

# Cellulose–Poly(acrylamide–acrylic acid) Interpenetrating Polymer Network Membranes for the Pervaporation of Water–Ethanol Mixtures. II. Effect of Ionic Group Contents and Cellulose Matrix Modification

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**ABSTRACT:** The separation properties in the dehydration of a water–ethanol mixture and the swelling behavior of interpenetrating polymer network (IPN) pervaporation membranes based on a cellulose or cellulose–hydroxyethyl cellulose (HEC) matrix and poly(acrylamide and/or acrylic acid) were investigated depending on the ionic acrylate groups content ( $\gamma$ ) in synthetic polymer chains (0–100 mol %), the HEC content in the matrix (0–50 wt %), and the temperature (25–60°C). The separation factor ( $\alpha$ ), permeation rate ( $P$ ), and separation index ( $\alpha P$ ) significantly improved with increasing  $\gamma$  values only for the separation of concentrated ethanol solutions (~86 wt %). For more dilute solutions of ethanol (~46 wt %), the  $P$  and  $\alpha P$  values also increased but no considerable increase in  $\alpha$  was observed. All types of membranes based on the cellulose matrix were characterized by a drastic decrease in the values of  $P$  at [EtOH]  $\geq$  90 wt % and, as a result, a decrease in the separation index ( $\text{kg m}^{-2} \text{h}^{-1}$ ) from ~2000 (for 86 wt % EtOH, 50°C) to ~240 (for 95 wt % EtOH, 50°C), which correlates with a decrease in the degree of membrane swelling. The modification of the cellulose matrix by introducing HEC into it makes it possible to increase considerably the membrane swelling in concentrated EtOH solutions and, hence, the  $\alpha P$  value to ~760 (95 wt % EtOH, 50°C). All types of IPN membranes exhibit a marked increase in both  $\alpha$  and  $P$  when the temperature increases from 25 to 60°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1452–1460, 2001

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

## INTRODUCTION

Dehydration of organic solvents, in particular ethanol, by pervaporation with the aid of polymer membranes is already being used in industry.<sup>1,2</sup> As compared with distillation processes traditionally used for these purposes, pervaporation processes are less power-consuming. However, it has

been pointed out that there are extensive possibilities for new developments. In fact, in spite of a great quantity of new membranes, only a few of them have the required characteristics: high separation factor ( $\alpha$ ), high permeation rate ( $P$ ), and high separation index ( $\alpha P$ ), as well as good mechanical strength and stability. For example, according to data in refs. 3 and 4, only membranes based on crosslinked poly(vinyl alcohol), chitosan, alginic acid, and poly(acrylic acid) polyion complexes are acceptable for industrial application which requires over a  $500 \text{ kg m}^{-2} \text{ h}^{-1}$  separation

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index for the dehydration of concentrated EtOH solutions.

It is known that the method of synthesizing composite materials with the structure of interpenetrating polymer networks (IPNs) provides ample possibilities for improving the properties of polymer materials including membranes.<sup>5-10</sup> In an earlier article,<sup>11</sup> we developed a method for the synthesis of a new type of both polyelectrolyte and uncharged cellulose-poly(acrylic acid or acrylamide) IPN membranes and investigated their pervaporation characteristics depending on the composition of the EtOH-H<sub>2</sub>O mixture to be separated (in the range of EtOH concentrations of 8-86 wt %) and the ratio of IPN components. The maximum separation index of the membranes that we have previously investigated was  $\sim 1500 \text{ kg m}^{-2} \text{ h}^{-1}$  (86 wt % EtOH, 50°C).

In this membrane type, cellulose plays the role of a matrix, and inside its physical network, a second network is formed. It consists of chains of a synthetic polymer: poly(acrylic acid) (PAA) or polyacrylamide (PAAm). For forming a synthetic polymer network, the method of synthesis of PAAm or PAA hydrogels was used. The peculiarity of this method is the application of macromolecular allyl polysaccharide crosslinking agents.<sup>12-14</sup> It was found, however, that the introduction of crosslinking agents into the reaction mixture during the formation of IPN membranes affects only slightly their swelling and transport properties.<sup>11</sup> In the absence of a crosslinking agent, the polymerization of monomers results in the synthesis of high molecular weight (to  $\sim 10^7 \text{ g/mol}$ ) PAAm or PAA and the physical IPN probably exists, although one cannot rule out grafting of synthetic chains onto the cellulose matrix as a result of chain-transfer reactions. It was shown that this method of IPN membrane preparation makes it possible to implement an optimum combination of functional properties of all IPN components: high mechanical strength and elasticity of the cellulose matrix and high separating characteristics of PAA and PAAm. It is significant that the high selectivity of IPN membranes is retained over a wide range of feed compositions. The latter feature is because the cellulose matrix limits the swelling of the synthetic component, in particular, when such a strong polyelectrolyte as PAA is used. In this connection, it should be noted that the selectivity of membranes based on PAA alone<sup>4</sup> decreases drastically with increasing water content in the mixture because of uncontrolled swelling.

In the present work, the study of the properties of the above IPN membrane type was continued over a wide range of feed compositions. The possibility of effective separation of more concentrated ethanol solutions (EtOH  $\geq 86 \text{ wt } \%$ ), including a mixture with an azeotropic composition, was studied most intensively. It was also of interest to evaluate changes in  $\alpha$  and  $P$  depending on the ionic group content ( $\gamma$ ) in PAA-PAAm chains of the synthetic IPN network and on temperature. The value of  $\gamma$  was controlled in the stage of IPN synthesis by varying the monomer ratio. To improve the transport characteristics of IPN membranes, the possibility of modifying the cellulose matrix was also investigated. For this purpose, matrices from a mixture of cellulose with hydroxyethyl cellulose (HEC) were prepared.

## EXPERIMENTAL

Acrylamide (AAM; Aldrich Chemicals, Milwaukee, WI) was recrystallized from benzene. Acrylic acid (AA; Aldrich Chemicals) was distilled under a vacuum at a pressure of  $\sim 18 \text{ Torr}$ . The fraction with a boiling point of 47°C was collected. All other reagents of analytical grade were used as received.

### Preparation of Cellulose Matrices

Films from commercial cellophane (Cph; Polymersynthesis, Vladimir City, Russia) 27  $\mu\text{m}$  thick, were used as cellulose matrices or else films were obtained using a previously developed method<sup>15</sup> by casting them from cellulose solutions or from its mixture with HEC (Cell and Cell-HEC films, respectively) in trifluoroacetic acid (TFAA). To cast films from TFAA, cotton linter and water-insoluble HEC with a low degree of substitution of hydroxyethyl groups (0.3) were used. These components were dissolved in TFAA; then, the solutions were poured onto glass and dried. The final films were washed with distilled water and dried. Cph films were washed in distilled water for 24 h to free them from low molecular weight impurities and then dried.

### Synthesis of IPN Membranes

To synthesize IPN membranes, Cph, Cell, and Cell-HEC initial matrices were immersed in an aqueous reaction solution containing AAM and AA in a ratio varying from 0:100 to 100:0 mol %. The initial concentrations of monomers in the reaction solution were 50 wt %. To initiate free-

radical polymerization, cobalt(III) acetate, proposed by us previously,<sup>12,13</sup> was used at a concentration of  $0.5 \times 10^{-3} M$ . The films, allowed to swell for 10 min in the reaction solution to the degree of equilibrium swelling, were placed between two glasses, pressed with clamps, and thermostated at 50°C. Free-radical polymerization started after an induction period of 10–15 min and was completed in 2 h. Subsequently, the membranes were washed with distilled water for 3 days to remove low molecular weight impurities and dried to a constant weight. Gravimetric analysis, carried out during washing, showed that IPN polymer components were not extracted in the process of washing in water. Membrane thickness was 30–50  $\mu\text{m}$ . Before measuring the degree of membrane swelling and their pervaporation characteristics, carboxyl groups in PAA-containing membranes were transformed into the salt PAA(K<sup>+</sup>) form. For this purpose, membranes were placed for 1 h in a 0.1M HCl solution, then for 1 h in water, and, finally, for 1 h in a 0.1M KOH solution with periodic stirring. The degree of equilibrium membrane swelling ( $Q$ ) in water and in EtOH–H<sub>2</sub>O mixtures 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. The error in the value of  $Q$ , after several measurements, was estimated to be  $\pm 7\%$ .

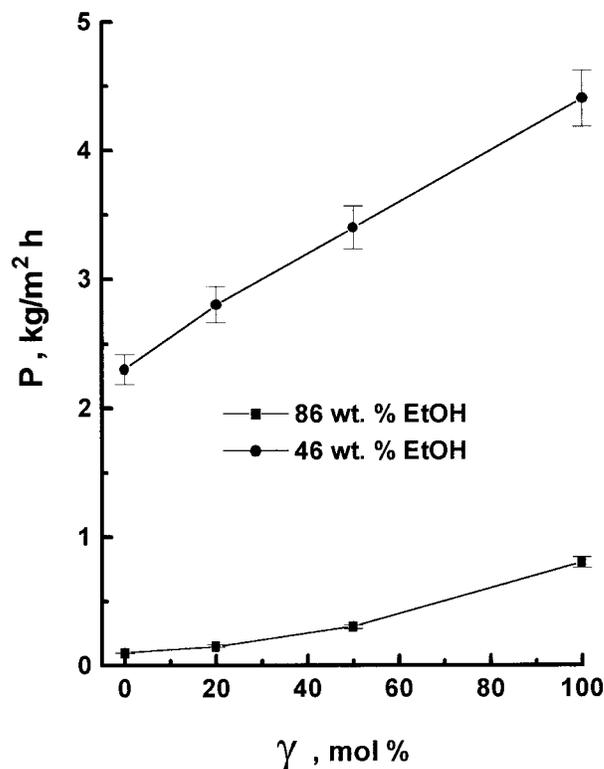
### Pervaporation

Experiments on pervaporation were carried out in a flange-type cell similar to that used in previous work.<sup>11</sup> The feed mixture temperature was controlled with the aid of a liquid thermostat and ranged from 25 to 60°C. The permeate was collected in a trap cooled with liquid nitrogen, weighed, and analyzed by using a chromatograph with a column 1 m long packed with Porapak Q and heated to 140°C. Helium was used as the carrier gas. The permeation rate of IPN membranes was normalized for the membrane thickness of 25  $\mu\text{m}$ . The value of  $\alpha$  was calculated from the equation  $\alpha = (x_a/x_b)/(y_c/y_d)$ , where  $x_a$  and  $x_b$  are the weight fractions of water and ethanol in the feed mixture, respectively, and  $y_c$  and  $y_d$  are the weight fractions of water and ethanol in the permeate, respectively. The error in the values of  $\alpha$  and  $P$ , after several measurements, was estimated to be  $\pm 5\%$ .

## RESULTS AND DISCUSSION

### Effect of Ionic Group Contents

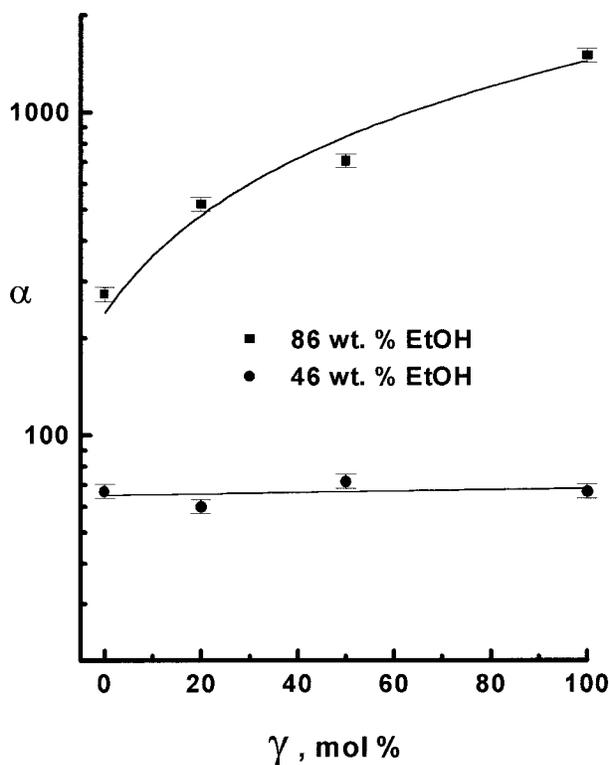
Figures 1 and 2 show the dependencies of the permeation rate and separation factor on the con-



**Figure 1** Effect of ionic acrylate group contents in PAA(K<sup>+</sup>)–PAAm polymer chains ( $\gamma$ ) on the permeation rate of the Cph–PAA(K<sup>+</sup>)–PAAm IPN membranes at 50°C.

tent of acrylate ionic groups in polymer PAA(K<sup>+</sup>)–PAAm chains of the synthetic network ( $\gamma$ ) for Cph–PAA(K<sup>+</sup>)–PAAm IPN membranes synthesized by using the Cph matrices. It is clear that in the separation of the EtOH concentrated solution (86 wt %) a considerable improvement in pervaporation characteristics of the IPN membranes with increasing  $\gamma$  is observed. It is accompanied by an increase in the values of  $P$  (from 0.1 to 0.8  $\text{kg m}^{-2} \text{h}^{-1}$ ) and  $\alpha$  (from 270 to 1500), which corresponds to an increase in separation index  $\alpha P$  from 27 to 1200  $\text{kg m}^{-2} \text{h}^{-1}$ . In the separation of a moderately concentrated solution of EtOH (46 wt %), the separation factor increases only slightly (50–70) with increasing  $\gamma$ , although an increase in  $P$  from 2.3 to 4.4  $\text{kg m}^{-2} \text{h}^{-1}$  is observed. The increase in  $\alpha$  in the first case (86 wt % of EtOH) may be explained by a higher affinity of ionic carboxylate groups for water as compared to that of amide groups in PAAm.

We take into consideration only functional groups of a synthetic polymer, because, as has been shown in our earlier work,<sup>11</sup> the cellulose matrix virtually does not provide any contribution to the selectivity of IPN membranes. When



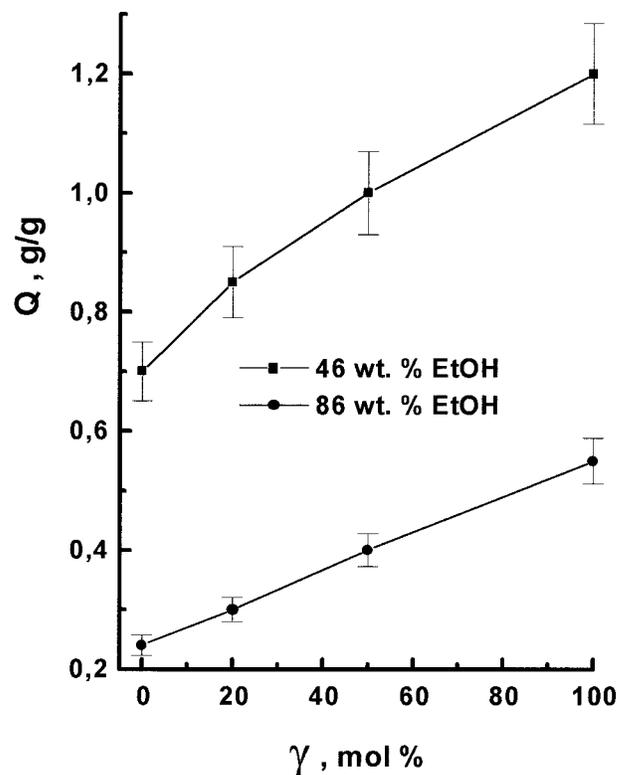
**Figure 2** Effect of  $\gamma$  on the separation factor of Cph-PAA(K<sup>+</sup>)-PAAm IPN membranes at 50°C.

separation takes place in 86 and 46% EtOH (50°C), the separation factor for the matrix is 11 and 3, respectively. This low matrix selectivity is caused by the presence of amorphous regions in it. These regions in IPN membranes are filled with a synthetic polymer which ensures high membrane selectivity. The observed increase in the permeation rate with increasing  $\gamma$  is evidently due to an increasing the degree of swelling of the membranes. Different degrees of swelling for various IPN membranes are shown in Figure 3. For the 86 wt % EtOH solution, the value of  $Q$  increases with  $\gamma$  from 0.24 to 0.55 g/g. The value of  $Q$  also increases from 0.7 to 1.2 g/g with the same increase in  $\gamma$  when a 46 wt % EtOH solution is separated, but, in this case, no considerable increase in  $\alpha$  is observed. The effect of constancy of  $\alpha$  with the variation of  $\gamma$  is probably caused by the mutual compensation of opposite effects of two factors: increase in affinity of polymer chains for water (increase in selectivity) and increase in the degree of membrane swelling (decrease in selectivity). As the degree of swelling increases, zones filled with free water appear in the polymer network.

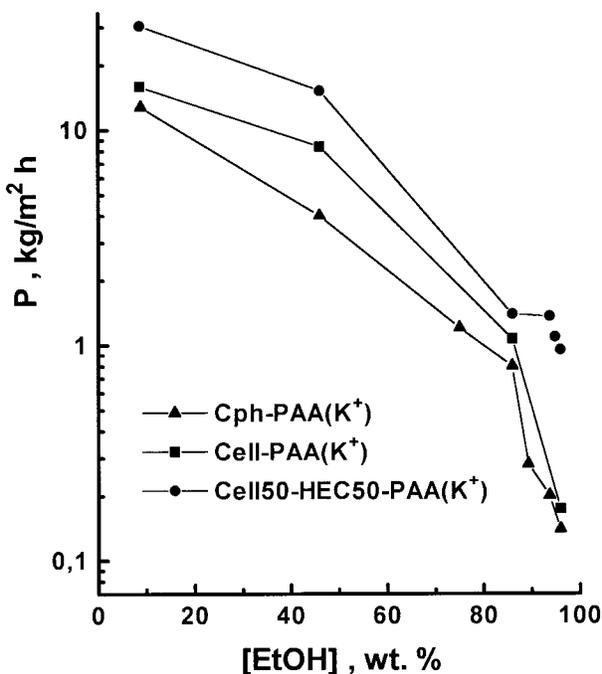
Ethanol is transported along these zones more freely than in less swollen networks. However, in the separation of 46 wt % EtOH, the selectivity

level of both ionic and nonionic IPN membranes remains relatively high. For comparison, it should be noted that composite membranes with a selective layer of PAA on a microporous support are not selective at the water concentration in the mixture to be separated >50 wt %.<sup>4</sup> In this case, the absence of selectivity for mixtures with a high water content may be associated with the fact that under these conditions the degree of swelling of the PAA layer is too high. As mentioned previously, the swelling of polyelectrolyte PAA chains in IPN membranes is limited due to the cellulose matrix. Indeed, we have shown<sup>11-14</sup> that the degree of swelling of PAA hydrogels synthesized under similar conditions attains  $10^2$ - $10^3$  g/g.

Figures 4 and 5 show the dependencies of  $P$  and  $\alpha$  for IPN membranes on the mixture composition in the range of [EtOH] = 9-95 wt %. The observed decrease in  $P$ , and increase in  $\alpha$  with increasing ethanol concentration, is usual behavior for hydrophilic pervaporation membranes. Similar behavior for this type of IPN membrane in the range of [EtOH] = 9-86 wt % was also described in our earlier work.<sup>11</sup> However, at [EtOH] >86 wt %, a drastic decrease in the mem-



**Figure 3** Effect of  $\gamma$  on the degree of equilibrium swelling of the Cph-PAA(K<sup>+</sup>)-PAAm IPN membranes at 25°C.



**Figure 4** Permeation rate of IPN membranes at 50°C versus EtOH concentration in the feed.

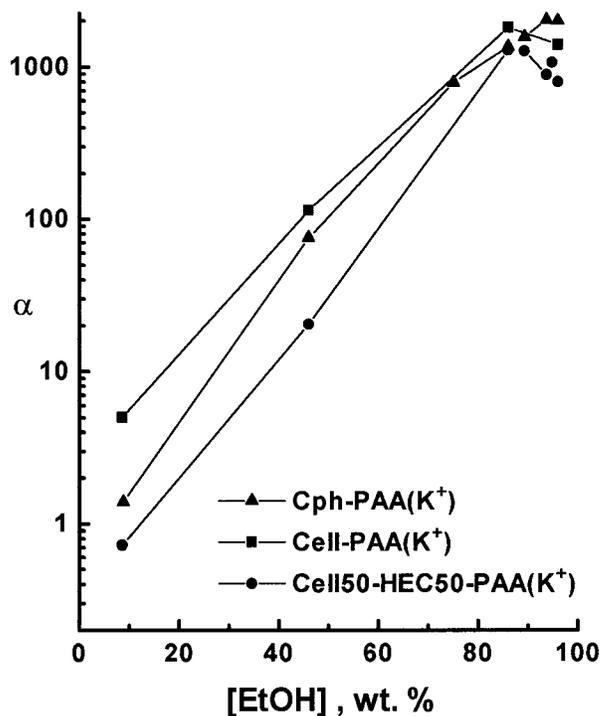
brane permeation rate is noted (Fig. 4). A decrease in  $P$  is observed both for Cph-PAA(K<sup>+</sup>) membranes synthesized with the application of commercial cellophane and for Cell-PAA(K<sup>+</sup>) membranes with a matrix obtained from the solution of cotton linter in TFAA. Hence, it is evident that a general relationship exists, which is characteristic of this type of IPN membrane. The selectivity level of IPN membranes in this range of EtOH concentrations remain high (Fig. 5); however, at [EtOH]  $\approx$  95 wt %, some decrease in the selectivity is observed for IPN membranes with a matrix cast from TFAA. The trend toward a decrease in the  $\alpha$  value is also observed for IPN based on the Cph matrices. We found previously<sup>11</sup> that the permeability level of this type of membrane is proportional to its degree of swelling. Hence, it is evident that the observed decrease in  $P$  is caused by the corresponding decrease in  $Q$ . In fact, Figure 6 shows that at [EtOH] > 86 wt % an abrupt decrease in the degree of swelling is observed for this type of IPN membrane.

A drastic decrease in  $Q$  and  $P$  values for membranes at [EtOH] > 86 wt %, and also the tendency to decreasing  $\alpha$  value, is evidently due to the fact that under these conditions the acrylate polymer chains have a tendency to collapse. In our earlier work,<sup>11</sup> we observed for PAA (Na<sup>+</sup>) hydrogels a marked decrease in the degree of swelling at

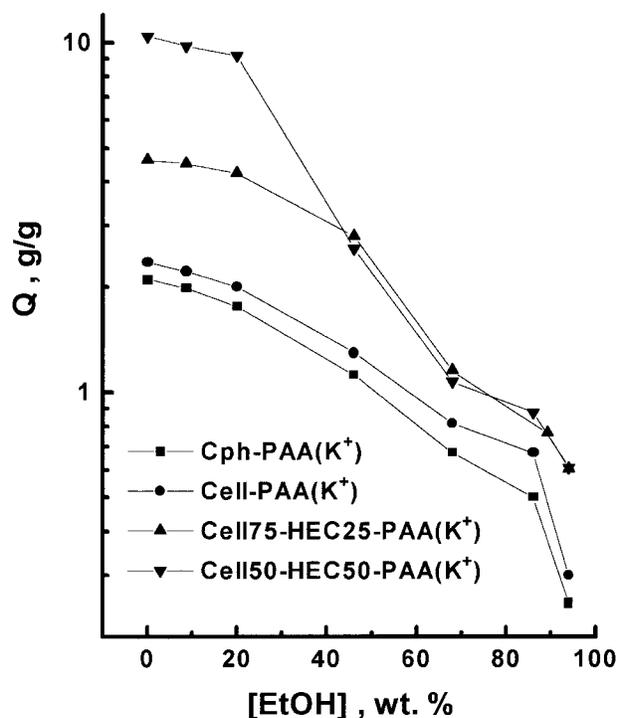
[EtOH] > 50 wt %. Tanaka showed that the collapse of polyelectrolyte gels can be understood in terms of the phase transition.<sup>16</sup> For the cellulose matrix at [EtOH] > 50 wt %, a collapse is not observed<sup>11</sup> because cellulose is not a polyelectrolyte. In the IPN structure, the cellulose matrix evidently hinders the collapse of PAA chains because of mutual interpenetration of chains composing IPN. The collapse was observed at higher EtOH concentrations (> 86 wt %) and it was not so pronounced as in the PAA hydrogels. The decrease in not only  $Q$  and  $P$  values but also in  $\alpha$ , under conditions of a collapse at [EtOH] > 86 wt %, is possibly because the collapse phenomenon is also related to a decrease in the effective degree of polymer chain ionization.

#### Effect of Cellulose Matrix Modification

It might be possible to increase the degree of IPN membranes swelling in concentrated EtOH solutions and, consequently, their permeation rate by modifying the cellulose matrix. Many cellulose derivatives are known to dissolve or swell extensively in ethanol. In this work, the method of matrix preparation from a mixture of cellulose with HEC was applied. Films cast from pure HEC are less mechanically stable than are those from



**Figure 5** Separation factor of IPN membranes at 50°C versus EtOH concentration in the feed.



**Figure 6** Degree of equilibrium swelling of IPN membranes versus EtOH concentration in the feed at 25°C.

cellulose, especially in the swollen form. At the cellulose:HEC ratio of 1:1 (by weight), films retain good mechanical strength. In this work, strength was determined only qualitatively: Films should at least be sufficiently strong to stand the procedure of IPN membrane preparation and testing. Figure 6 shows the  $Q$ -[EtOH] curves for IPN membranes containing 25 and 50 wt % HEC in the matrix [Cell 75-HEC 25-PAA(K<sup>+</sup>) and Cell 50-HEC 50-PAA(K<sup>+</sup>)]. It can be seen that membranes of this type actually have a much higher degree of swelling over the entire concentration range of EtOH than that of membranes which do not contain HEC. Moreover, for dilute EtOH solutions (up to 20 wt %), the value of  $Q$  increases

considerably with increasing HEC content in the matrix. At high EtOH concentrations, the  $Q$  value is approximately equal for membranes containing 25 and 50 wt % HEC in the matrix. The increase in the degree of IPN membrane swelling also leads to a higher permeation rate over the entire concentration range of EtOH [Figs. 4 and 5 show, for simplicity, only the data for the Cell50-HEC50-PAA(K<sup>+</sup>) membrane]. However, a considerable difference between the curves of  $P$ -[EtOH] dependence is observed at [EtOH] > 86 wt %. For Cell-HEC-PAA(K<sup>+</sup>) IPN membranes, no drastic decrease in the  $P$  value in this EtOH concentration range is observed.

The selectivity level of the Cell50-HEC50-PAA(K<sup>+</sup>) membrane in the separation of concentrated EtOH solutions (86–95 wt %) is slightly lower than those of Cell-PAA(K<sup>+</sup>) and Cph-PAA(K<sup>+</sup>) membranes (Fig. 5). For more dilute solutions of EtOH, the membrane containing HEC in the matrix loses selectivity to a much greater extent, and for 8–20 wt % EtOH, it is already not selective, which is understandable because, under these conditions, its degree of swelling is too high (~10 g/g).

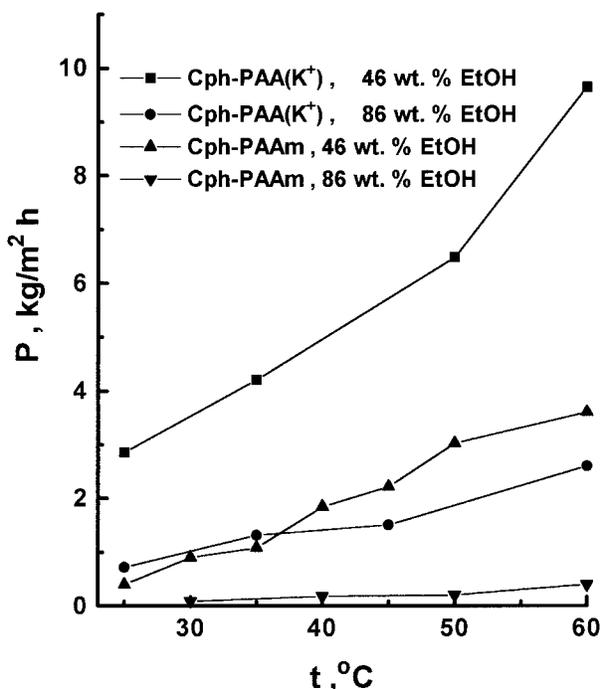
In Table I, functional characteristics ( $\alpha$ ,  $P$ , and  $\alpha P$ ) for Cell-PAA(K<sup>+</sup>), Cell75-HEC25-PAA(K<sup>+</sup>), and Cell50-HEC50-PAA(K<sup>+</sup>) IPN membranes are given at three different feed mixtures of 46, 86, and 95 wt % EtOH. It can be seen that, for 95 wt % EtOH, the separation index increases markedly with increasing HEC content in the matrix: from 238 to 700 kg m<sup>-2</sup> h<sup>-1</sup> because of an increasing permeation rate. In the separation of 86 wt % EtOH, the values of  $\alpha P$  for Cell-PAA(K<sup>+</sup>) and Cell50-HEC50-PAA(K<sup>+</sup>) membranes are approximately equal. In the separation of a more dilute solution containing 46 wt % EtOH, the value of  $\alpha P$  decreases from 958 to 310 kg m<sup>-2</sup> h<sup>-1</sup> with increasing HEC content in the matrix.

Comparison of these data with those on the swelling of both membranes containing HEC

**Table I** Transport Properties of Cell-PAA(K<sup>+</sup>), Cell 75-HEC 25-PAA(K<sup>+</sup>), and Cell 50-HEC 50-PAA(K<sup>+</sup>) IPN Membranes at 50°C Depending on the HEC Content in the Matrices ( $C_{\text{HEC}}$ )

$C_{\text{HEC}}$ (wt %)	46 wt % EtOH			86 wt % EtOH			95 wt % EtOH		
	$\alpha$	$P^a$	$\alpha P^a$	$\alpha$	$P^a$	$\alpha P^a$	$\alpha$	$P^a$	$\alpha P^a$
0	114	8.4	958	1814	1.1	1995	1400	0.17	238
25	30.3	21.2	642	860	1.4	1204	1176	0.45	529
50	20.4	15.2	310	1282	1.4	1795	800	0.95	760

<sup>a</sup> In kg m<sup>-2</sup> h<sup>-1</sup>.



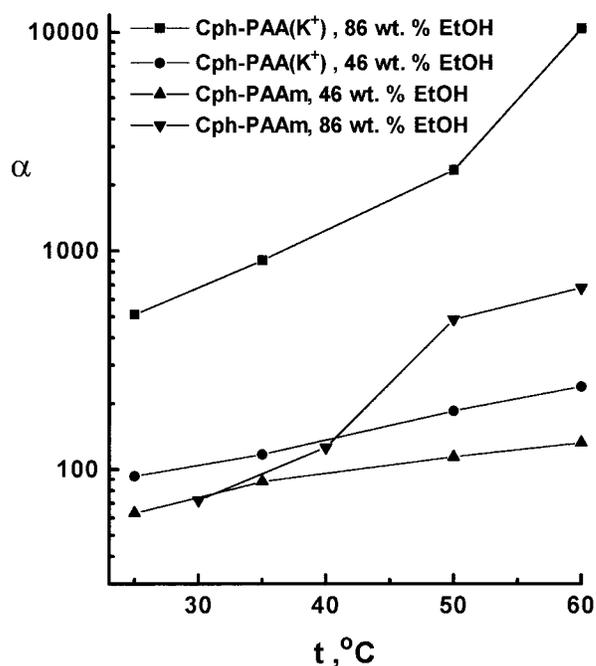
**Figure 7** Temperature dependence on the permeation rate of IPN membranes.

shows that their  $P$  values and, consequently, the  $\alpha P$  values are not determined by the degree of swelling alone. It might be suggested that the separation properties of these membranes are also affected by the degree of compatibility of the matrix components (cellulose and HEC). Hence, it is evident, that in the separation of the azeotropic mixture, modified membranes have an essential advantage over nonmodified membranes. The value of  $\alpha P$  at 50°C for the azeotropic mixture is  $760 \text{ kg m}^{-2} \text{ h}^{-1}$ , which, according to its effective performance in industrial processes. It should also be pointed out that this value is attained at a lower temperature (50°C) than in ref. 3 (data were obtained at 100°C).

#### Effect of Temperature

The temperature dependence of  $P$  and  $\alpha$  in the range of 25–60°C for IPN membranes with a matrix from Cph is shown in Figures 7 and 8. It can be seen that with increasing temperature a marked increase in both  $P$  and  $\alpha$  is observed, which is of particular interest. In fact, the increase in  $P$  with increasing temperature for diffusion-type membranes is a usual dependence, whereas selectivity usually changes only slightly with increasing temperature or even decreases.

Karakane et al.<sup>4</sup> found that, for composite membranes with a selective PAA layer, in addition to increasing  $P$ , a slight decrease in  $\alpha$  was observed in the range of 50–70°C. Liang and Ruckenstein<sup>10</sup> observed a decrease in  $\alpha$  for IPN membranes based on PVA–PAAm, with a temperature increase from 30 to 75°C. A similar dependence was also detected for membranes based on a chitosan–PAA polyelectrolyte complex.<sup>17</sup> Karakane et al.<sup>4</sup> and Shieh and Huang<sup>17</sup> supposed that a temperature increase leads to increasing mobility of the polymer chains, which, in turn, leads to an increasing free volume in the polymer and facilitates sorption and diffusion of components of the mixture to be separated. This favors an increase in  $P$  and a decrease in  $\alpha$ . For cellulose–acrylate IPN membranes, the anomalous increase in  $\alpha$  with increasing temperature observed by us may be explained by the improved compatibility between cellulose and synthetic components in the IPN structure at elevated temperatures. This leads to an increasing degree of homogeneity of IPN membranes on a supramolecular level. The results of our previous works<sup>11,18</sup> showed that the structure of IPN is more homogeneous than is that of the cellulose matrix. This conclusion was based on a comparison of data on transport properties of the cellulose matrix and IPN membranes and their structures obtained by small-angle neutron scattering (SANS). The structure of the cel-



**Figure 8** Temperature dependence on the separation factor of IPN membranes.

lulose matrix is much more microheterogeneous because both amorphous and crystalline regions are present. The presence of amorphous regions explains the relatively low matrix selectivity in the separation of EtOH-water mixtures. The filling of amorphous regions by synthetic chains probably leads to the formation of a more ordered structure, and as a result, membrane selectivity increases sharply. SANS data showed that large voids with a size of  $\sim 110$  Å observed in the matrix structure are transformed into smaller voids with a size of  $\sim 30$  Å.<sup>18</sup>

It might be suggested that with increasing temperature homogenization of IPN membrane structural elements [amorphous regions filled by PAA(K<sup>+</sup>) or PAAm chains] takes place on a lower size scale ( $<30$  Å), which leads to a decreasing free volume in the IPN structure. To draw more definite conclusions, a more detailed investigation of the temperature dependence of the IPN membrane structure is required. The difference in the temperature behavior between the IPN membrane type studied by us and the IPN membranes based on PVA-PAAm<sup>10</sup> can also be explained not only by the difference in chemical composition but also by the difference in the procedure of IPN membranes preparation. In ref. 10, the PAAm network is formed first in the presence of the PVA solution and subsequently the crosslinking agent for PVA is introduced. In our case, AAm polymerizes inside the cellulose matrix. In these cases, the microstructures must evidently differ greatly.

The Arrhenius plot constructed from the data on the temperature dependence of  $P$  for different types of IPN membranes is shown in Figure 9. The values of the observed activation energy ( $E_a$ ) for the IPN membranes are listed in Table II. For polyelectrolyte membranes with a Cph matrix, the values of  $E_a$  are approximately equal: 6.7 and 6.8 kcal/mol for the separation of 46 and 86 wt % EtOH, respectively. These values are close to those observed in ref. 4.  $E_a$  is 6.2 kcal/mol for composite membranes based on PAA diffusion layers on a PAN support. For polyelectrolyte IPN membranes with the Cell-HEC matrix, the value of  $E_a$  is slightly lower (5.1 and 5.9 kcal/mol for 46 and 86 wt % EtOH, respectively). The observed activation energy of a nonionic Cph-PAAm membrane is higher than that for polyelectrolyte membranes (12.3 and 9.5 kcal/mol for 46 and 86 wt % EtOH, respectively). This is also in agreement with the data in ref. 10 in which the value of  $E_a$  for nonionic PVA-PAAm IPN membranes was 8.9–10.2 kcal/mol in the separation of 85 wt % EtOH.

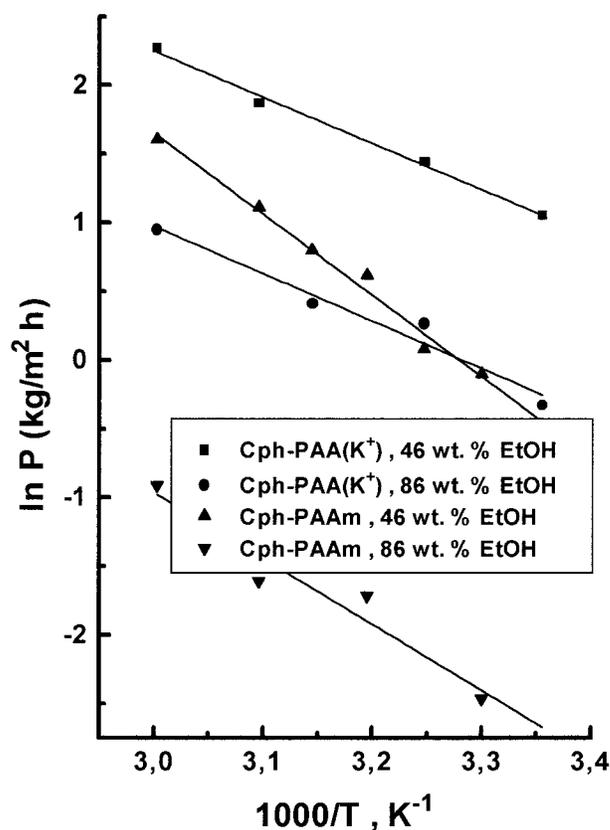


Figure 9 Arrhenius plots of the permeation rate of IPN membranes.

## CONCLUSIONS

In the separation of concentrated EtOH solutions ( $\geq 86$  wt %), the separation factor and the permeation rate of IPN membranes increase with an increasing content of ionic acrylate groups in polymer chains of the synthetic network. This is caused by a higher affinity of ionic acrylate groups for water as compared with that of amide groups. In the separation of moderately concentrated EtOH solutions (46 wt % EtOH), no marked increase in  $\alpha$  is observed when the content of ionic groups increases from 0 to 100 mol %. In this case, it is evidently more desirable to use nonionic membranes, taking into consideration membrane stability under the conditions of their long performance, so as to avoid the well-known effect of counterion elimination from polyelectrolyte membranes.

The separation index for polyelectrolyte IPN membranes with a cellulose matrix in the separation of 86 wt % EtOH attained  $\sim 2000$  kg m<sup>-2</sup> h<sup>-1</sup> (50°C), but in the separation of the azeotropic EtOH-water mixture, it decreases to  $\sim 240$  kg m

**Table II Feed Concentration Dependence of the Observed Activation Energy of the Permeation Rate for Different Types of IPN Membranes**

[EtOH] (wt %)	$E_a$ (kcal/mol)		
	Cph-PAA(K <sup>+</sup> )	Cph-PAAm	Cell50-HEC50-PAA(K <sup>+</sup> )
46	6.7	12.3	5.1
86	6.8	9.5	5.9

$h^{-1}$ , mainly as a result of decreasing  $P$  because of a sharp decrease in the degree of swelling of IPN membranes. The modification of the cellulose matrix by introducing HEC into it makes it possible to increase considerably the degree of membrane swelling (at EtOH >86 wt %) and, correspondingly, their permeation rate and separation index in the separation of the azeotropic composition also increase.

The values of  $P$  and  $\alpha$  for all types of IPN membranes increase with increasing temperature in the range of 25–60°C. It is most probable that the increase in  $\alpha$  is due to improved compatibility of IPN components with increasing temperature and to the formation of a more homogeneous IPN structure on the supramolecular level.

## REFERENCES

1. Staudt-Bickel, C.; Lichtentaller, R. N. *Vysokomol Soedin* 1994, 36, 1924.
2. Feng, X.; Huang, R. Y. M. *Ind Eng Chem Res* 1997, 36, 1048.
3. Sander, U.; Soukup, P. *J Membr Sci* 1988, 36, 463.
4. Karakane, H.; Tsuyumoto, M.; Maeda, Y.; Honda, Z. *J Appl Polym Sci* 1991, 42, 3229.
5. Sperling, L. H. *Mater Eng* 1980, 92, 66.
6. Sperling, L. H. In *Interpenetrating Polymer Networks; Advances in Chemistry Series 239*; Klempner, D.; Sperling, L. H.; Utracki, L. A., Eds.; American Chemical Society: Washington, DC, 1994; pp 3–38.
7. Lee, D. S.; An, J. H.; Kim, S. C. In *Interpenetrating Polymer Networks; Advances in Chemistry Series 239*; Klempner, D.; Sperling, L. H.; Utracki, L. A., Eds.; American Chemical Society: Washington, DC, 1994; pp 463–485.
8. Lee, Y. K.; Tak, T.-M.; Lee, D. S.; Kim, S. C. *J Membr Sci* 1990, 52, 157.
9. Billard, P.; Nyuyen, Q. T.; Leger, C.; Clement, R. In *Third International Symposium Euromembrane' 97, Progress in Membrane Science Technology, Book of Abstracts, University of Twente, The Netherlands, June 23–27, 1997*; pp 326–328.
10. Liang, L.; Ruckenstein, E. *J Membr Sci* 1995, 106, 167.
11. Buyanov, A. L.; Revel'skaya, L. G.; Kuznetsov, Yu. P.; Shestakova, A. S. *J Appl Polym Sci* 1998, 69, 761.
12. A. L.; Buyanov, Revel'skaya, L. G.; Nud'ga, L. A. *Russ Patent* 1 481 236, 1989.
13. Buyanov, A. L.; Revel'skaya, L. G.; Petropavlovskii, G. A. *Zh Prikl Khim* 1989, 62, 1854 (*J Appl Chem USSR* 1990, 1723).
14. Buyanov, A. L.; Revel'skaya, L. G.; Petropavlovskii, G. A. *Polym Mater Sci Eng* 1992, 66, 119.
15. Bushin, S. V.; Astapenko, E. P.; Belyaeva, E. V.; Khripunov, A. K.; Tsvetkov, V. N. *Polym Sci Ser A* 1999, 41, 681. Translated from *Vysokomol Soedin Ser A* 1999, 41, 1021.
16. Tanaka, T. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Eds.; Wiley: New York, 1987; Vol. 7, pp 514–531.
17. Shieh, J.-J.; Huang, R. Y. M. *J Membr Sci* 1997, 127, 185.
18. Buyanov, A. L.; Revel'skaya, L. G.; Khripunov, A. K.; Kuznetsov, Yu. P.; Lebedev, V.T.; Torok, Gy.; Cser, L. In *International Symposium, New Approaches in Polymer Synthesis and Macromolecular Formation, Book of Abstracts, St. Petersburg, Russia, June 16–20, 1997*; p 110.