Cellulose–Poly(acrylamide or acrylic acid) Interpenetrating Polymer Network Membranes for the Pervaporation of Water–Ethanol Mixtures

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ABSTRACT: A new type of interpenetrating polymer network (IPN) pervaporation membranes based on cellulose and synthetic polymers was developed. They were prepared by free-radical polymerization of acrylamide or acrylic acid in the presence (or absence) of the crosslinking agent (allyldextran or *N,N'*-methylenebisacrylamide) within cellophane films swollen in the reaction mixture. The swelling behavior of these membranes in water–ethanol solutions and their separation characteristics were investigated depending on the polyacrylamide (PAAm) or poly(acrylic acid) (PAA) content in the IPN (C_p) and for ionic cellulose–PAA membranes depending on the degree of neutralization of carboxylic groups and on the type of counterions. IPN membranes were selective over a wide range of ethanol concentration in the feed. The separation factor (α) and the permeation rate (P) significantly improved with increasing C_p in IPN membranes, especially for the cellulose–PAA(K^+ form) membranes (for 86% EtOH feed at 50°C, and α and P values reached 1500 and 1.6 kg/m^2 h, respectively). The results for ionic and nonionic IPN membranes were compared. The separation characteristics of membranes were in good correlation with their swelling behavior. The α values of the membranes depended on the affinity of the IPN polymer chains functional groups for water. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 761–769, 1998

Key words: membrane; interpenetrating polymer network; cellulose; poly(acrylamide or acrylic acid); pervaporation

INTRODUCTION

The dehydration of organic solvents by pervaporation through membranes is attracting increasing interest in industry as an energy-efficient process.[1,2] Cellulose has long been studied as a membrane in a wide variety of applications,[3] including ethanol–water separation.[4–6] Cellulose membranes exhibit good mechanical characteristics but their selectivity with respect to water in pervaporation processes is relatively low. Thus, the separation factor for cellophane membranes does not exceed 10 for 90 wt % EtOH at 30°C.[5] Polyelectrolyte cellulose derivatives, such as carboxymethylcellulose (CMC), are much more selective because of the presence of highly hydrophilic ionic groups.[7] Moreover, membranes containing poly(acrylic acid) (PAA), which is a polyelectrolyte with a high charge density, exhibit a higher level of selectivity than does CMC.[8,9] The separation factor of membranes based on CMC increased from 500 to 2000 when 20% PAA was added to casting solutions for increasing the ionic group content.[7] However, the permeation rate of these highly selective membranes is relatively low (0.05 kg/m^2 h at 25°C). In contrast to films from CMC, membranes based on CMC–PAA mixtures were turbid, which indicated phase separation of the polymers.[7] On the other hand, it is known that the

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formation of composite materials according to the principle of interpenetrating polymer networks (IPNs) preparation makes it possible to combine incompatible or partially compatible polymers and provides unique possibilities for controlling their mechanical and physicochemical properties.[10,11] It is necessary to note that only few publications refer to IPN membranes for gas or liquid separation.[12–18] Thus, it has been shown[12] that polyurethane–polystyrene IPN membranes have a higher separation factor for gas separation than have membranes prepared by the blending of the same polymers because a more compatible mixture is formed. Various types of IPN membranes including membranes based on polyurethane–poly(methyl methacrylate–acrylic acid) copolymers for the pervaporation of water–ethanol mixtures were prepared and investigated.[13–15] The use of the IPN technique for the formation of the highly selective pervaporation membranes based on polyacrylamide–poly(vinyl alcohol) copolymers has been shown to be efficient.[16] This type of IPN membranes has a separation factor up to 4100 and a permeation rate of about 0.06–0.1 kg/m^2 h for 95 wt % ethanol solution at 75°C.

The aims of the present investigation were, first, the development of a new method for the preparation of composite pervaporation IPN-type membranes based on cellulose and acrylic polymers and, second, the study of transport properties of these membranes in the separation of water–ethanol mixtures depending on their composition.

EXPERIMENTAL

Materials

Industrially manufactured cellophane (Vladimir city) 27-μm thick containing 10 wt % of glycerol as a plasticizer was washed in distilled water for 24 h to remove low molecular weight impurities and vacuum-dried over P_2O_5 to a constant weight. Acrylamide (AAm) (Aldrich Chemicals) was recrystallized twice from benzene. Acrylic acid (AA) (Aldrich Chemicals) was distilled under a vacuum at a pressure of 18 Torr. A fraction with a boiling temperature of 47°C was chosen. All other reagents were of analytical grade and used without additional purification.

Synthesis of IPN Membranes

To synthesize IPN cellulose–polyacrylamide (C–PAAm) and cellulose–poly(acrylic acid) (C–PAA) membranes, cellophane films were allowed to swell in aqueous reaction solutions of AAm or AA for 10 min to the degree of swelling close to the equilibrium state. Subsequently, these monomers were subjected to free-radical polymerization or copolymerization with a crosslinking agent inside the swollen films. Allyldextran (AD) and *N,N'*-methylenebisacrylamide (MBA) were used as crosslinking agents. AAm and AA initial concentrations in the reaction solution (C_m) were varied from 10 to 50 wt % (1.4–7.4M) and from 19 to 75 wt % (2.7–11M), respectively. AD and MBA concentrations (C_{c-a}) were 0.6 and 0.15 wt % (with respect to the monomer). To initiate free-radical polymerization, cobalt(III) acetate proposed by us previously[19] was used at a concentration of $0.5 \cdot 10^{-3}M$.

After impregnation in the reaction solution, the films were immediately placed between two glasses which were fixed with cramps and placed for 3 h in a thermostat at 25°C (for the preparation of C–PAAm membranes) and at 50°C (for the preparation of C–PAA membranes). Subsequently, the membranes were placed in distilled water for 5 days for removing low molecular weight compounds and then vacuum-dried over P_2O_5 to a constant weight for the gravimetric determination of PAAm and PAA content. PAAm content in IPN membranes was also determined by elemental analysis for nitrogen. The protons of the PAA were exchanged by K^+ or Na^+ ions by soaking the acid membranes in an aqueous solution of the desired alkaline hydroxide. The thickness of the IPN membranes obtained was in the range of 40–50 μm. The degree of membrane equilibrium swelling (Q) was determined from the equation $Q = (W_s - W_d)/W_d$, where W_s and W_d are the weights of swollen and dry membranes, respectively.

Synthesis of Hydrogels

Reaction mixtures for hydrogel synthesis were prepared in a similar way as those used in the synthesis of IPN membranes. Free-radical copolymerization of AAm or AA with a crosslinking agent (AD or MBA) was carried out at $C_m = 30$ wt %. AAm homopolymerization was carried out with the C_m value ranging from 10 to 50 wt %. The intrinsic viscosity ($[\eta]$) values of PAAm were determined in water at 25 ± 0.05°C using an Ubbelohde viscometer. The synthesis and analysis of hydrogels and PAAm are described in greater detail in refs. 19–22.

Pervaporation

Experiments on pervaporation were carried out in a flange-type cell. The temperature of the feed solution was kept constant using a thermostat. The effective area of the membrane placed on a porous plastic plate was $1.32 \cdot 10^{-3}$ m^2. A constant downstream pressure (1–3 Torr) was maintained with a vacuum pump. The permeate was collected in a liquid nitrogen trap, weighed, and analyzed with a refractometer (for [EtOH] > 5 wt %) or a chromatograph equipped with a 1-m-long Porapak Q packed column heated at 140°C. Helium was used as the carrier gas.

The pervaporation performance was determined by steady-state mass transfer. The permeation rate (P) was obtained from the expression $P = G/S \cdot t$, where G is the total permeate amount during the time interval t and S is the effective membrane surface area. These data were normalized with respect to the membrane thickness of 25 μm. The separation factor (α) was calculated using the expression

$$\alpha = (W_a/W_b)/(W_c/W_d)$$

where W_a, W_b, W_c, and W_d are the weight fractions of water and ethanol in the feed mixture and in the permeate, respectively.

RESULTS AND DISCUSSION

As mentioned above, the membranes were prepared by free-radical polymerization of AA or AAm within cellophane films swollen in the reaction mixture. For forming a synthetic polymer network, the previously developed method of the synthesis of high-swelling hydrogels was used. The peculiarity of this method is the application of macromolecular allyl polysaccharide crosslinking agents.[18–22] AD with a low molecular weight was used (10,000 g/mol), because the penetration of high molecular weight compounds into cellophane swollen in the reaction solution is limited. For synthetic chains crosslinking MBA was also employed as a widely used "standard" low molecular weight crosslinking agent.

IPN Membranes Composition

Table I gives data on the contents of PAAm or PAA in membranes synthesized with variation of the initial monomer concentration in the reaction solution. The results of gravimetric and elemental analysis give approximately the same values for all C–PAAm membranes. The table also lists data on the calculated contents of PAAm and PAA in IPN membranes obtained by using the amount of the monomer that the membranes absorb upon swelling in the reaction solution. It was assumed in the calculations that the monomer concentration in swollen IPN membranes and in the reaction solution is the same. Close agreement between the calculated and experimental values shows that virtually the entire monomer is polymerized inside the swollen cellophane films, and the resulting polymer, even in the absence of the crosslinking agent, is fixed in the cellophane physical network and is not extracted upon washing in water. This can easily be explained by the fact that the size of the molecules of the synthetic polymer greatly exceeds the maximum size of the regions in the cellophane network that are free for diffusion. The data in Table II show that AAm homopolymerization (in the absence of the crosslinking agent) results in the synthesis of PAAm with the intrinsic viscosity $[\eta] = 7.80–14.8$ dL/g (depending on the initial monomer concentration). The macromolecules having this $[\eta]$ value actually have high molecular weights and large dimensions. The estimation of the molecular weight (M_w) and the radius of gyration (R_G) of PAAm from eqs. (1) and (2)[23,24] gives the values of $M_w = (3–7) \cdot 10^6$ g/mol and $R_G = 975–1613$ Å:

$$[\eta] = 1.00 \cdot 10^4 \cdot M_w^{0.755} \tag{1}$$

$$R_G = 0.147 \cdot M_w^{0.69} \tag{2}$$

Some macromolecules of a synthetic polymer can also be grafted onto the cellulose (Cell–OH) network by covalent bonds because of chain-transfer reactions developed according to the scheme

$$\text{Cell–OH} + M_n^{\bullet} \rightarrow \text{Cell–O}^{\bullet} + M_n$$

$$\text{Cell–O}^{\bullet} + M_n^{\bullet} \rightarrow \text{Cell–O–}M_n$$

where $M_n^{\bullet}$ is a growing macroradical of PAAm or PAA.

Swelling Behavior of Membranes and Hydrogels

The specificity of pervaporation membranes is known to be mainly determined by the level of membrane material interaction with the components of the mixture to be separated. Hence, it

Table I Content of PAAm or PAA(H^+) in Membranes Formed with the Variation of Initial Monomer Concentration in the Reaction Solution

		Wt % of PAAm or PAA(H^+)		Mol % of PAAm or PAA(H^+)	
Membrane	C_m (wt %)	Calculated	Experimental[a]	Calculated	Experimental[b]
C–PAAm	10	7.8	6.5	16.2	15.3
C–PAAm	20	14.5	17.4	27.9	26.7
C–PAAm	30	20.3	19.8	36.7	35.4
C–PAAm–AD	30	20.3	21.3	36.7	35.2
C–PAAm–MBA	30	20.3	21.8	36.7	39.8
C–PAAm	40	25.4	24.2	43.7	43.2
C–PAAm	50	29.8	28.6	49.2	47.1
C–PAA(H^+)	10	13.9	12.7	26.7	—
C–PAA(H^+)	38	24.4	24.0	42.1	—
C–PAA(H^+)	53	31.1	30.9	50.4	—
C–PAA(H^+)–AD	53	31.1	31.6	50.4	—
C–PAA(H^+)–MBA	53	31.1	32.3	50.4	—
C–PAA(H^+)	75	38.9	41.3	59.0	—

[a] Gravimetric analysis.
[b] Elemental analysis.

was of interest to compare the behavior during the swelling of IPN membranes and crosslinked polymers contained in them (cellulose, PAAm, and PAA hydrogels) with respect to water and its mixtures with ethanol.

Data on the equilibrium swelling of several nonionic (C–PAAm) and ionic [C–PAA (H^+, Na^+, K^+)] IPN membranes as well as cellophane depending on the ethanol content in ethanol–water mixtures are shown in Figure 1. It can be seen that ionic C–PAA (Na^+, K^+) membranes for which the degree of equilibrium swelling (Q) attains 3 g/g (300 wt %) exhibit the highest degree of swelling in water. The Q value for cellophane and nonionic IPN membranes is approximately one-third (1 g/g). With increasing ethanol concentration, the Q value decreases considerably for all membrane types except ionic C–PAA(H^+) membranes for which it changes only slightly in the range of [EtOH] = 0–70 wt % and amounts to 1.7–1.5 g/g. Chemical crosslinking of synthetic PAAm or PAA chains in IPN membranes has no effect on their behavior during swelling over the entire range of EtOH concentration. Thus, the Q–[EtOH] curves coincide for membranes synthesized both without crosslinking agents and in the presence of AD or MBA at concentrations of 0.60 and 0.15 wt % (with respect to the monomer), respectively. Figure 1 shows, for simplicity, only the data for the C–PAA(H^+) and C–PAA(H^+)–AD membrane pair.

Table II Properties of Water-Soluble PAAm Synthesized with the Variation of Initial Monomer Concentration in the Reaction Solution

C_m (wt %)	[η] (dL/g)	$M_w \cdot 10^{-6}$ (g/mol)	R_g (Å)
20	7.80	3.00	975
30	9.50	3.92	1141
40	12.6	5.69	1422
50	14.8	7.05	1613

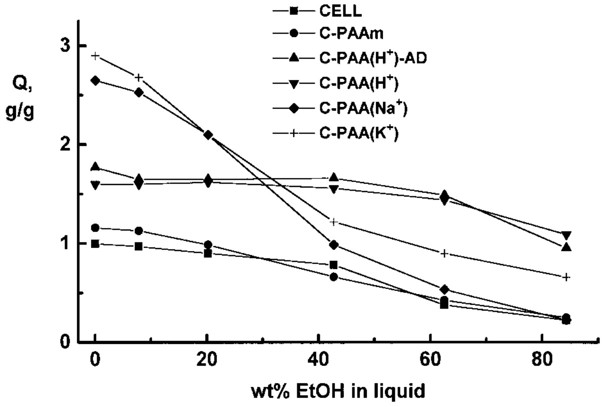

Figure 1 Effect of ethanol concentration on the swelling of cellophane and IPN membranes in water–ethanol mixtures at 20°C. Synthesis conditions: C_m = 50 and 53 wt % for C–PAAm and all types of C–PAA membranes, respectively.

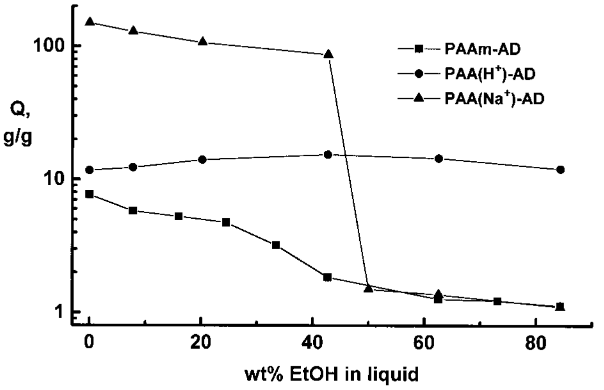

Figure 2 Effect of ethanol concentration on the swelling of hydrogels (crosslinked by AD) in water–ethanol mixtures at 20°C. Synthesis conditions: C_m = 50 and 53 wt % for PAAm and PAA hydrogels, respectively.

Figure 2 shows the Q–[EtOH] curves for ionic and nonionic hydrogels synthesized at the same monomer and AD concentration as that in the membrane synthesis. Polyelectrolyte PAA(Na^+)–AD hydrogels exhibit the degrees of swelling that exceed by one order of magnitude those of nonionic hydrogels. This effect is known to be caused by the high contribution to the swelling pressure of ionic gels of the counterion osmotic pressure and the electrostatic repulsion of charges fixed on polymer chains.[25] The degree of swelling of PAA(H^+)–AD hydrogels which are in the acid form is much lower than that for PAA(Na^+)–AD hydrogels because PAA is a weak acid, and in the acid form, carboxylic groups are only partially dissociated. On the other hand, the degree of swelling of PAA (Na^+)–AD gels with increasing ethanol concentration in ethanol–water mixtures drops abruptly at [EtOH] $>$ 50 wt % and decreases to low values (1.2–1.1 g/g), whereas that of PAA(H^+)–AD hydrogels only slightly depends on the mixture composition, and in concentrated ethanol solutions, these gels swell relatively greatly (12–15 g/g). A sharp decrease in the degrees of swelling (collapse) for polyacrylate hydrogels at [EtOH] $>$ 50 wt % has also been observed in the work.[26] It is known that this phenomenon can be understood in the terms of phase transition in the gels.[27] The absence of a collapse for PAA(H^+)–AD hydrogels in the same condition is evidently due to the affinity of alcohol molecules for COOH groups resulting from hydrogen-bond formation.

The comparison of the data in Figures 1 and 2 shows that correlation exists between the behavior of PAAm and PAA hydrogels during swelling and that of IPN membranes containing these polymers. This correlation is revealed both by an increase in the degree of swelling in the water of IPN membranes and gels in the following order: PAA(Na^+, K^+) $>$ PAA(H^+) $>$ PAAm and by the character of changes in the degree of swelling with increasing ethanol concentration in the mixtures. However, the range of changes in the degree of swelling for hydrogels and IPN membranes differs by one or two orders of magnitude. It may be assumed that the cellophane physical network limits to a great extent the swelling of the synthetic chains contained in it. The pressure of the swelling of nonionic PAAm chains is insufficient to move apart the framework of cellulose hydrogen bonds, as follows from the coincidence of Q–[EtOH] curves for C–PAAm membranes and cellophane. On the other hand, the tendency of PAA(Na^+, K^+) polyelectrolyte chains to swell is so high that it leads to a threefold increase in the degree of swelling in water of the C–PAA(Na^+, K^+) IPN membranes over that in cellophane. The synthetic chains in the network structure of IPN membranes are far from the state of equilibrium swelling, and, therefore, the chemical crosslinking of these chains does not exert a considerable effect on the degree of equilibrium swelling of the IPN membranes.

Pervaporation

Effect of the Composition of IPN Membranes

Figures 3 and 4 show the dependencies of the separation factor and the permeation rate of C–

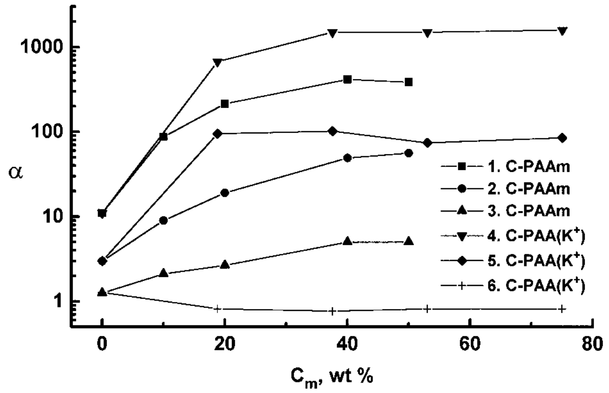

Figure 3 Separation factor of C–PAAm and C–PAA (K^+) IPN membranes at 50°C versus initial monomer concentration in the IPN synthesis. Symbols 1,4; 2,5; and 3,6 correspond to the ethanol concentration in the water–ethanol mixtures: 86, 46, and 8 wt %, respectively.

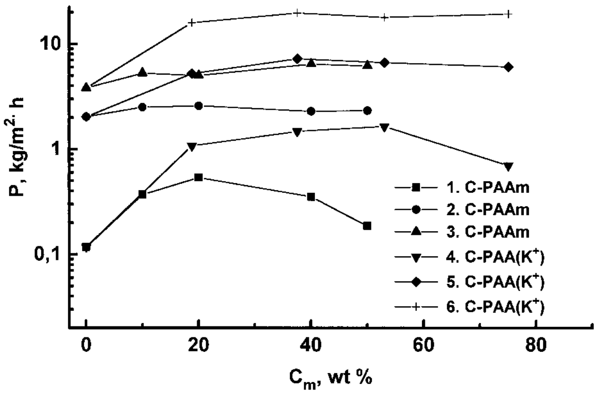

Figure 4 Permeation rate of C−PAAm and C−PAA(K$^+$) IPN membranes versus initial monomer concentration in the synthesis at 50°C. The membranes and conditions are the same as in Figure 3.

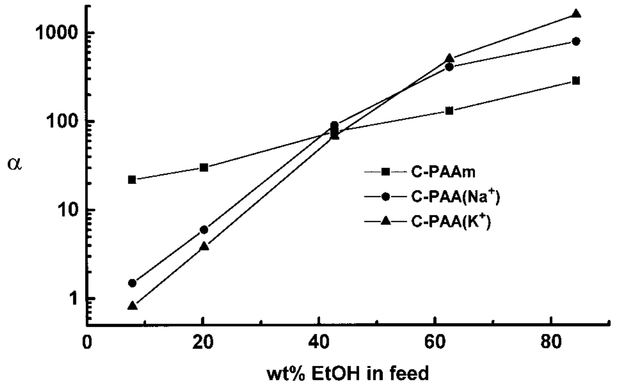

Figure 5 Effect of feed composition on the separation factor of IPN membranes at 50°C. Synthesis conditions: C_m = 50 and 53 wt % for C−PAAm and C−PAA (Na$^+$, K$^+$) membranes, respectively.

PAAm and C−PAA(K$^+$) membranes on the initial monomer concentration in the synthesis (C_m) determined at an ethanol concentration in the feed of 8, 46, and 86 wt %. The experimental values of $C_m = 0$ correspond to the data for the initial cellophane. It is clear that for ethanol concentrations in the feed of 46 and 86 wt % the separation factor increases markedly when C_m increases to 30 wt %. When C_m increases further, the value of α changes only slightly. Polyelectrolyte C−PAA (K$^+$) membranes exhibit the highest selectivity ($\alpha = 1500$) in the separation of concentrated solutions of ethanol ([EtOH] = 86 wt %). Under these conditions, the separation factor for nonionic C−PAAm membranes is much lower (400). Figure 4 shows that the permeation rate of all types of IPN membranes increases over that of cellophane membranes. A particularly drastic increase in P is observed for polyelectrolyte membranes. There is a significant maximum on the P versus C_m dependence for data obtained in 86 wt % EtOH. The permeation rate of the membranes as compared to cellophane increases but decreases with a further increase in C_m. The maximum on the P–C_m curves is more pronounced for nonionic C−PAAm membranes. In this case, the swelling factor cannot influence the results because the values of Q for nonionic membranes synthesized at different C_m and for cellophane are virtually identical. It may be assumed that in this case membrane performance depends on the level of hydrophilicity and packing density of the polymer chains in the IPN structure. Since PAAm exhibits higher hydrophilicity than does cellophane, the increase of its concentration in the membrane initially leads to increasing P. With a further increase in PAAm concentration in the membranes, polymer chain density increases to such an extent that it begins to hinder the diffusion of the water molecules. The degree of membrane swelling in 86 wt % EtOH is very low, and this effect of density is quite possible.

Effect of Feed Composition

Figures 5 and 6 show the dependencies of the separation factor and the permeation rate on the ethanol content in the feed. With a decrease in this content, the separation factor drops for both ionic and nonionic membranes, but this drop is more pronounced for the former (Fig. 5). At 10 wt % of EtOH, ionic membranes are not selective, whereas the selectivity of nonionic membranes attains a value of 20. The separation factors for ionic membranes with Na$^+$ or K$^+$ as a counterion differ

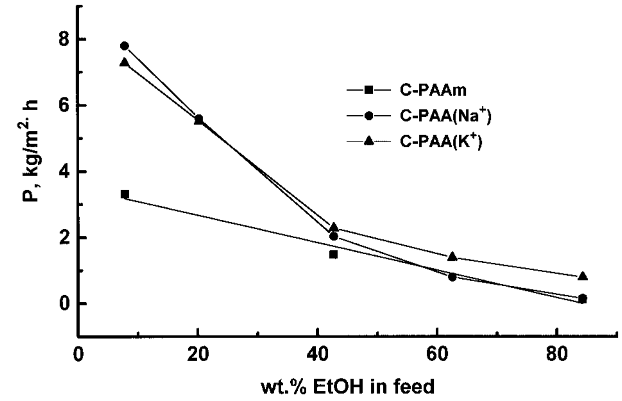

Figure 6 Effect of feed composition on the permeation rate of membranes at 50°C. The membranes are the same as in Figure 5.

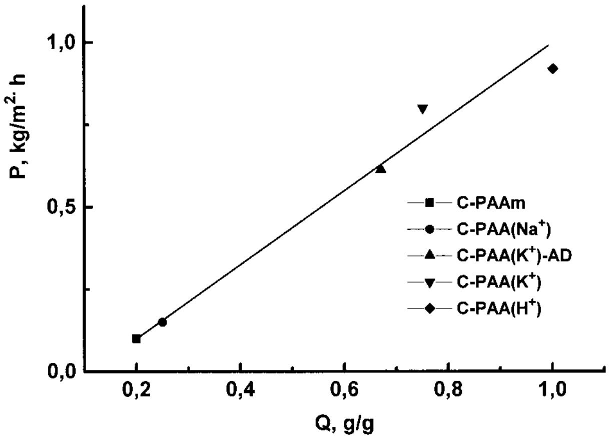

Figure 7 Permeation rate of membranes (86 wt % EtOH at 50°C) versus degree of their equilibrium swelling. Synthesis conditions: C_m = 50 and 53 wt % for C–PAAm and all types of C–PAA membranes, respectively.

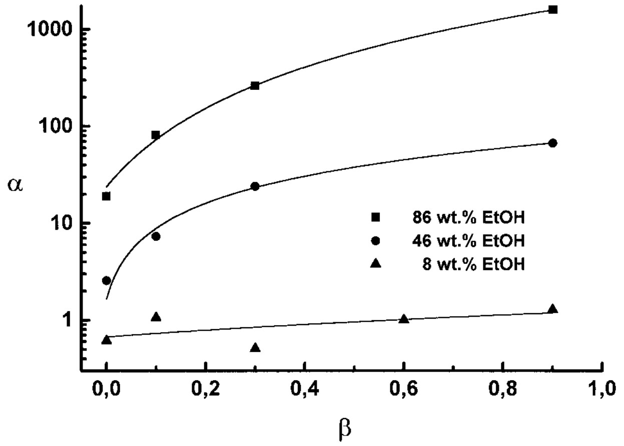

Figure 8 Effect of the degree of neutralization of carboxylic groups on the separation factor of C–PAA(H^+/Na^+) IPN membranes at 50°C. C_m = 53 wt %.

only slightly. The absence of selectivity of polyelectrolyte membranes in dilute EtOH solutions can be caused by their higher degrees of swelling than those of C–PAAm membranes. At this degree of swelling, regions with low polymer density are probably formed in the network structure. The molecules of both water and ethanol molecules are freely transported through these regions.

At lower ethanol concentration, the permeation rate of both membrane types increases but this increase is more drastic for ionic membranes at [EtOH] < 50 wt % in the feed (Fig. 6). These data are in good agreement with those on membrane swelling obtained depending on the composition of the EtOH–H_2O mixtures (Fig. 1). The comparison of the permeation rate for different types of membranes obtained at an equal EtOH concentration in the feed shows that the P value is approximately proportional to the degree of swelling. This is shown in Figure 7 in which the $P - Q$ dependence is given for the C–PAAm and C–PAA (H^+, Na^+, K^+) membranes.

Effect of the Degree of Neutralization of Carboxylic Groups

The effect of the degree of neutralization of carboxylic groups (β) on the separation factor and the permeation rate of polyelectrolyte membranes is shown in Figures 8 and 9. In more concentrated ethanol solutions (46–86 wt %), the substitution of H^+ counterions by Na^+ counterions leads to an increase in the separation factor by more than one order of magnitude. The relatively low selectivity of the membranes containing PAA in the H^+ form is in agreement with the data for membranes based on PAA in the H^+ or salt form.[7] This effect is in correlation with the good swelling of C–PAA(H^+) IPN membranes in concentrated ethanol solutions and, as noted above, it is evidently due to the affinity of alcohol molecules for COOH groups resulting from hydrogen-bond formation. When dilute EtOH solutions (8 wt %) are separated, the value of α is close to unity for all β values. In other words, under these conditions, polyelectrolytic membranes do not exhibit selectivity with respect to water regardless of the degree of neutralization of the carboxylic groups.

In dilute ethanol solutions (8 wt %), the P

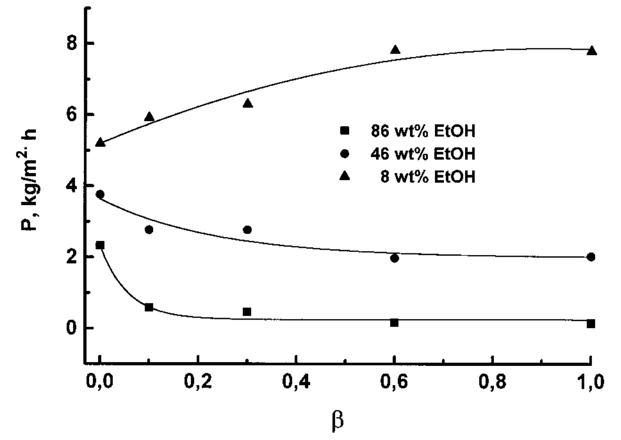

Figure 9 Effect of the degree of neutralization of carboxylic groups on the permeation rate of C–PAA(H^+/Na^+) IPN membranes at 50°C. The membranes are the same as in Figure 8.

Table III Transport Properties of IPN Membranes Synthesized in the Presence (or Absence) of the Crosslinking Agent (AD or MBA) at 50°C

Membrane	86 wt % EtOH		46 wt % EtOH	
	α	P (kg/m^2 h)	α	P (kg/m^2 h)
C–PAAm	416	0.21	49	1.36
C–PAAm–AD	530	0.22	57	1.48
C–PAAm–MBA	605	0.16	43	1.20
C–PAA(K$^+$)	1510	0.80	74	2.28
C–PAA(K$^+$)–AD	1670	0.67	76	2.06
C–PAA(K$^+$)–MBA	1590	0.50	63	2.22

value increases with increasing β, which evidently takes place as a result of an increasing degree of membrane swelling. In more concentrated ethanol solutions (46–86 wt %), IPN membranes in the H$^+$ form exhibit a higher degree of swelling than do those in the Na$^+$ and K$^+$ forms. Hence, under these conditions, P drops with increasing β.

Effect of Chemical Crosslinking of Synthetic Chains

It can be seen from Table III that the introduction of crosslinking agents, AD or MBA, into the reaction mixture during the formation of C–PAAm and C–PAA IPN membranes affects only slightly their transport properties. For membranes crosslinked with the aid of MBA, a certain decrease in performance in 86 wt % EtOH is observed. This effect may be related to the well-known tendency of MBA molecules to homopolymerization with the formation of dense crystalline aggregates inside the network[28,29] which hinder mass transfer through the membrane. It is clear that this effect is manifested just under those conditions when the membranes exhibit a low degree of swelling.

The slight effect of chemical crosslinking on the swelling and pervaporation behavior of the IPN membranes is evidently caused by the peculiarities of their structure. As can be seen from the description of synthesis, membranes are synthesized according to the principle of the preparation of IPNs: Monomer polymerization takes place inside the cellophane physical network. In the absence of the crosslinking agent, the physical interpenetrating network probably exists, although, as already mentioned, one cannot rule out grafting as a result of chain-transfer reactions. When a crosslinking agent is introduced into the reaction mixture, a synthetic chemical network is formed inside this cellophane network. It is possible to evaluate the molecular weight of the polymer chains between chemical crosslinking junctions M_c of the synthetic network using eq. (3)[29]:

$$M_c = 2C_m\, M_{\text{unit}}/fC_{c-a} \tag{3}$$

where f is the crosslinking agent functionality and M_{unit} is the molecular weight of the monomer unit.

The value of M_c characterizes the crosslinking density of an ideal network with a defectless structure in which all the crosslinking agent has reacted with the monomer.[29] For networks crosslinked with the aid of AD and MBA, M_c = 30,000 and 60,000 g/mol, respectively. It is probable that these values greatly exceed the molecular weight of the polymer chains between physical entanglements of synthetic and cellulose chains. In this case, the effect of chemical crosslinking of the synthetic chains on IPN membrane properties must actually be slight.

The IPN microstructure can profoundly affect membrane properties, and this problem requires special consideration. It may be assumed that the distribution density of synthetic chains in IPNs is markedly inhomogeneous. Cellulose materials are known to contain both crystalline and amorphous regions. The degree of crystallinity of cellophane estimated by X-ray diffraction was about 40%.[30] Since amorphous regions swell to a much greater extent, it is probable that it is in these regions that monomers are preferably polymerized. Thus, in the IPN synthesis, synthetic chains probably fill the defective regions of cellophane, which is the reason for its low selectivity during pervaporation. On the other hand, the filling of this region by synthetic polymers makes the structure of the IPN system more ordered, providing their high performance in comparison with that of cellophane.

CONCLUSION

All the results obtained show that in the membrane type being investigated the cellophane network serves mainly as a mechanical framework, rendering the membrane dense and elastic and limiting the swelling of the synthetic polymer, which in the absence of this framework would have been too great for pervaporation purposes. The high membrane performance, in particular in concentrated ethanol solutions, is ensured by the synthetic polymer.

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