

Poly(vinyl alcohol)/Poly(vinyl pyrrolidone) Interpenetrating Polymer Network: Synthesis and Pervaporation Properties

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ABSTRACT: Novel interpenetrating polymer network membranes were made from poly(vinyl alcohol)/poly(vinyl pyrrolidone) blends of different compositions. The two polymer components were independently crosslinked chemically with glutaraldehyde and photochemically with 4,4'-diazostilbene-2,2'-disulfonic acid disodium salt. The membrane performances were studied in pervaporation of tetrahydrofuran (THF)/water and THF/methanol mixtures.

It was found that the membranes were excellent in THF dehydration, but much less efficient for the separation of THF/methanol mixtures. The pervaporation results were consistent with the membrane swelling data. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2808–2814, 2003

Key words: pervaporation; membranes; interpenetrating networks (IPN); crosslinking; swelling

INTRODUCTION

Poly(vinyl alcohol) (PVA) is often used as hydrophilic membranes for the dehydration of organic solvents by pervaporation.¹ However, the low membrane permeability attributed to the high PVA crystallinity limits the performances of PVA membranes in pervaporation. To lower the crystallinity and thus to increase the membrane permeability, PVA modification or blending of PVA with a hydrophilic component capable of reducing the PVA crystallinity was envisaged by different authors.² The membranes made of cyclodextrin/PVA blend³ and chitosan/PVA blend membrane⁴ showed markedly increased fluxes. Nevertheless, polymer blending generally gives rise to membranes with low selectivity (and stability in solvent) attributed to the reduction of the number of PVA crystallites. Because the crystallites act as chain crosslinks, their reduction causes larger membrane swelling in the solvents, and consequently a larger flux, but lower selectivity and stability.

The crosslinking of the hydrophilic polymer blends makes them resistant to water-rich media, thus reducing the risk of membrane deterioration upon an accidental overshoot in water content in the pervaporation process. Because the extent of membrane swelling

in solvents is also limited by the crosslinks, the selectivity is expected to be equivalent to that of the semi-crystalline PVA membrane.

In the present work, we investigated the use of interpenetrating polymer network (IPN) membranes prepared by specifically crosslinking PVA with glutaraldehyde on the one hand, and poly(vinyl pyrrolidone) (PVP) with 4,4'-diazostilbene-2,2'-disulfonic acid disodium salt (DAS) under ultraviolet light, on the other hand. Although PVA can be crosslinked by diacids like succinic or maleic acid, a high temperature is generally required.^{5,6} Glutaraldehyde in the presence of an acid as a catalyst is a well-known agent for PVA crosslinking at much lower temperature⁷ and was therefore chosen for the purpose. Because of the absence of reactive groups in its chemical structure, PVP is more difficult to crosslink. We chose DAS⁸ because of its ability, under UV light, to substitute a hydrogen on the substituted carbon of the polymer backbone and link with it. The membranes were next used to separate THF/water and THF/methanol mixtures by pervaporation. The membrane swelling properties in these liquid mixtures were also studied to explain the membrane behavior in pervaporation.

EXPERIMENTAL

Materials

PVA (average molecular weight 80,000; hydrolysis degree > 99.8%) was bought from Shanghai Jinshan Petroleum Corp. PVP (average molecular weight 360,000), DAS, and glutaraldehyde (as 25% aqueous solution) were bought from Acros. Tetrahydrofuran (THF) and methanol were analytical reagents (purchased from Shanghai Feida Trading Company), and water was deionized water.

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Membrane preparation

We prepared the 5 wt % PVA and 5 wt % PVP solutions by heating the polymer in water under stirring. The solutions were mixed in proper proportions to obtain the desired polymer compositions in the final blends, and were filtered. A 4 wt % DAS aqueous solution was prepared in parallel in a dark room and added to the polymer blend solutions, together with 5 wt % glutaraldehyde (aqueous). After removal of the bubbles, the solutions were cast onto a cellulose acetate (CA) film fixed on a glass plate, which was heated in an oven at 40°C for drying. All these operations were carried out in the dark. The dried membranes were next irradiated with an ultraviolet lamp (rated power, 125 W; wavelength, 290–400 nm), for PVP crosslinking. After irradiation, the membrane was peeled off the CA support and heated in an oven at 80°C for 20 min, to crosslink the PVA. The obtained IPN membranes had a thickness in the range of 20–30 μm .

The reported weight fraction of DAS was based on the weight of PVP in the membrane, and that of glutaraldehyde was based on the weight of PVA in the membrane.

Measurements of membrane pervaporation properties

The pervaporation setup and cell were previously described elsewhere.⁹ The membrane was first mounted in the cell and the vacuum was pumped out on the downstream side. The membrane surface area was 28 cm² and the pressure on the downstream side was 30–50 Pa. The liquid mixture was poured into the cell and the permeate was collected in cold traps cooled in liquid nitrogen. Several permeate fractions were sampled out in different traps, until the steady state was reached. The composition of the steady-state permeate was analyzed with a gas chromatograph (Varian Associates, Palo Alto, CA) equipped with a 2 m-Porapak Q column and a thermal detector. In the pervaporation of water-THF or methanol-THF mixtures, the membranes were characterized by their selectivity, which was expressed as the water content C' (in wt %) or the methanol content in the permeate C'_m (in wt %), and the permeation flux J (gm⁻² h⁻¹). The latter was calculated from the weight of the permeate fraction collected during a fixed length of time.

Solubility and swelling degree measurement

A preweighed sample was immersed in a solvent mixture and allowed to reach sorption equilibrium at 40°C (for at least 10 h). The swollen sample removed from the solvent mixture was then wiped with paper tissue to remove the surface liquid, and immediately weighed. It was next dried in an oven under vacuum at 60°C to give the sample a constant weight after its conditioning in the studied solvent mixture.

The swelling degree characterizes the ability of the membrane to absorb the liquid mixture:

$$\text{Degree of swelling (\%)} = \frac{W - W'}{W'} \times 100$$

The solubility represents the fraction of the membrane extracted by the liquid mixture:

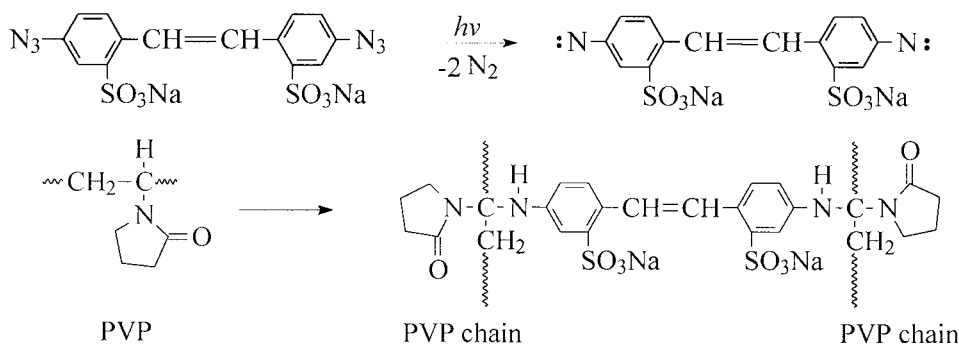
$$\text{Solubility (\%)} = \frac{W_0 - W'}{W_0} \times 100$$

where W_0 , W , and W' are the membrane weight before swelling, after swelling, and after redrying of the swollen sample, respectively.

RESULTS AND DISCUSSION

On the mechanism of the polymer photocrosslinking by DAS

DAS is a hydrophilic, diazo photocrosslinking agent, which is suitable for water-soluble polymers. Its crosslinking mechanism was reported in previous studies.^{8,10} Under UV irradiation, DAS would lose two nitrogen molecules to become an active dinitrene compound¹¹ whose nitrene groups are either in the state of singlets or triplets.¹¹ The dinitrene compound would react under the more active form of the singlet¹¹ by insertion into two C—H bonds to give interchain or intrachain crosslinks with substituted amine groups. Because the tertiary carbon is the most reactive,¹¹ the pyrrolidone-substituted carbon atoms of PVP would react with the DAS according to the following scheme:



A second reaction can also occur, especially at high DAS concentration: coupling of two DAS molecules into a dimer, whose bronze color can be easily detected.^{8,10} When the dimer formation occurs, it lowers the overall efficiency of crosslinking; thus the DAS concentration was strictly controlled in the reaction system.

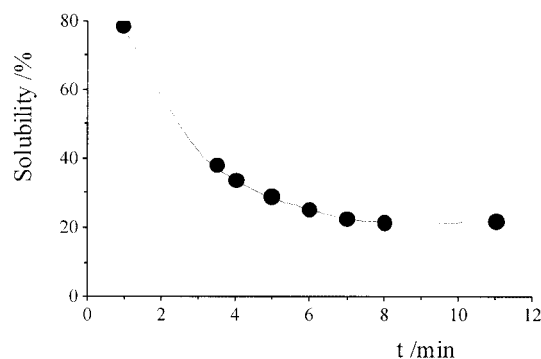
We were not able to detect the DAS characteristic peaks (of sulfonate and aromatic rings) in the infrared spectra of the crosslinked blends. This was probably because of the low content of the crosslinking agents in the blends.

Effect of crosslinking conditions on the solubility of PVA/PVP blends

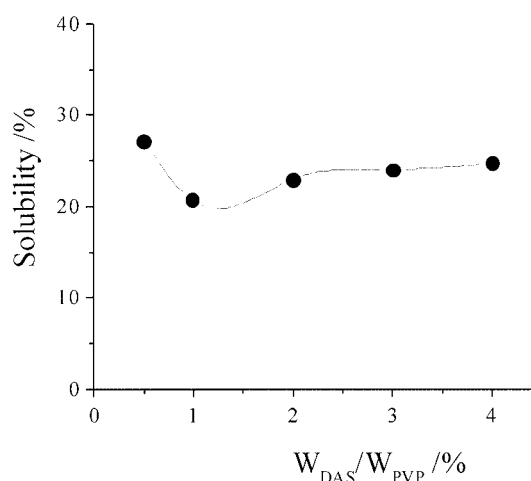
PVA and PVP are perfectly compatible polymers because of the hydrogen-bond interactions between PVP CO-groups and PVA OH-groups.¹² The small amounts of glutaraldehyde and DAS do not significantly change the polymer compatibility. FTIR analysis shows the PVA/PVP interactions¹³: the stretching band of OH progressively shifts to lower values (3410 to 3260 cm^{-1}) when the PVA content increases from 20 to 100%, indicating a switch of the $\text{CO}\cdots\text{HO}$ hydrogen bonds between the polymers to the multiple H-bonds in PVA. A similar shift of the $\text{C}=\text{O}$ band around 1696 to 1664 cm^{-1} attributed to the $\text{CO}\cdots\text{HO}$ hydrogen bond was also observed. Because of the H-bond interactions, the PVA crystallization was increasingly hindered when the PVP content increases (peaks at 1142 cm^{-1}).¹³ The crosslinking prevents the PVA fraction in the blends from crystallizing, thus stabilizing the membrane properties. No change in the PVA crystallinity-related peak at 1142 cm^{-1} was detected after the membrane use in pervaporation experiments.

DAS, according to its crosslinking mechanism, could react with PVA as well as with PVP. However, the solubility data showed that there was no effective PVA crosslinking by DAS. PVA films were completely dissolved in hot water after treatment with DAS under UV irradiation. The viscosity of the recovered PVA was reduced after irradiation in the dry state with γ -ray or UV-ray. It seems that PVA-chain scissions prevail in the procedure of PVA treatment with DAS under UV irradiation, probably because of the lack of stability of the resulting nitrene insertion derivatives. Although chain scissions caused by high-energy photons lead to radicals, which can in turn combine by pairs into crosslinks, the formed macroradicals have too limited a mobility in the dry polymer films to be able to generate crosslinks by radical recombination.

With respect to the DAS photocrosslinking mechanism, the crosslinking density increases with the efficiency of DAS conversion into dinitrenes (i.e., the quantum yield of DAS decomposition). The longer the irradiation time and the more intensive the light, the



(a)



(b)

Figure 1 Effect of irradiation time (a) and DAS content (b) on the solubility of PVP in water. Radiation distance: 7 cm.

higher the DAS concentration and the greater the absorbed energy.

At a fixed UV-source power, the intensity of light increases with a decrease in irradiation distance. However, if the irradiation distance is too short, the evolved heat will melt the blend membrane, and lead to a nonuniform blend modification. A compromise was found for an irradiation distance of 7 cm. Figure 1(a) shows that the solubility of PVP in hot water decreases with increasing irradiation time, indicating an increase of the PVP crosslinking density. When the irradiation time exceeds 8 min, the membrane solubility is no longer altered, which can be attributed to either a total depletion of DAS or a nonefficient crosslinking of short chains. Figure 1(b) shows that there is an optimum experimental condition for PVP insolubilization by DAS. When the DAS content was

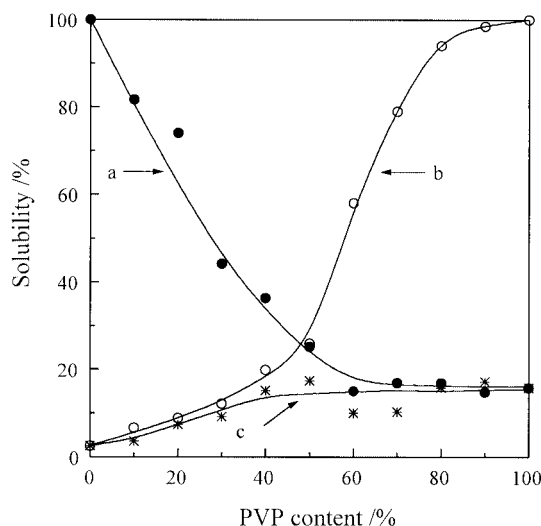


Figure 2 Effect of crosslinking agent on solubility of blend membrane in water: (a) DAS, 2%; (b) glutaraldehyde, 5%; (c) DAS, 2%; glutaraldehyde, 5%.

too low, there are too few crosslinking points to make an sufficiently large network of polymer chains, and part of the crosslinked chains remains extractable. If the DAS content is too high, the DAS decomposition rate is high, leading to a high dinitriline concentration and a high probability of bimolecular coupling of DAS molecules, and eventually to an intrachain crosslinking. The membrane solubility is not reduced, and even increased, because of a loss of interchain crosslinks. When that membrane is immersed in ethanol, the solvent medium turns orange, indicating the decomposition of DAS and its bimolecular coupling. When the DAS content is in the range 1–2 wt %, the solubility is the lowest. Thus, the DAS content was set to 2% for further experiments.

Polymer component extraction from photocrosslinked PVA/PVP blends

Changes in the solubility of the PVA/PVP blend membranes depend on their composition and on the nature of the crosslinking agent. When DAS alone is used as the crosslinking agent, the membrane solubility decreases first with the PVP content in the membrane, then tends to a residual solubility in water about 18 wt % [Fig. 2(a)]. Similarly, the membrane solubility increases with the PVP content in the membrane because of the lack of the ability for glutaraldehyde to crosslink PVP [Fig. 2(b)]. The DAS/glutaraldehyde mixture must specifically crosslink the two polymer components into intermingled PVA and PVP networks (i.e., IPN membranes). Figure 2(c) effectively shows that the solubility of the membranes sequentially crosslinked with such a mixture remains low in the whole composition range of the blend membranes.

In the following sections, the term PVA/PVP IPN membrane refers to the membranes sequentially crosslinked with glutaraldehyde and DAS-UV light.

Dehydration of THF with PVA/PVP IPN membranes

THF forms an azeotropic mixture with water at 95 wt %. The PVA/PVP IPN membrane show very high selectivity to water at 5 wt % in THF, whatever its composition (Fig. 3). The high water selectivity can be explained by the high affinity to water of both PVA and PVP. PVA shows high selectivity to water in a great number of organic solvents. PVP is also a good polymer for THF dehydration because its radiochemical grafting onto inert polytetrafluoroethylene (PTFE) films imparts a good selectivity to PTFE.¹⁴ It is interesting to note that the permeation flux increases with the PVP content in the membrane, without loss of selectivity. The flux increases sharply at around 40 wt % PVP in the membrane (Fig. 3), but tends to level off at about 80 wt %. The sharp increase in the permeation flux at PVP contents higher than 50% in the membranes is attributed to the disappearance of the PVA crystallinity, but not to the dual crosslinking. The PVA crystallites in the membranes play a double role: (1) reduce the absorbed solvent and (2) restrict the swelling of the membrane by a physical crosslinking effect. The disappearance of the PVA crystallinity at high PVP contents was evidenced in our previous study by DSC and IR studies^{12,13}; when it occurs, the membranes are freed from this physical crosslinking effect, leading to the observed increase in permeation flux (whereas the chemical crosslinks still operate as usual). The absence of a further increase in the permeation flux for PVP contents higher than 80% is related to the crosslinking of both polymer components in the membrane. The membrane is not able to swell more be-

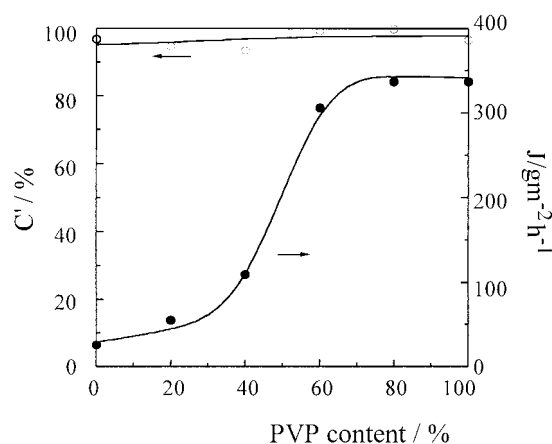


Figure 3 Effect of PVP content on the IPN membrane performances for the dehydration of THF by pervaporation at 40°C; feed, 5 wt % of water in THF. (Crosslinking agents: DAS, 2 wt %; glutaraldehyde, 5 wt %).

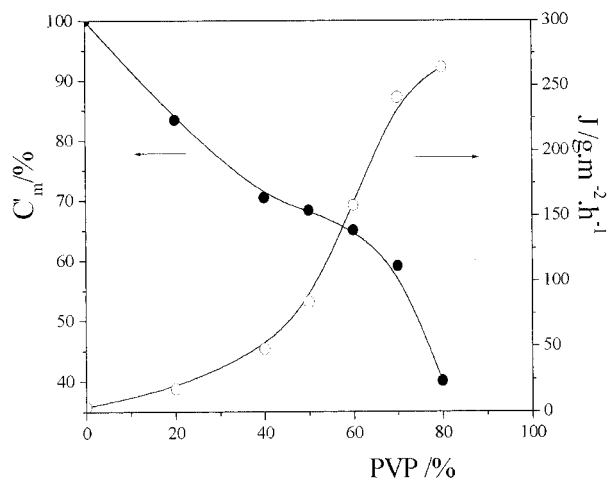


Figure 4 Effect of PVP content on the pervaporation properties of a 5:95 THF/MeOH mixture through a PVA/PVP IPN membrane at 40°C (DAS, 2%; glutaraldehyde, 5%).

cause of this dual crosslinking, as shown by the data on the membrane swelling in hot water. Such a relationship between the permeation flux and the swelling is generally observed in pervaporation. Thus, the IPN membrane containing 80 wt % PVP would be the best membrane for the THF dehydration. Such a membrane is much less fragile than the pure PVP membrane because of the film-forming properties of the PVA component.

Pervaporation of THF/methanol mixture

Influence of membrane composition

The outstanding separation performances of the IPN membranes in the pervaporation of the THF/water mixture prompted us to examine other mixtures. However, when we used PVA/PVP IPN membranes to separate the methanol/THF mixture, the membranes appeared to be less selective. Although the selectivity to methanol was high for the membranes of low PVP contents, the flux was low. Moreover, the selectivity decreases when the PVP content increases (Fig. 4). The difference in the behaviors of the two systems probably arises from (1) the stronger sorption by the membranes of water, compared with methanol, from mixtures with THF; and (2) the greater interactions of THF with methanol than with water. As a result, the selectivity toward methanol in THF is always lower than that toward water in THF.

The results also indicate that the PVA component plays a key role in the selectivity of the membrane to methanol in THF, whereas the PVP component imparts the permeability to the membrane. The sharp decrease in the membrane selectivity at a PVP content in the membrane around 20 wt % is attributed to the fact that PVP shows not only a lower affinity toward methanol compared with water, but also exhibits hy-

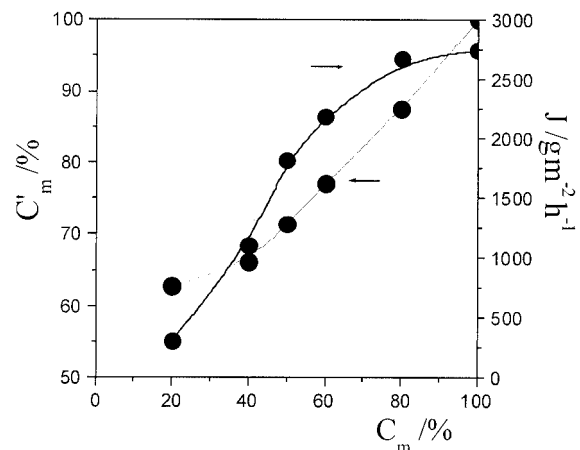


Figure 5 Effect of methanol content on pervaporation properties of tetrahydrofuran-methanol mixture on PVA/PVP IPN membrane. (DAS, 2%; glutaraldehyde, 5%; $T = 20^\circ\text{C}$; PVA/PVP = 40/60).

drogen-bond interactions with PVA and blocks the PVA crystallization.¹³ As a result, THF molecules penetrate more easily into the membrane,¹⁴ thus leading to a lower membrane selectivity.

Influence of feed composition

The composition of the liquid mixture to be treated generally has a strong influence on the membrane properties in pervaporation.^{15,16} Figure 5 shows an increase in the permeation flux through the membrane, and a reasonable decrease in selectivity, when the methanol content in the mixture increases. The pure THF flux through the membrane was relatively high compared with that of other solvents, in agreement with the trend in material swelling shown in Table I.

Influence of temperature

It is well known that the diffusion coefficient of molecular species in polymer materials increases exponentially with temperature according to an Arrhenius-like equation. Such a diffusivity increase generally gives rise to an Arrhenius-type (exponential) increase in the total permeation flux with the pervaporation temperature.¹⁷ Figure 6 shows that the total flux of

TABLE I
Effect of DAS Content on the Swelling Degree of PVA/PVP IPN Membranes at 40°C (glutaraldehyde content 5%; PVA/PVP = 40/60)

DAS (%)	Percentage swelling			
	THF	THF/MeOH (95/5)	MeOH	Water
2	9.6	31.4	63.7	1590
3	14.3	34.5	86.9	1850
4	20.5	36.4	92.6	2180

methanol/THF permeation through the IPN membrane containing 60 wt % PVP deviates from the general behavior. Not only does the permeation flux increase much less sharply with temperature, it also decreases when the pervaporation temperature exceeds about 40°C. The change in selectivity with temperature is the reverse of that of the permeation flux.

Although the situation appears to be abnormal, its interpretation turns out to be possible on the basis of other data. In fact, the flux increase and the permselectivity decrease in the range of low pervaporation temperature are quite classical; we need only to interpret the reverse situation at high temperatures. FTIR analyses evidenced a crystallinity increase in the membrane after the pervaporation experiment at 50°C. Thus, the PVA crystallinity increase was induced both thermally and by the solvent¹⁸ during the pervaporation experiment, when the temperature was high enough for a fast PVA crystallization. Because the crystallites are quasi-impermeable, the permeation flux is drastically reduced when the crystallization proceeds (i.e., in the pervaporation) at high temperatures. Consequently, the membrane swelling decreases, leading to a selectivity increase. We effectively observed that the membrane was permanently altered; that is, the permeation flux did not go back to its high value when the membrane, which experienced the PVA crystallization, was used again at lower temperatures.

Influence of DAS content

If the crosslinking density of the IPN membrane increases, the THF permeability would decrease because of the reduction of the polymer segment mobility. The pure THF flux through the membrane can thus be used as a measure of the crosslinking density. Table II shows a sudden increase in pure THF flux at 3 wt % of

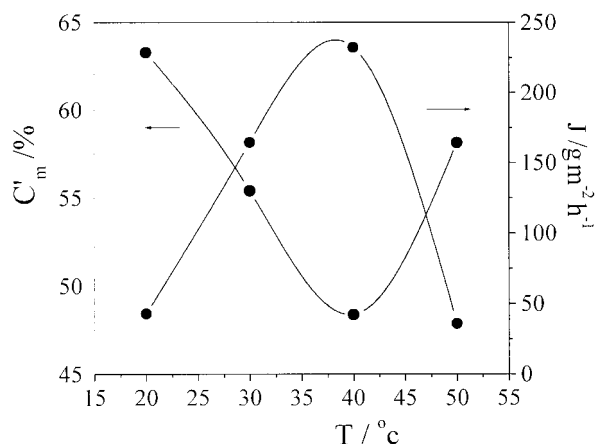


Figure 6 Effect of temperature on the pervaporation properties of a 5 : 95 tetrahydrofuran-methanol mixture through a PVA/PVP IPN membrane at 40°C (DAS, 2%; glutaraldehyde, 5%).

TABLE II
Effect of DAS Content on the Properties of Pervaporation of Pure Tetrahydrofuran at 20°C Through PVA/PVP (40/60) IPN Membranes (glutaraldehyde content 5%)

DAS (%)	1	2	3	4
$J/\text{gm}^{-2}\text{h}^{-1}$	257	251	1160	1540

DAS in the polymer blend system. Such an increase in pure THF flux suggests a decrease in the crosslinking density. It should be noted that the crosslinking density depends on the efficiency of the transformation of DAS into an effective dinitrene crosslinker.⁷ However, when the DAS content was too high, the dinitrene concentration is also high. At high dinitrene concentration, the probabilities of bimolecular coupling reaction and intramolecular crosslinking would increase at the expense of the intermolecular crosslinking.

Membrane swollen properties in different solvents

In the process of solvent separation by pervaporation, membrane swelling inevitably occurs as a result of solvent sorption, leading to a flux increase and a selectivity drop. The larger the swelling of the membrane in a solvent, the greater the solvent-membrane affinity, and the more it is preferentially permeated. To analyze the affinity between IPN membrane and different solvents, we separately measured the swelling degree of the IPN membranes with different DAS contents in THF, methanol, water, and THF/methanol 95 : 5 mixture.

Table I shows that the swelling degree is higher for pure methanol than that for the mixture and pure THF. The swelling degree in water is one order of magnitude greater than that for methanol. This explains the exceptional selectivity of the membranes to water in THF compared with that to methanol. Table I also shows that the membrane swelling degree increases with the DAS content in the membrane beyond 2 wt %. These data are consistent with the interpretation based on the above-suggested decrease in the intermolecular crosslinking density when the DAS content exceeds 2 wt %.

CONCLUSIONS

Membranes made of interpenetrating (IPN) polymer networks were conveniently prepared from PVA/PVP blends by specific crosslinking the polymer components with glutaraldehyde and with a water-soluble photocrosslinking reagent, 4,4'-diazostilbene-2,2'-disulfonic acid disodium salt. The membranes had good film-forming property and stability.

The membranes showed fairly good pervaporation characteristics toward the THF/methanol mixture. The pervaporation data indicate the decisive role of

PVA in the membrane selectivity. The PVP component improves the flux, but at a certain expense of the selectivity. The membranes exhibit both excellent flux and selectivity to water in THF because of their very strong affinity to water. It was found that there is an optimum value of the DAS content for the membrane with the best separation performance.

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