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M. C. Burshe[a]; S. A. Netke[a]; S. B. Sawant[a]; J. B. Joshi[a]; V. G. Pangarkar[a]
[a] DEPARTMENT OF CHEMICAL TECHNOLOGY, UNIVERSITY OF BOMBAY, MUMBAI, INDIA

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Pervaporative Dehydration of Organic Solvents

M. C. BURSHE, S. A. NETKE, S. B. SAWANT, J. B. JOSHI,
and V. G. PANGARKAR*
DEPARTMENT OF CHEMICAL TECHNOLOGY
UNIVERSITY OF BOMBAY
MATUNGA, MUMBAI 400 019, INDIA

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ABSTRACT

Pervaporative separation of acetone/water and isopropanol (IPA)/water systems has been studied in the water-lean range of composition of the feed mixtures. Poly(vinyl alcohol) (PVA) membranes crosslinked with citric acid, adipic acid, maleic acid, glutaraldehyde, and glyoxal were used for this purpose. The sorption characteristics of all the membranes indicate that these membranes have a good sorption selectivity for water in view of the hydrophilic nature of PVA. The type of crosslinker used for crosslinking has been shown to have an important bearing on the permeation characteristics of the membranes. Thus, the trifunctional citric acid yields the highest selectivity but lowest flux. A comparison of the productive capacities of the various membranes indicates that the glutaraldehyde crosslinked membrane has the maximum productive capacity for IPA dehydration whereas maleic acid crosslinked membrane yields the highest productive capacity for acetone dehydration.

Key Words. Poly(vinyl alcohol); Crosslinking; Pervaporation; Acetone; Isopropanol; Dehydration

INTRODUCTION

Pervaporation (PV) is an effective alternative membrane process used to remove water from aqueous–organic mixtures where concentration of

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* To whom correspondence should be addressed.
FAX: 91 22 4145614
E-MAIL: vgp@udct.ernet.in

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water is low. Essential characteristics of a PV membrane in industrial application for dehydration of organics are high selectivity coupled with a reasonably high flux for water. Poly(vinyl alcohol) (PVA) is the polymer used to make the active layer of the commercially available membranes for dehydration by PV. There are a number of industrial plants for dehydration of ethanol employing moderately crosslinked PVA membranes supplied by GFT (1).

Pervaporation membrane consists of a thin active/permselective layer followed by a porous support. In principle, good preferential sorption leads to high selectivity in a PV process. The permselective layer should selectively sorb the faster permeating species which is normally a good solvent for a polymer comprising this layer. However, if the interactions between the preferentially sorbed component and the membrane material are very strong, these can lead to excessive swelling of the membrane. Excessive swelling dilates the polymer lattice and results in loss of mechanical strength and permselective properties of the membrane. This problem is generally overcome by crosslinking the active layer of the polymer membrane. Crosslinking improves both membrane stability and selectivity but lowers the flux. In view of this, an optimization is required which will result in a membrane with high selectivity at an acceptable flux.

Yoshikawa et al. (2) reported that the introduction of imide groups into the membrane structure can be very effective for selectivity with respect to water. This is due to the high polarity and hydrogen bonding interactions of the imide group with water. Huang and Yeom (3) studied the effect of crosslinking density of amic acid crosslinked membrane for dehydration of ethanol. They observed an increase in selectivity for water up to 12% crosslinking, beyond which the selectivity decreased. Yamada et al. (4) investigated formaldehyde and glutaraldehyde crosslinked PVA membranes for dehydration of ethanol. It was found that glutaraldehyde crosslinked membranes afford higher selectivities as compared to formaldehyde crosslinked membranes, but the permeation rates were low with glutaraldehyde crosslinked membranes. Dehydration of a number of organic systems, e.g., ethanol, isopropanol, and acetic acid, are industrially important. Isopropanol (IPA) and water form an azeotrope at 0.87 weight fraction of IPA. Huang et al. (5) reported separation of IPA–water by aromatic poly(etherimide) membranes. Separation of acetone-rich mixtures with water can be conveniently effected by distillation up to 95–97 wt% acetone. Beyond this concentration however, the relative volatility is relatively low. As a result, large reflux ratios/large number of theoretical stages are required for further enrichment of acetone. There are many applications where an acetone content of 99.8 wt% is required. For such

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applications a hybrid process comprising distillation up to 90–95wt% acetone and subsequent pervaporative dehydration to 99.8% acetone will be more economical. Dehydration of acetone using GFT's PVA membrane has been studied by Wesslein et al. (6).

In this study, the preformance of crosslinked poly(vinyl alcohol) membranes was evaluated for the separation of IPA–water and acetone–water mixtures. The effect of the functional group of crosslinker on the separation performance was studied for the above systems. The study was restricted to the following concentration ranges: 1) IPA 70 to 98 wt% and 2) acetone 85 to 98 wt%. For IPA concentrations lower than 70 wt% and acetone concentrations lower than 80 wt%, distillation is a highly favourable alternative. Performance of the membranes for the separation of aqueous–organic mixtures was evaluated by obtaining the flux and selectivity for the particular system. Flux is a function of membrane thickness. Therefore, the flux values reported in this work were normalized to 10 μm thickness. Selectivity is expressed as

$$\alpha = \frac{\dfrac{C^f}{1 - C^f}}{\dfrac{C}{1 - C}} \tag{1}$$

The separation factor, β, is given by

$$\beta = C^f/C \tag{2}$$

C^f and C are the weight fractions of the faster permeating species (water in this case) in the permeate and in the feed, respectively. Pervaporation is generally described by the sorption–diffusion model. The sorption behavior can be evaluated by calculating the sorption coefficient. The sorption data also give the boundary concentrations of permeating species in the upstream layer of the membrane (7). A classical example of these calculations for the water–ethanol mixture is given by Neel (7). Neel et al. (8) defined the productive capacity, Q_P, of a unit pervaporator as follows:

$$Q_P = J_P(\beta - 1) \tag{3}$$

This definition allows a comparison of performance of different membranes for a given system.

EXPERIMENTAL

Membrane Casting

PVA was kindly supplied by Polychem Ltd., Mumbai, India. The PVA, Polynol 117, was 99% hydrolyzed and the average molecular weight was

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75 kD. PVA flakes were gradually dissolved in deionized water at 90°C and boiled for 2 hours to produce a transparent 8 wt% PVA solution. For chemical crosslinking with citric acid, adipic acid, and maleic acid, calculated amounts of the crosslinking agents were dissolved in the PVA solution. After the membrane was cast, water was allowed to evaporate at 30°C and then the membrane was subjected to thermal treatment at 150°C for 1 hour. The glutaraldehyde and glyoxal crosslinked PVA membranes were prepared as per the procedure of Yamada et al. (4). The membranes were prepared in a manner such that 5% crosslinking density was obtained. Crosslinking density here refers to the percentage of OH groups of PVA which have been bound by the crosslinker.

Sorption Studies

Films of known weight of the membranes prepared as described above were immersed in aqueous solutions of acetone and in aqueous solutions of IPA of different known concentrations. The films were allowed to equilibrate for 48 hours at 30°C. The films were then removed and weighed after the superfluous liquid was wiped with tissue paper. The increase in weight is due to the water and acetone or IPA sorbed by the membrane. The amount of water in the membrane phase was analyzed by Karl Fisher Titrator. The amount of acetone//IPA sorbed was obtained by material balance.

Permeation Studies

The equipment used for PV experiments was the same as that used by Netke et al. (9). The membrane was allowed to equilibrate for 1 hour with the feed solution before the commencement of PV experiments. After steady state was attained, the permeate was collected in traps immersed in liquid nitrogen. The permeate composition was determined using a Bausch and Lomb refractometer. Permeation studies were carried out at 30°C. The downstream pressure was maintained at 1 mmHg in all the experiments.

Determination of Membrane Crystallinity

The crystallinity of the membrane was determined by means of DSC Dupont 9900. The heat of fusion values were calculated for each crosslinked membrane. Crystallinity was calculated by using the following equation:

$$\%\ \text{Crystallinity} = (\Delta Hf_c/\Delta Hf_{cs}) \times 100 \tag{4}$$

where ΔHf_c is the heat of fusion at crystallization for the crosslinked membrane and ΔHf_{cs} is the heat of fusion at crystallization for the standard.

RESULTS AND DISCUSSION

Sorption Studies

Figures 1 and 2 give the variation in sorption of water for water–acetone and water–IPA, respectively, for PVA membranes with different crosslinkers. It can be observed that sorption of water by the membrane varies depending upon the nature of the crosslinking agent. Greater sorption of water exhibited by the citric acid crosslinked membrane is probably due to the higher intermolecular space between the PVA chains. Sorption in PVA occurs because of hydrogen bonding between the OH group of PVA and water. Initially when water concentration is low, sorption is predominantly due to the hydrogen bonding between the OH group and water, and the isotherm is almost linear. As the water concentration is increased, all the OH groups of PVA are probably bonded. Subsequently, sorption occurs on the BET sites (10). The curve tends to flatten out in the higher

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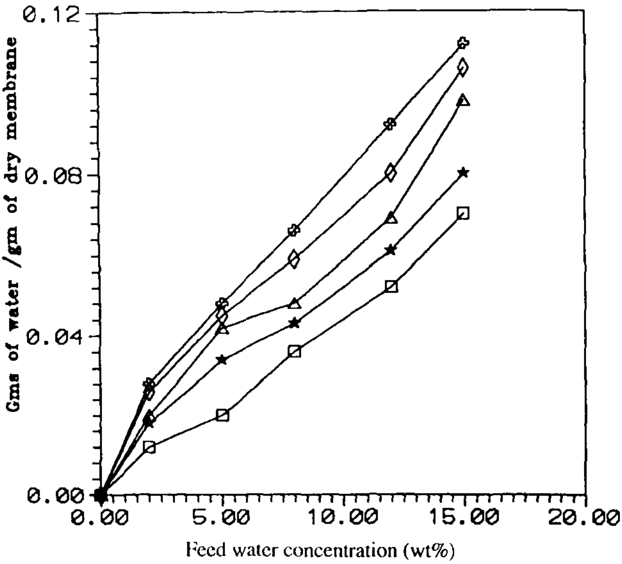

FIG. 1 Sorption plot for water. System: water–acetone–crosslinked PVA. (✣) 5% citric acid crosslinking agent, (◇) 5% adipic acid crosslinking agent, (△) 5% maleic acid crosslinking agent, (★) 5% glutaraldehyde crosslinking agent, (□) 5% glyoxal crosslinking agent.

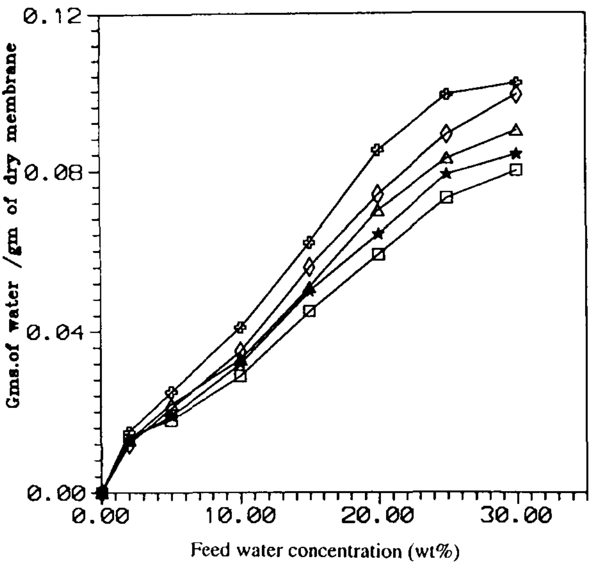

FIG. 2 Sorption plot for water. System: water–IPA–crosslinked PVA. (✣) 5% citric acid crosslinking agent, (◇) 5% adipic acid crosslinking agent, (△) 5% maleic acid crosslinking agent, (★) 5% glutaraldehyde crosslinking agent, (□) 5% glyoxal crosslinking agent.

concentration region and resembles the curve for Roger's Type II isotherm (10). Extent of water sorption for IPA–water mixtures levels off at a water concentration greater than 25 wt% (Fig. 2). For the acetone–water system such a plateau is not observed (Fig. 1). The range of water concentration studied for the IPA–water system is 0–30% by weight whereas that for acetone–water is 0–15% by weight. It is likely that the water sorption isotherm for the acetone/water/PVA system (Fig. 1) may also level off at higher water weight percent (of the order of 25–30 wt%) which has not been covered. A comparison of the sorption data shows that the trifunctional citric acid yields greater sorption than the bifunctional adipic acid and maleic acid. This is probably due to the difference in the number of ester groups in the corresponding membranes which are: citric acid crosslinked membrane (3) > adipic acid crosslinked membrane and maleic acid crosslinked membrane (2). The hydrophilicity of the ester group (11) is the probable cause of this behavior.

The aldehyde crosslinked membranes yield greater total sorption but less water sorption. Glutaraldehyde crosslinked membrane yields a mar-

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ginally greater (10%) water sorption compared to the glyoxal crosslinked membrane.

Permeation Studies

Figures 3 and 4 give the variation of fluxes with feed concentration for the acetone–water and IPA–water systems, respectively. Flux of water increases with an increase in the feed concentration of water owing to the higher sorbed water concentration and the consequent plasticization of membrane. In the present systems the glyoxal crosslinked PVA membranes showed the highest flux values for all feed water concentrations. Glyoxal acts as an intramolecular crosslinking agent for PVA, as the molecular chain length of glyoxal is too short to link two different molecules of PVA. In the case of glutaraldehyde, an intermolecular bridge is formed where the crosslinking takes place between two different molecules, which makes the structure compact. This compact structure is likely to hinder chain motion, and hence causes a decrease in the water flux as compared

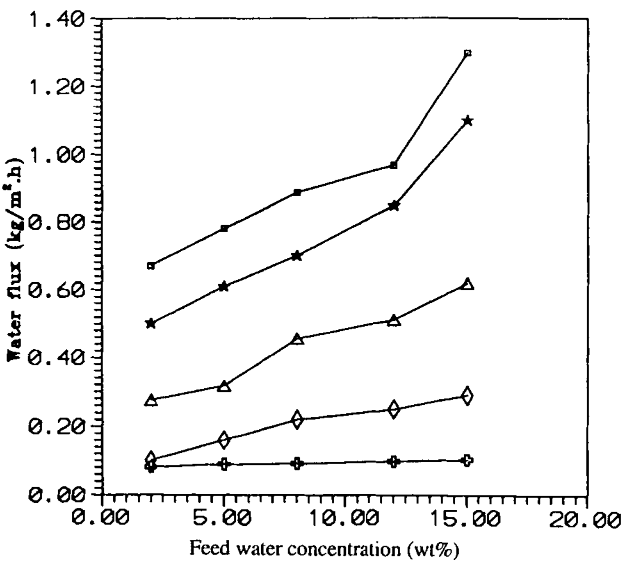

FIG. 3 Variation of water flux with feed water concentration for acetone–water system. (✚) 5% citric acid crosslinking agent, (◇) 5% adipic acid crosslinking agent, (△) 5% maleic acid crosslinking agent, (★) 5% glutaraldehyde crosslinking agent, (□) 5% glyoxal crosslinking agent.

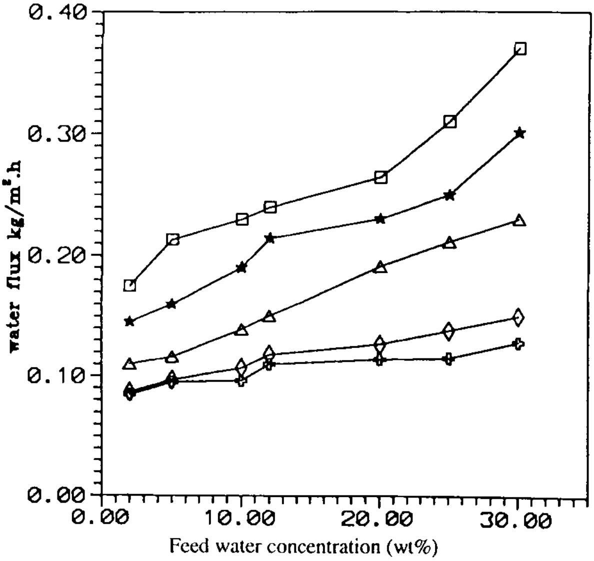

FIG. 4 Variation of water flux with feed water concentration for IPA–water system. (✣) 5% citric acid crosslinking agent, (◇) 5% adipic acid crosslinking agent, (△) 5% maleic acid crosslinking agent, (★) 5% glutaraldehyde crosslinking agent, (□) 5% glyoxal crosslinking agent.

to glyoxal crosslinked PVA. Low flux values were observed for citric acid crosslinked membranes. This is due to the trifunctional carboxylic acid groups of citric acid which give a larger number of sites for crosslinking between different PVA molecules. This results in a more compact structure of the membrane because the chain mobility is reduced, as mentioned above. The extent of compactness can be explained on the basis of crystallinity of the membrane. The values of crystallinity of the membranes are given in Table 1. Thus, for instance, the more crystalline citric acid crosslinked membrane yields the highest selectivity but the lowest flux. Permeation fluxes for maleic acid and adipic acid crosslinked membranes were higher compared to citric acid because these two acids are bifunctional carboxylic acids, which on crosslinking give less compact structures than citric acid. The flux values are higher for the acetone–water system than the IPA–water system.

Effect of Functional Group of the Crosslinker

In order to study the influence of the functional group of the crosslinker, the above prepared membranes were studied for the pervaporation of

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TABLE 1
Effect of Crosslinking Agent on Flux and Selectivity of Water. Acetone and IPA Feed Concentration 95% by Weight. Temperature: 30°C

			System			
			Acetone–water		IPA–water	
Crosslinking agent	Nature of groups formed on crosslinking with PVA	% Crystallinity	H_2O flux[a] (kg/h·m^2)	Selectivity	H_2O flux[a] (kg/h·m^2)	Selectivity
Citric acid	Triester group	41	0.089	192	0.095	741
Adipic acid	Diester group	38.5	0.16	153	0.097	481
Maleic acid	Diester group	38	0.32	118	0.116	321
Glutaraldehyde	Diether group	35	0.78	95	0.194	116
Glyoxal	Diether group	32	0.61	57	0.213	86

[a] Normalized flux: 10 μm membrane thickness.

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IPA–water and acetone–water systems. The results are presented in Table 1. From the results it is evident that the citric acid crosslinked membrane yields the highest selectivity for both systems. This high selectivity can be explained on the basis of formation of ester groups as a result of crosslinking between PVA and citric acid. These groups in the membrane produce a larger number of sites for the interaction of water through hydrogen bonding. The ester group has a hydrophilic character which can cause an increase of the sorption selectivity of the membrane and, as a consequence, can increase the separation factor in PV experiments (11). In the case of glyoxal and glutaraldehyde crosslinkers, ether groups are formed which are less hydrophilic than the ester group of polyacids. Therefore, these membranes showed lower selectivity than the one crosslinked with polyacids.

Membrane Appearance and Stability

Studies on membrane stability require extended continuous pervaporation experiments running into several weeks/months. Since such tests were not carried out, only visual observations about the membranes and their appearances are reported here. After the pervaporation experiments, PVA membranes crosslinked with polyaldehydes (glyoxal and glutaraldehyde) were found to have less mechanical strength and stability. This is probably due to a progressive hydrolysis of crosslinks which are of ether or acetal type of difunctional agents (12). The acid crosslinked membranes, however, did not show such deterioration in mechanical strength.

TABLE 2
Observations Made for Various Crosslinked PVA Membranes

Crosslinking agent	Membrane appearance
Citric acid	Transparent
Maleic acid	Transparent
Adipic acid	Slightly opaque
Glutaraldehyde	Slightly transparent
Glyoxal	Slightly transparent

Table 2 gives some of the observations made for the various membranes used in this study.

Effect of Feed Concentration

It can be observed from Figs. 3 and 4 that the permeate flux increases with the water content in the mixture. This can be explained on the basis

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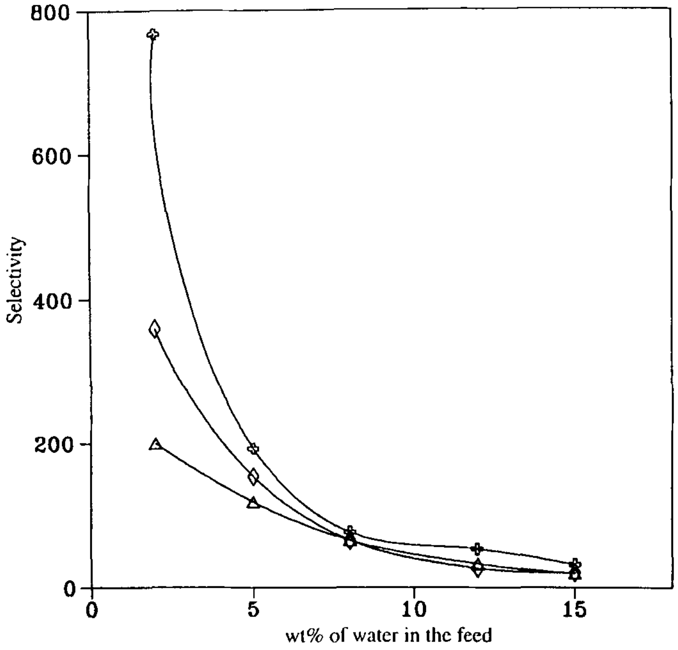

FIG. 5 Variation of selectivity with wt% of water in the feed for acetone–water system. (✣) 5% citric acid crosslinking agent, (◇) 5% adipic acid crosslinking agent, (△) 5% maleic acid crosslinking agent.

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of an increase in membrane sorption. However, with increasing feed concentration of water, the selectivity decreases, probably due to membrane plasticization. The structure of the membrane has a strong influence on the permeation and separation of binary mixtures, especially when one of the components is a plasticizing agent for the polymer (13). Water swells the amorphous regions of the polymer matrix. With increasing concentration of water in the feed, the extent of swelling of the amorphous regions of the polymer increases. This leads to an increase in flexibility of polymer chains, and hence permeation is less selective. Figures 5 and 6 give the variation of permeation selectivity with respect to the concentration of water in the feed for the PVA membranes crosslinked with citric acid, adipic acid, and maleic acid for IPA–water and acetone–water systems, respectively. PVA membranes crosslinked with citric acid yielded the highest selectivity compared to the other crosslinked PVA membranes for IPA–water and acetone–water systems. Figures 7 and 8 give the variation of selectivity with respect to the concentration of water in the feed for the PVA membranes crosslinked with glutaraldehyde and glyoxal for IPA–water and acetone–water systems, respectively. Among these two

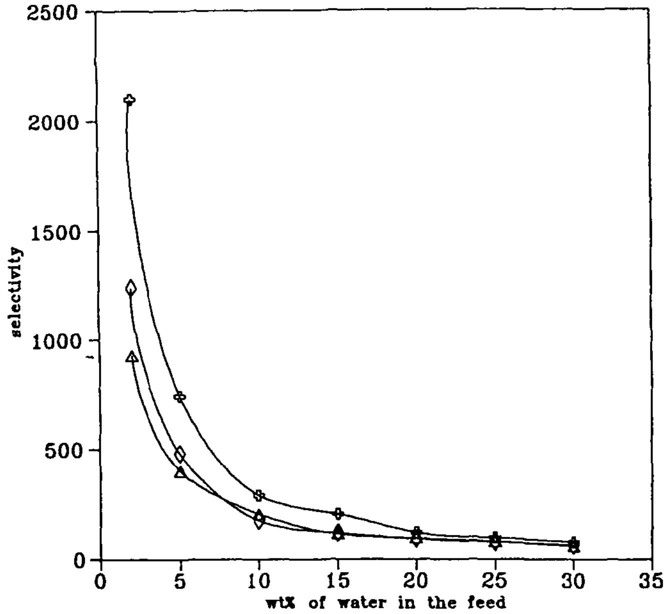

FIG. 6 Variation of selectivity with wt% of water in the feed for IPA–water system. (✢) 5% citric acid crosslinking agent, (◇) 5% adipic acid crosslinking agent, (△) 5% maleic acid crosslinking agent.

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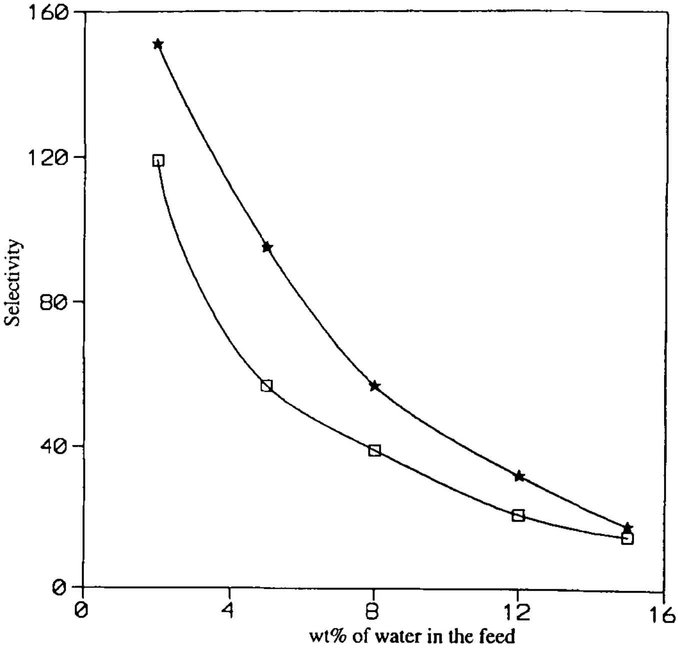

FIG. 7 Variation of selectivity with wt% of water in the feed for acetone–water system. (★) 5% glutaraldehyde crosslinking agent, (□) 5% glyoxal crosslinking agent.

crosslinked membranes, higher selectivity was obtained for water with PVA membranes crosslinked with glutaraldehyde for both systems.

Choice of Crosslinker

As mentioned earlier, the productive capacity of a membrane is a good guide for selection of the membrane for an industrial application. Table 1 gives a summary of the performance of the membranes for the two systems studied in the present work. Considerable information is available in the literature on dehydration of IPA with various membranes. However, in most of these cases the membrane thickness is not reported. Thus, direct comparison of the present data with the literature data is not possible. Table 3, based on the present work, indicates that for IPA dehydration glutaraldehyde is the optimum crosslinker (productive capacity of 3.54). For acetone dehydration maleic acid (productive capacity of 12.66) is evidently the best crosslinker.

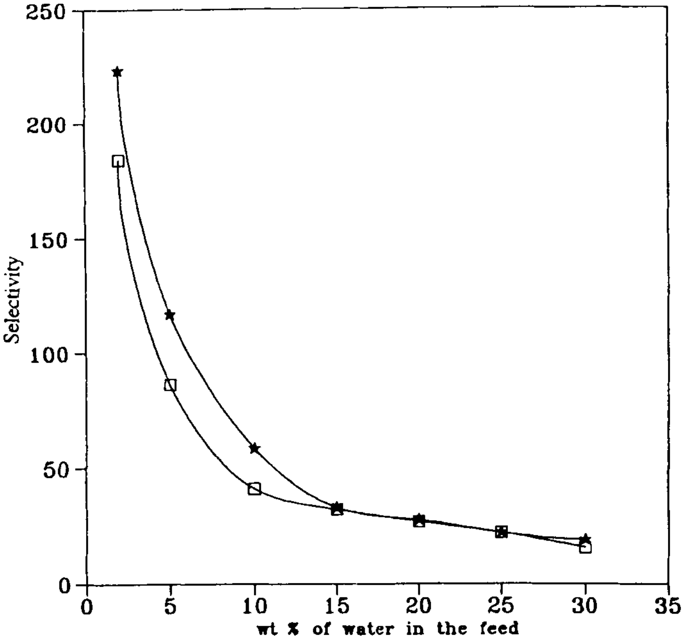

FIG. 8 Variation of selectivity with wt% of water in the feed for IPA–water system. (★) 5% glutaraldehyde crosslinking agent, (☐) 5% glyoxal crosslinking agent.

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TABLE 3
Productive Capacities of Crosslinked PVA Membranes for IPA–Water and Acetone–Water Systems

	Productive capacity, Q_P	
Crosslinking agent	IPA–water	Acetone–water
Citric acid	1.75	1.53
Adipic acid	1.77	2.69
Maleic acid	1.7	12.66
Glutaraldehyde	3.54	4.96
Glyoxal	2.28	8.54

CONCLUSION

The results reported in this work indicate that the type of crosslinker has a significant effect on the pervaporation performance of PVA membranes in dehydration applications. The productive capacity, which considers both the separation ability and flux, has been used to select the optimum crosslinker for the two systems studied. The best crosslinkers in terms of the productive capacity (among those studied) are glutaraldehyde and maleic acid for the acetone–water and the IPA–water systems, respectively.

ACKNOWLEDGMENT

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SYMBOLS

α	selectivity of a membrane (dimensionless)
β	separation factor of a membrane (dimensionless)
C^f	weight fractions of water in the permeate.
C	weight fraction of water in the feed.
Q_P	productive capacity (kg/h·m^2)
J_P	flux of water (kg/h·m^2)
ΔHf_{cs}	heat of fusion at crystallization for the standard PVA (J/g)
ΔHf_c	heat of fusion at crystallization for the sample (J/g)

REFERENCES

1. GFT Deutche Carbone, Geschaftseinheit GFT, Firmenschsthaller Str., 19 6680 Neunkirchen, Germany.
2. M. H. Yoshikawa, K. Sanui, and N. Ogata, "Separation of Water and Ethanol by Pervaporation through Polymer Membrane Containing *N*-Substituted Imide Groups," *Polym. J., 2*, 363 (1985).
3. R. Y. M. Huang and C. K. Yeom, "Pervaporation Separation of Aqueous Mixtures Using Crosslinked Poly(Vinyl Alcohol) [PVA]. II. Permeation of Ethanol–Water Mixtures," *J. Membr. Sci., 51*, 273 (1990).
4. S. Yamada, T. Nakagawa, and T. Abo, "Pervaporation of Water–Ethanol with PVA-Fluoropore Composite Membrane," in *Proceedings of the 3rd International Conference on Pervaporation Processes in the Chemical Industry, Nancy, September 19–22, 1989* (R. Bakish, Ed.), Bakish Materials Corp., Englewood, NJ, p. 64.
5. R. Y. M. Huang and X. Feng, "Dehydration of Isopropanol by Pervaporation Using Aromatic Polyetherimide Membranes," *Sep. Sci. Technol., 28*(11&12), 2035–2048 (1993).

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6. M. Wesslein, A. Heintz, and R. N. Lichtenthaler, "Pervaporation of Liquid Mixtures through Poly(Vinyl Alcohol) (PVA) Membranes. I. Study of Water Containing Binary Systems with Complete and Partial Miscibility," *J. Membr. Sci.*, *51*, 169–179 (1990).
7. J. Neel, "Fundamental and General Engineering Aspects of Pervaporation," in *Proceedings of the 1st International Conference on Pervaporation Processes in the Chemical Industry, Atlanta, Georgia, February 23–26, 1986*, Bakish Materials Corp., Englewood, NJ 1987, pp. 10–40.
8. J. Neel, Q. T. Nguyen, R. Clement, and L. Le Blanc, "Fractionation of a Binary Liquid Mixture by Continuous Pervaporation," *J. Membr. Sci.*, *15*, 43–62 (1983).
9. S. A. Netke, S. B. Sawant, J. B. Joshi, and V. G. Pangarkar, "Sorption and Permeation of Aqueous Picolines through Elastomeric Membranes," *Ibid.*, *94*, 163 (1993).
10. C. E. Rogers, *Polymer Permeability* (J. Comyn, Ed.), Elsevier Applied Science Publishers, New York, NY, 1985.
11. R. Nobrega, A. C. Habert, M. E. F. Garcia, R. J. Esposito, and C. P. Borges, "Separation of Ethanol/Water Mixtures by Pervaporation through Polyvinyl Alcohol Membranes," in *Proceedings of the 3rd International Conference on Pervaporation Processes in the Chemical Industry, Nancy, September 19–22, 1989* (R. Bakish, Ed.), Bakish Materials Corp., Englewood, NJ, p. 326.
12. Q. T. Nguyen, A. Essamri, Z. H. Ping, J. Neel, and H. Brueschke, "Optimization of Polymer Membranes for the Dehydration of Hot Organic Acids by Pervaporation," in *Proceedings of the 5th International Conference on Pervaporation Processes in the Chemical Industry, Nancy, March 11–15, 1991* (R. Bakish, Ed.), Bakish Materials Corp., Englewood, NJ, p. 67.
13. J. E. Mark, *Studies in Physical Properties of Polymers* (ACS Symp. Ser. 280), Washington, D.C., 1984, Chapter 2.

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