

Water–Alcohol Separation by Pervaporation Through Zeolite-Modified Poly(Amidesulfonamide)

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Received 9 November 2000; accepted 16 November 2000

ABSTRACT: Pervaporation membranes were fabricated by blending different amount of zeolite NaA or NaX with three types of poly(amidesulfonamide) (PASA). The zeolite-filled membranes were characterized by IR spectroscopy, SEM, sorption measurements, and wide-angle X-ray diffraction. By adding the proper amount of NaA into the polymer casting solutions, the resultant zeolite-filled membranes exhibited improvement in both selectivity and permeability in the separation of 10% aqueous solutions of ethanol and propan-1-ol, as compared with the zeolite free membrane. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1323–1329, 2001

Key words: poly(amidesulfonamide); zeolite; pervaporation; dehydration of alcohol

INTRODUCTION

Membrane technology represents one of the most effective and energy-saving means for several separation processes, including ultrafiltration (UF) reverse osmosis (RO), pervaporation (PV), and gas separation.¹ Membrane materials play a pivotal role in determining the effectiveness of the process. Therefore, the development of new membrane materials with outstanding separation characteristics is vital to sustain and expand the growth of membrane separation technology. In response to this research opportunity, we have synthesized and characterized a series of homopolymers and copolymers of poly(amidesulfonamide)s (PASA).^{2,3} Furthermore, the potential use of these membrane materials in RO and UF processes was demonstrated.⁴ To further extend the utility of this new class of materials, we have recently reported the pervapo-

ration characteristics of some selected PASA in dehydration of alcohols.⁵ Reminiscent to the pervaporation performance of other glassy polymers, most of these materials exhibit a fairly high separation factor albeit a permeation flux below $35 \text{ g m}^{-2} \text{ h}^{-1}$ in the pervaporation separation of aqueous alcohol mixtures. For a true prospect of the application in pervaporation, the permeation flux through the membranes requires further improvement. We have some success in modifying the separation characteristics of the material by introducing organic pending groups to the backbone of the polymer through *N*-alkylation of the sulfonamide moieties.⁴ By contrast, the transport properties of membranes for the separation of aqueous alcohol mixtures can be improved by the addition of zeolites to the polymer matrix.^{6,7} The present work represents our effort to upgrade the separation characteristics of PASA by blending with inert hydrophilic zeolites.

EXPERIMENTAL

Materials

PASA1-3 (Fig. 1) were synthesized by low-temperature solution polycondensation as described else-

Contract grant sponsor: Research Committee of the HKBU; Contract grant number: FRG/97-98/I-25.

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Journal of Applied Polymer Science, Vol. 82, 1323–1329 (2001)
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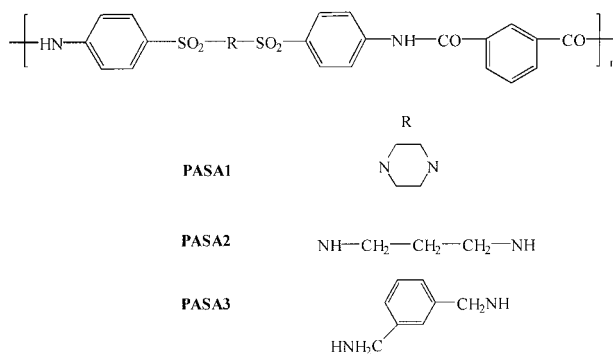


Figure 1 Structure of PASA.

where.² *N,N*-Dimethylacetamide (DMAc) (Fluka) was dried on 4 Å molecular sieves (Merck) before use. Absolute ethanol was purchased from Merck. Zeolite $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \times \text{XH}_2\text{O}$ (4 Å) (NaA) (Aldrich) and $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \times \text{XH}_2\text{O}$ (10 Å) (Fluka) were used as received.

Membrane Preparation

Pure polymer membranes were prepared as reported previously.⁵ The zeolite-filled membranes were prepared by adding a calculated amount of zeolite into the polymer solution (Table I). The mixture was stirred for 2 days to obtain a homogeneous casting solution. The solutions were cast on a glass plate with an applicator, and the solvent was allowed to evaporate 70°C for 24 h. They

were then immersed in deionized water to yield zeolite-filled membranes.

Membrane Characterization

Scanning electron microscopy (SEM) (Jeol T330) was used to investigate the morphology of the membranes. Zeolite-filled membranes were also characterized by infrared (IR), Raman spectroscopy, and wide-angle X-ray diffraction (WAXD). The degree of swelling (DS; %) of the membrane defined by

$$\text{DS} = \left(\frac{\text{weight of swollen membrane}}{\text{weight of dry membrane}} - 1 \right) \times 100\%$$

was determined as described previously.⁵

Pervaporation Experiments

The pervaporation apparatus used in this investigation was fabricated in-house, as reported in the previous study,⁵ with an effective membrane area in the cell of 33.18 cm². The membrane was supported by a filter paper over a perforated metal disc 6.5 cm in diameter. The cell was loaded with 250 mL of 90 wt % aqueous ethanol at 20°C. A constant downstream pressure was maintained at 0.5 mm Hg by a vacuum pump (Edwards E2M-15). The permeate was condensed in a cold trap

Table I Formulation of Various Zeolite-Filled PASA Casting Solutions and Degree of Swelling (%) of Some Selected Zeolite-Filled Membranes

Polymer	$[\eta]_{\text{intrinsic}}$ (dL g ⁻¹) ^a	Type of Zeolite	Concentration of Zeolite ^b (wt %)	DS ^c (%)	
				Water	Ethanol
PASA1	0.85	—	—	9.18	16.36
PASA1	0.85	NaA	2	—	—
PASA1	0.85	NaA	5	9.51	13.94
PASA1	0.85	NaA	8	—	—
PASA1	0.85	NaX	2	—	—
PASA2	1.36	—	—	9.84	19.31
PASA2	1.36	NaA	2	12.17	18.02
PASA2	1.36	NaA	4	—	—
PASA2	1.36	NaA	6	13.22	21.43
PASA2	1.36	NaX	2	15.37	23.62
PASA2	1.36	NaX	3.5	—	—
PASA3	0.75	NaA	2	—	—

^a Viscosity in DMAc solution at 25.00 ± 0.05°C.

^b The concentration of PASAs in all casting solutions is 13.5% by wt.

^c Average value over three determinations, with a RSD below 5%.

cooled by liquid nitrogen, and the permeate rate (J) was obtained by measuring the weight of the permeate. A Hayesep DB column (1 m) in combination with a thermal conductivity detector (TCD) was used to analyze both the feed and permeate composition by means of a Shimadzu gas chromatography. The separation factor $\alpha_{\text{H}_2\text{O}/\text{EtOH}}$ was calculated from the following equation:

$$\alpha_{\text{H}_2\text{O}/\text{EtOH}} = \frac{Y_{\text{H}_2\text{O}}/Y_{\text{EtOH}}}{X_{\text{H}_2\text{O}}/X_{\text{EtOH}}}$$

where X_i and Y_i are the weight fractions of species in the feed and permeate, respectively.

RESULTS AND DISCUSSION

Morphology of the Zeolite-Filled Membranes

SEM was employed to study the morphology of the zeolite-filled membranes. Typical SEMs of 5% NaA-filled PASA1 membrane are shown in Figure 2. Several features of the pictures are worth commenting on. The surface view of the micrograph shows that there are no macroscopic voids within the membrane matrix. The low permeation flux observed for the zeolite-filled membranes supports the absence of macroscopic voids. Under the prescribed fabricated conditions, the zeolite particles disperse uniformly within the polymer matrix. The size of the zeolite was found to be around 5 μm . In contrast, the appearance of empty pores observed in the cross-sectional view of the membrane indicates that the adhesion between the polymer and the zeolite particle is fairly weak. The pore formation as observed is presumably the result of the peeling of zeolite particles during the sample preparation of the cross section, using the liquid nitrogen cracking technique. Attempts to strengthen the adhesion between zeolites and polymer by thermal treatment proved fruitless. IR and Raman spectra of some selected zeolite-filled membranes appeared to be identical before and after heat treatment at $\leq 150^\circ\text{C}$.

Sorption

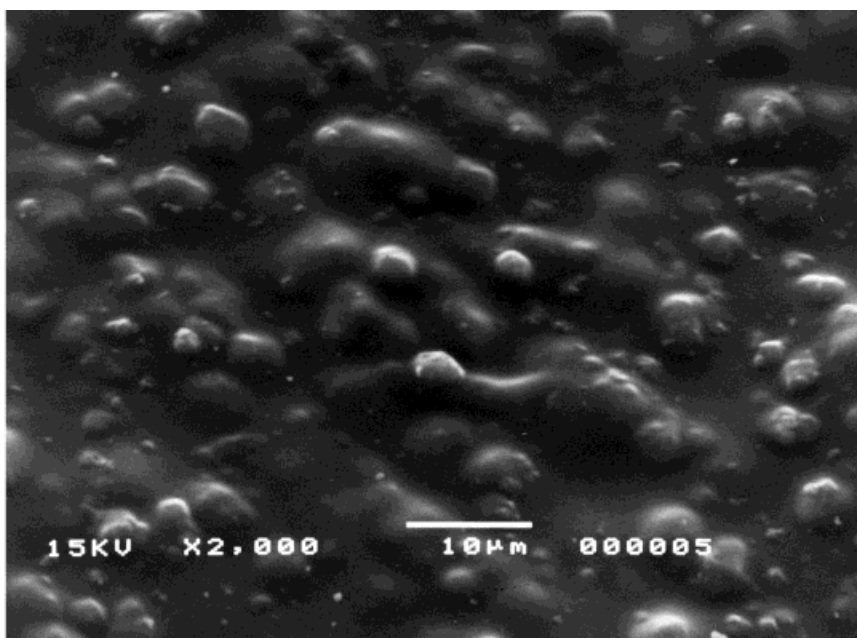
The DS of both PASA and zeolite-filled membranes in pure water and ethanol was quite substantial, and in all cases exceeded 9% (Table I, column 5 and 6). Reminiscent to the sorption properties of PASA membranes, the extent of DS of zeolite-filled PASA membranes was found to be

greater in pure ethanol than in pure water, even though both NaX and NaA zeolite are known to be hydrophilic. By contrast, upon the addition of zeolite, the DS of the modified PASA membranes in pure water increased (Table I, column 5). The results were consistent with the fact that both A type and X type zeolite are hydrophilic and possessing pores much greater than the kinetic diameter of water molecule (i.e., $\sim 2.65 \text{ \AA}$).

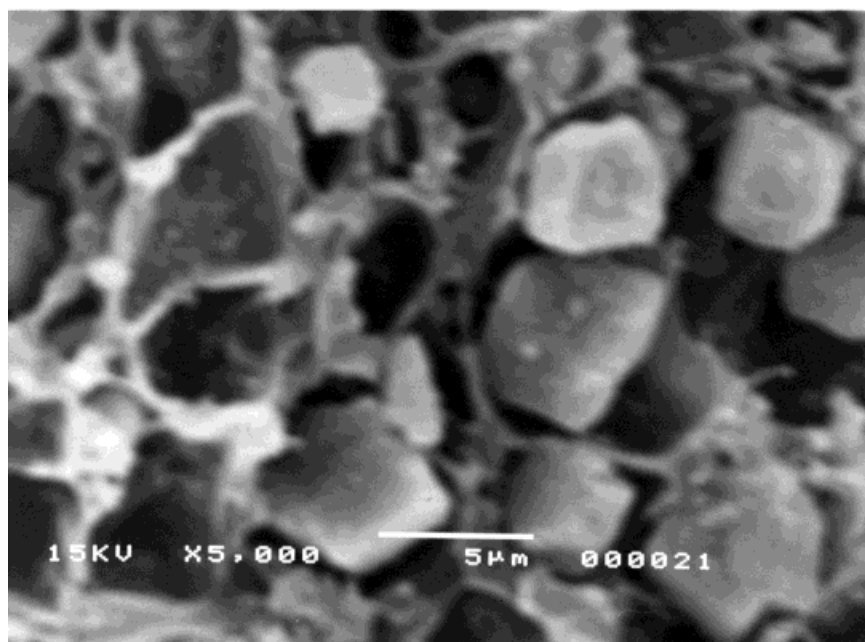
When the sorption process attained an equilibrium, additional amount of water will fill up some of the pores of the zeolite, resulting in an overall increase in DS. The sorption behavior of zeolite-filled PASA membranes in pure ethanol was much complicated. NaX with larger pore size could accommodate additional amount of ethanol (kinetic diameter $\sim 4.7 \text{ \AA}$) (Table I). The sorption behavior of zeolite-filled PASA membranes will be used to rationalize their PV performance (see below).

Crystallinities

The presence of crystallites in glassy polymers such as PASA would deter the permeability of the penetrants in the PV process which in turn may reduce its permeation flux. To monitor the effect of the zeolite additives on the degree of crystallinity of the polymer system is of great significance in understanding the separation characteristics of the membranes in the PV process. The degree of crystallinity for the parent and zeolite-filled PASA membranes was investigated by X-ray ($2\theta = 5\text{--}40^\circ$). The results obtained for the PASA1 and PASA2 series are shown in Figure 3. As shown by XRD study and structural consideration of the polymer backbone, PASA2 possesses a higher degree of crystallinity than that of PASA1. For the loosely packed PASA1, considerable amount of free volume may exist within the polymer matrix. Thus, the general shape of the XRD pattern of zeolite-filled PASA1 membranes is very similar. The sharp diffraction maxima of zeolite is enhanced as its content in the membrane is increased. In contrast, Figure 3b shows the crystallinity of zeolite-filled PASA2 membranes decreased significantly compared with that of the parent membrane; 2% of zeolite additive amounting to about 13% by weight of the final membrane content, would be sufficient to cause a sharp reduction of the crystallinity in the polymer matrix. This, in turn, would have a pronounced effect on changing the permeability of the membranes (see below).



(a)



(b)

Figure 2 Scanning electron microscopy of 5% zeolite (NaA)-filled PASA1 membrane. (a) Surface view; (b) cross-sectional view.

Thickness of the Membranes

For the glassy type symmetric nonporous polymer membranes, a limiting membrane thickness value of ~ 15 μm was required for pervaporation membranes to exhibit stable performance.⁸ Fur-

ther increase the thickness of the membrane would enhance the separation factor in the expenses of suppressing the permeation flux. The first question warranting our attention is to determine the desired thickness of the zeolite-filled

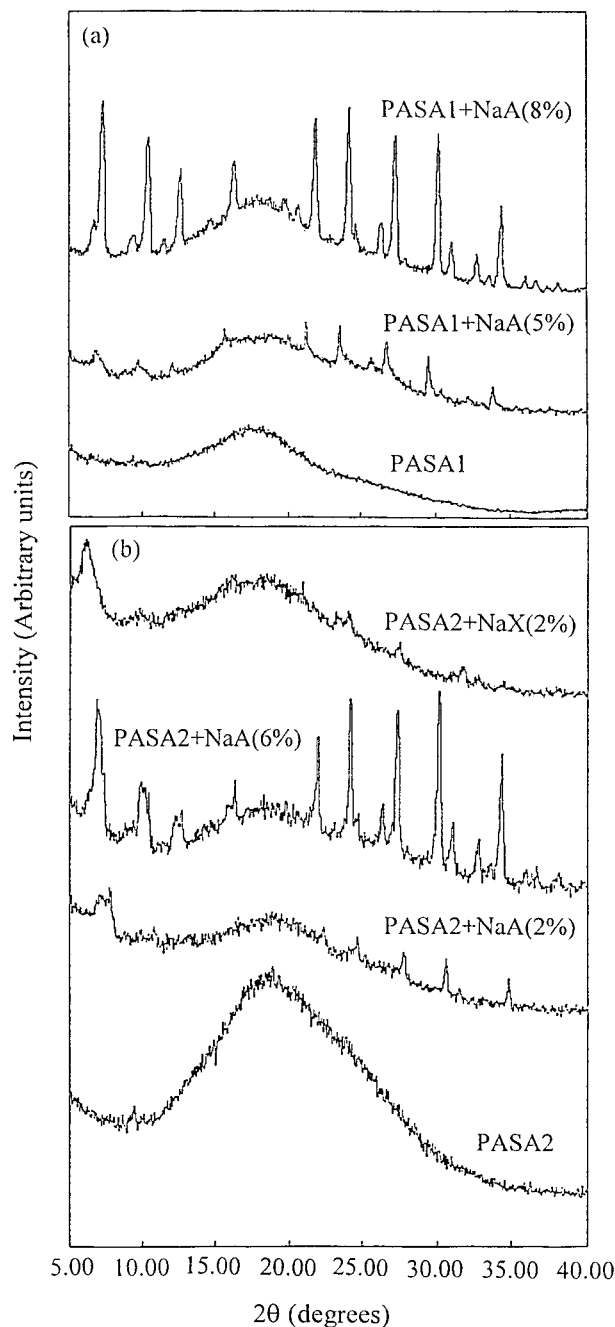


Figure 3 X-ray diffraction diagrams of zeolite-filled PASA membranes. (a) PASA1 series; (b) PASA2 series.

membranes that would exhibit good compromise of separation characteristics. A 5% NaA-modified PASA1 membrane was chosen as a representative membrane, which was subjected to the thickness study. Results of such study are shown in Table II. Drastic improvement in separation factor of the membranes took place when the thickness of the membrane was changed from 24 to 33 μm .

Further increase in the thickness of the membrane will only reduce the flux and with no effect on the separation factor of the membranes. Thus, the thickness of all subsequent zeolite-filled membranes would be kept at $\sim 30\text{--}35 \mu\text{m}$.

Pervaporation Properties

It has been widely accepted that under reduced pressure conditions the transport of a volatile substance through a PV membrane comprises of three steps: a sorption step at the membrane upstream face, followed by a diffusion through the dense polymer film and a desorption into the vacuum. Under high vacuum, on the downstream side of the polymer film, the desorption is considered a fast step. Therefore, the overall separation characteristics of a membrane depends on a delicate balance of three intrinsic properties of the penetrants of the mixture: affinity to the membrane, the size of the penetrating molecules and their vapor pressure. Considering the pervaporation separation of aqueous alcohol solutions, the relative affinity of alcohol and water molecules to the membrane could be assessed experimentally by sorption measurements. To match our anticipation, by blending the PASA with hydrophilic zeolites (i.e., either NaA or NaX type), the permeation flux of all zeolite-filled PASA membranes was found to be enhanced proportional to the amount of the zeolite added (Table III, column 3). The results of sorption measurements described above corroborated to this observation. The higher content of zeolite added, the greater the DS of the filled PASA membranes and the faster the permeation flux of the membranes. Understandably, the effect of the flux enhancement was more pronounced if NaX was used in place of NaA (Table III, entry 2 vs 5 and entry 7 vs 10). The

Table II Effect of Membrane Thickness of 5% NaA-Modified PASA1 Membranes on Pervaporation Separation of 90% wt % Ethanol- H_2O Mixture

Thickness of the Membrane (μm)	Permeation Flux J ($\text{g}/\text{m}^2\text{h}$)	Separation Factor α	Pervaporation Separation Index (PSI) ($\text{g}/\text{m}^2\text{h}$)
20	138.54	16.9	2,341
24	131.37	19.1	2,509
33	32.09	70.8	2,273
37	17.80	76.2	1,355

Table III Characteristics of Membranes Derived from the Parent Polymer and the Zeolite-Modified Polymers in Pervaporation of 90% Wt Ethanol–Water Mixture at 20°C

Entry	Polymer	Zeolite Content by Wt in the Modified Membrane (%)	Permeation Flux J (g/m ² h)	Separation Factor α	Pervaporation Separation Index (PSI) (g/m ² h)
1	PASA1	0	19.59	51.0	999
2	+2% NaA (4 Å)	12.9	32.87	42.51	1,397
3	+5% NaA	28.5	32.09	70.84	2,273
4	+8% NaA	37.2	96.01	18.21	1,748
5	+2% NaX (10 Å)	12.9	53.41	26.37	1,408
6	PASA2	0	4.52	191.20	864.2
7	+2% NaA	12.9	5.91	777.10	4592.7
8	+4% NaA	22.8	8.65	59.28	512.8
9	+6% NaA	30.8	15.02	21.80	327.4
10	+2% NaX	12.9	18.61	30.10	560.2
11	+3.5% NaX	20.6	82.08	4.73	388.2
12	PASA3	0	3.70	355.80	1316.5
13	+2% NaA	12.9	7.23	753.40	5313.3

large pore size (10 Å) present in NaX would accommodate more water and facilitate the diffusion of the penetrants. At the outset of this investigation, as indicated by the XRD pattern and the structural consideration, PASA2 and PASA3 are regarded as densely packed glassy polymers, whereas the intermolecular interaction within PASA1 matrix is considerably weaker. In the dehydration of 90% ethanol-water mixture by PV through PASA2, the separation factor was explicitly established as⁴

$$\alpha_{\text{H}_2\text{O}/\text{EtOH}} = \alpha_{\text{sorption}} \alpha_{\text{diffusion}}$$

$$191 = (8.01) \times (23.87)$$

In other words, using PASA2 as the membrane barrier, the PV separation of ethanol–water mixtures is diffusion controlled. In a relative sense, we believe that the separation process of PASA1 will be controlled with equal importance by sorption and diffusion.

When 4 Å NaA zeolite was added to PASA1 and PASA2 at a level of 5% and 2%, respectively, the DS of NaA zeolite-filled PASA in water increased, whereas it decreased in ethanol. With such a low level of additives, presumably, the zeolitic crystallites spread in the polymer bulk forming isolated zeolite islands and the membrane behaves essentially as that of the unmodified PASA membranes. By contrast, the small pore size of NaA

would also favor the preferential permeation of water molecules. The complementary effects of the zeolite additive on sorption and diffusion would improve membrane performance in terms of both flux rate and separation factor. As measured by the pervaporation separation index (PSI), substantial improvement of membranes in separation characteristics (i.e., entry 3, 7, 13 vs 1, 6, 12 in Table III) was achieved by the zeolite modification approach. Clearly, such extent of improvement will not take place if NaX was used because its large pore size (10 Å) would not discriminate the diffusion of both water and ethanol molecules. It is worth noting that when the amount of NaA zeolite in PASA1 and PASA2 was further increased to 8% and 4% (i.e., 37% and 23% by weight of the modified membrane content), respectively, the separation factor was abruptly diminished. At this relatively high level of additives, a drastic change in the bulk of polymer is envisaged. Many pores within the zeolite/modified polymer interface will be inevitably created since the cohesion between the zeolite and the polymer is weak.

Use of the zeolite-filled PASA1 and PASA2 membranes was extended to the pervaporation separation of other water alcohol mixtures. The results are summarized in Table IV. For the separation of water–methanol mixture, no improvement was found when zeolite-filled PASA mem-

Table IV Characteristics of Membranes Derived from the Parent Polymer and the Zeolite-Modified Polymers in Pervaporation of Water-Alcohol Mixtures Containing 90% Wt % Alcohol at 20°C

Polymer	Water–Methanol		Water–Ethanol		Water–Propanol	
	Permeation Flux J (g/m ² h)	Separation Factor α	Permeation Flux J (g/m ² h)	Separation Factor α	Permeation Flux J (g/m ² h)	Separation Factor α
PASA1	26.45	6.10	16.17	51.50	6.92	∞
+5% NaA	164.3	1.68	32.09	70.84	14.15	∞
+8% NaA	311.2	1.53	96.01	18.21	31.27	1294
PASA2	13.06	24.08	4.51	191.2	2.17	∞
+2% NaA	14.40	11.95	5.91	777.1	4.60	∞
+4% NaA	22.20	9.51	8.65	59.28	6.91	2774
+6% NaA	58.60	4.18	15.02	21.79	9.49	100.6

branes were employed. In contrast, in comparison with the parent polymer membrane, both 5% NaA-modified PASA1 membrane and 2% NaA-modified PASA2 again exhibited a much improved separation characteristics in the separation of water-propanol mixture. In addition, the present finding agreed with the separation characteristics observed for other glassy polymeric materials in PV processes.⁹ For the homologous series of methanol, ethanol and 1-propanol, Table IV shows that the permeation flux of each of the zeolite-filled PASA membranes increases as the size of the penetrating molecules decreases. Membrane selectivity is found to depend on the bulkiness of the alcohol molecules.

CONCLUSIONS

In summary, we have demonstrated that modification of pervaporation membranes by blending with suitable amount of hydrophilic zeolite such as NaA (4A) is an effective means to improve their separation characteristics (i.e., selectivity and

permeation flux) in the separation of 10% aqueous ethanol and propan-1-ol, as compared with the zeolite free membrane.

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