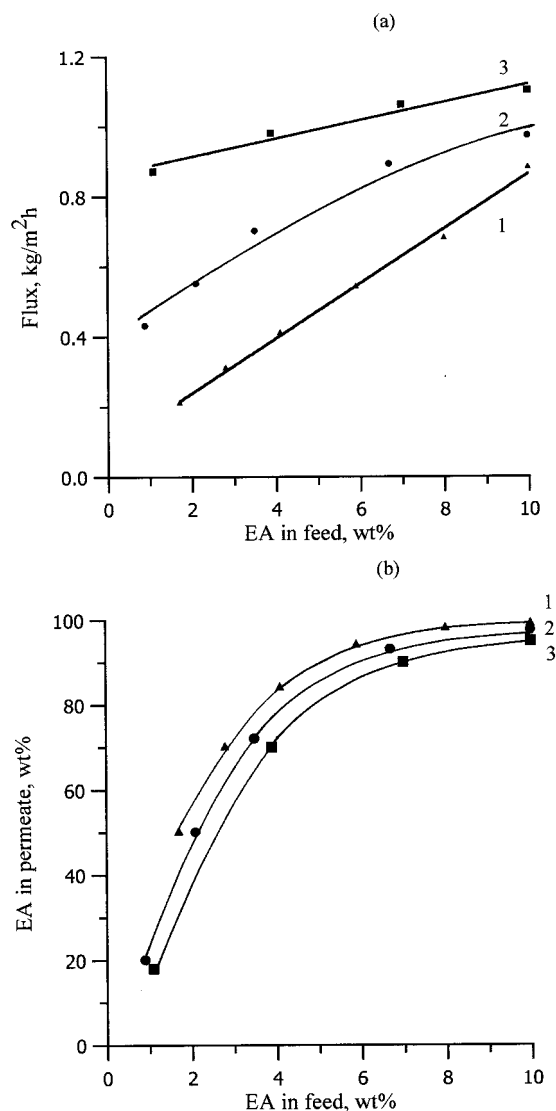


Figure 2 Dependence of (a) flux and (b) EA content in the permeate on the EA content in the feed for the PV of dilute EA aqueous solutions through (1) PI–PAA-1/PPO, (2) PI–PAA-2/PPO, and (3) PI–PAA-2- Cu^+ /PPO composite membranes at 50°C.

PAA top layer and the PPO skin layer in the zone of diffusion mass transfer were thin. Hence, the achieved level of permeability and selectivity in the PI–PAA/PPO composite membranes was of practical significance for their application for concentrating dilute aqueous EA solutions.

PV of the ethanol/water mixture

The separation of the ethanol/water mixture with the PI–PAA-1/PPO composite membrane was studied in a wide feed-content range. Figure 3 shows the dependence of flux and selectivity on water content in the feed. The permeate was enriched by water in the entire feed-content range. However, the PV of the ethanol/water mixture when the composite mem-

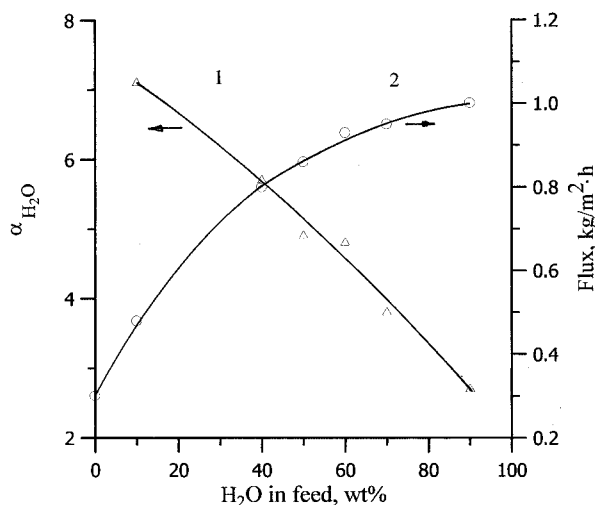


Figure 3 Dependence of (1) selectivity and (2) flux on the water content in the feed for the PV of the ethanol/water mixture through the PI-PAA-1/PPO composite membrane at 50°C.

branes were used was less selective than when the homogeneous membranes ($\alpha_{H_2O} = 2.7$ and 7.1 for the PI-PAA-1/PPO composite membrane and $\alpha_{H_2O} = 11$ and 55 for the homogeneous PI-PAA-1 membrane in the PV of 10 and 90% ethanol aqueous solutions) were used. The analysis of the transport properties of the PPO homogeneous membrane (Tables II and III) shows that the PPO support contribution to the total selectivity of the composite membranes in the PV of the ethanol/water mixture was slight. The PI-PAA-1 top layer took an active role in mass transfer. The decrease in the composite membrane selectivity was probably determined by the fact that the PI-PAA layer

was thin (2–4 μm). Under the conditions of more intense mass transfer, this layer swelled on the entire cross-section, in contrast to swelling in the thicker (20 mm) homogeneous membranes.

PV of the ethylacetate/ethanol mixture

A third possible combination of substances listed in Table II, the EA/ethanol mixture, was also tested. The PV of the EA/ethanol mixture was studied over a wide feed-content range with PI-PAA-1/PPO composite membrane. Figure 4 shows the dependence of permeability and selectivity on the EA content in the feed. The EA/ethanol mixture separation occurred with low selectivity and the permeate became enriched with EA. This result correlated with the data on the sorption and permeation of EA and ethanol in PI-PAA-1 and PPO films (Table II). It was apparent that the predominant EA permeation through the PI-PAA-1/PPO composite membrane was caused by the predominant EA sorption as compared with ethanol sorption in both the PI-PAA-1 and PPO components.

PV of the methanol/CH mixture

The methanol/CH mixture was used as a model of the methanol/methyl-*t*-butyl ether (MTBE) mixture. MTBE finds its application as an antiknock additive to gasoline. The positive result in the PV of methanol/CH mixtures can be used in MTBE purification from impurities during its synthesis.^{12,27}

The PV of the methanol/CH mixture in a wide feed-content range was studied with the PI-PAA-1/PPO composite membrane. Figure 5 shows the depen-

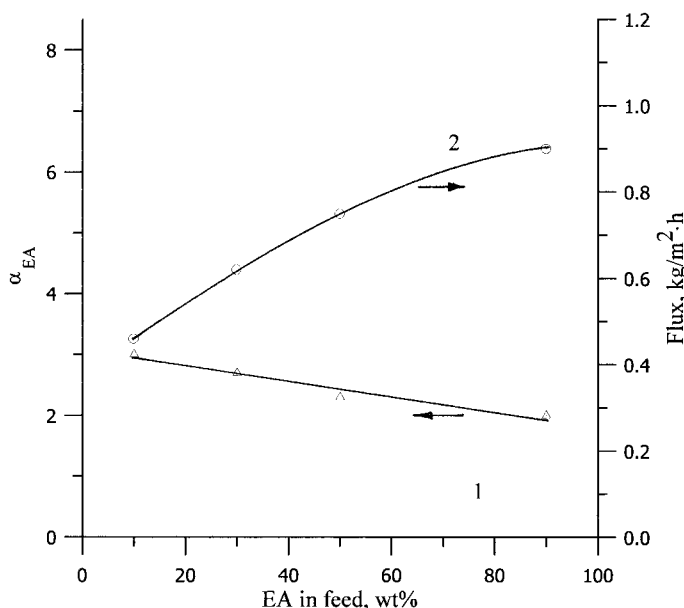


Figure 4 Dependence of (1) selectivity and (2) flux on the EA content in the feed for the PV of the EA/ethanol mixture through the PI-PAA-1/PPO composite membrane at 50°C.

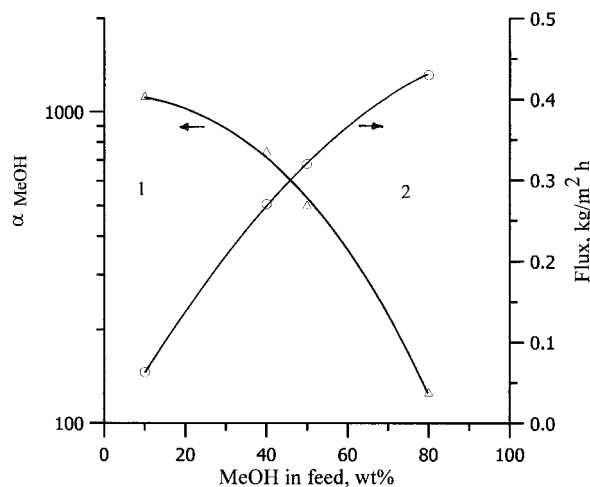


Figure 5 Dependence of (1) selectivity and (2) flux on the methanol content in the feed for the PV of the methanol/CH mixture through the PI-PAA-1/PPO composite membrane at 50°C.

dence of flux and selectivity on the methanol content in the feed. The permeate was enriched by methanol in the entire feed-content range. At low methanol concentration in the feed, the selectivity of methanol removal exceeded 10^3 .

The study of equilibrium swelling showed the absence of CH sorption ($S \cong 0$) in both PI-PAA-1 and PPO. The degree of equilibrium sorption of methanol in PI-PAA-1 and PPO were in close agreement ($S \cong 8-11$). Consequently, in the PV of the methanol/CH mixture, the directions of selective mass transfer through polymers comprising composite membrane coincided. This made it possible to achieve a high selectivity level.

CONCLUSIONS

The PV of aqueous/organic and organic/organic mixtures through composite membranes containing a PI-PAA top layer with different chemical structures on asymmetric porous PPO support was studied. The sorption and transport properties of homogeneous membranes from polymers comprising the composite membranes were investigated to explain the specific features of PV through the composite PI-PAA/PPO membranes.

In the PV of aqueous/organic mixtures, PI-PAA/PPO composite membranes exhibited dehydration properties for aqueous solutions of ethanol, isopropanol, and acetone. For the EA/aqueous mixture, this membrane exhibited organophilic properties and selectivity inversion in favor of EA. In the separation of EA mixtures with water and ethanol, predominant EA permeation resulted from predominant EA sorption as compared with that of water and ethanol in both the PI-PAA and PPO components. However, the PPO contribution was the principal factor. The skin-layer

(free of pores) surface of the PPO support was the lowest boundary of diffusion mass-transfer zone in the composite membrane and exhibited a very high thermodynamic affinity to EA.

In the PV of the methanol/CH mixture through composite PI-PAA/PPO membranes, methanol removal was highly selective. The high selectivity was due to the coincidence of selective mass-transfer direction through polymers comprising the composite membranes.

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