Removal of *n*-Butanol from Aqueous Solutions by Ion–Exchange Membranes Containing Organic Counterions

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ABSTRACT: The pervaporation of aqueous butanol solutions was investigated using thin-film composite membranes composed of a poly(vinylidene fluoride) substrate coated with a sulfonated poly(2,6-dimethyl-1,4-phenelene oxide) polymer. The polymer was ion-exchanged with quaternary ammonium cations having aliphatic substituents of various chain lengths. The pervaporation of aqueous *n*-butanol solutions using these membranes gave a permeate more concentrated in *n*-butanol; therefore, they were alcohol-selective. The separation factor increased and the permeate flux decreased as the chain lengths of the aliphatic substituents were increased. Hence, the masstransport properties of such membranes can be controlled or altered to yield some desired permselectivity by the introduction of a proper counterion. It was observed that the *n*-butanol flux was small relative to the total flux and, therefore, the water flux dominated the total permeate flux. The degree of swelling of the membranes and its effect on membrane performance was investigated as well. As the *n*-butanol content was increased, the swelling of the membranes increased greatly. High membrane swelling caused a reduction in the separation factor. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 47-58, 1999

Key words: pervaporation; sulfonated polyphenylene oxide; TFC membranes; organic counterions

INTRODUCTION

There have been many studies on water-selective ion-exchange pervaporation membranes for the separation of aqueous organic mixtures. These membranes have mostly been used to dehydrate ethanol solutions. However, a few studies have reported the selective separation of organic liquids by pervaporation. Organic permselective membranes may be applied directly to separate or concentrate organic compounds from dilute aqueous solutions if their permselectivities are high enough. Wenzlaff et al.¹ studied the performance of ionexchange membranes in the sorption and pervaporation of water–ethanol solutions. They used cation-exchange and anion-exchange membranes with different counterion loading, that is, H^+ , Li^+ , Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Al^{3+} for the cation-exchange membranes and OH^- , Cl^- , $SCN^$ and SO_4^{2-} for the anion-exchange membranes. All the membranes studied demonstrated preferential water sorption.

Cabasso and Liu² also separated alcohol/water mixtures by pervaporation using Nafion hollowfiber membranes loaded with various cations (H⁺, Li⁺, Na⁺, K⁺, Cs⁺, Ca²⁺, and Al³⁺). They found as well that the permeation rates and separations were highly dependent on the type of counterion. For the alkali-cation series, the flux decreased in

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the sequence $H^+ > Li^+ > Na^+ > K^+ > Cs^+$ and the sequence was reversed for the separation factor. Therefore, a desired flux and separation could be obtained by exchanging the counterions without changing the membrane material. According to Cabasso and Liu, the rather low value for the apparent energy of activation of transport (less than 6 kcal/mol) indicates that the mass transport in these membranes may occur through discrete paths within the membranes and not by the solution-diffusion model.

In a later study, Cabasso et al.³ employed flatsheet ion-exchange sulfonated polyethylene membranes loaded with the same cations (H^+, Li^+, Li^+) Na^+ , K^+ , and Cs^+) to separate a solution of isopropanol-water near the azeotropic composition and a solution of ethanol-water containing 15 wt % water. The separation of such compositions using a conventional distillation process consumes much energy; however, the results obtained by Cabasso et al. prove that one-stage separation is attainable when a proper ion-exchange membrane is used. An even lower value for the apparent activation energy of transport (approximately 5 kcal/mol) was recorded for this membrane, compared to the previous Nafion membrane. The later value is close to the activation energy for the mobility of water in water (4.5 kcal/mol). According to Cabasso et al., this suggests that the mass transport occurs through hydration shell and water clusters.

Cabasso et al.⁴ also studied the effect of counterions on the transport of isopropanol/water mixtures through flat-sheet Nafion ion-exchange membranes in pervaporation. These membranes preferentially absorbed water. With these membranes, both permeants had nearly the same apparent activation energies, indicating the possibility that both components were transported through the same discrete paths.

In the studies mentioned above involving ionexchange membranes, the membranes always showed preferential removal of water. Pasternak and Dorawala,⁵ however, produced membranes which permeated alcohol preferentially by incorporating organic counterions in flat-sheet ion-exchange membranes. The membranes employed were commercial perfluorinated Nafion-H 117 into which quaternary ammonium cations with various aliphatic substituents were incorporated. The ion-exchange membranes selectively removed the alcohol from isopropanol/water, *n*-butanol/water, and ethanol/water solutions. In all three cases, the ions with longer-chain aliphatic substituents had greater affinity toward the organic component in the feed and therefore showed higher separation factors. The pervaporation experiments were carried out at 50 and 70°C. At higher temperatures, the separation factor increased. For the pervaporation of 1.5% *n*-butanol aqueous solutions at 70°C, the separation factors obtained increased from 1.1 to 9.8 in the cation sequence $N^+(octyl)_4 > N^+(heptyl)_4 > N^+(hexyl)_4$ $> N^+(pentyl)_4$.

In the present study, modified poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was used as the selective layer to investigate the pervaporation of butanol solutions. It is well known that PPO is an attractive material for the preparation of membranes because it possesses excellent mechanical properties both at room temperature and at elevated temperatures. It is also resistant to a number of chemical reagents and is less expensive than Nafion. It may be noted that membranes from unmodified PPO are water-selective in pervaporation experiments when they were used to separate waterethanol mixtures.

Thin-film composite membranes composed of a poly(vinylidene fluoride) (PVDF) substrate coated with sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) were used to conduct the abovementioned study. The polymer was ion-exchanged with quaternary ammonium cations having various aliphatic substituents. The effect of changing the chain lengths of the aliphatic substituents in the membrane was studied. The membranes were evaluated for *n*-butanol/water separation by per-vaporation for different feed concentrations. The degree of swelling of the membranes and its effect on the performance of the membranes were also investigated.

EXPERIMENTAL

Materials and Membrane Preparation

Quaternary ammonium bromide, NR_4Br , with various aliphatic substituents (R = butyl, pentyl, hexyl, heptyl, octyl) was purchased from Aldrich (Milwaukee, WI). Commercial, flat-sheet PVDF OSMO AP-10 membranes were kindly supplied by Osmonics (Minneapolis, MN) and used as a substrate material. PPO of intrinsic viscosity 0.46 dL/g in chloroform at 25°C manufactured by General Electrics (Parkersburg, WV) was used as the starting polymer material. SPPO was synthesized by reacting PPO with a stoichiometric quantity of



Figure 1 Schematic diagram of pervaporation apparatus.

chlorosulfonic acid in a chloroform media according to the method described by Plummer et al.⁶ Composite membranes were prepared by coating a substrate membrane (OSMO AP-10 ultrafiltration membrane) with a solution containing 1 wt % of SPPOH (IEC = 2.0 meq/g of dry polymer) in a chloroform/methanol (20/80) solvent mixture. Thereafter, a second coating was immediately applied using the same procedure. The membrane was left to dry under ambient conditions for 24 h.

The incorporation of the organic counterions was performed as follows: Solutions of 0.5M quaternary ammonium bromide in isopropanol were prepared and 25 mL of the solutions was poured onto the PVDF/SPPO membranes. The solution was allowed to react with the SPPO for 24 h. The treated membranes then underwent three 30-min washes in 50/50 isopropanol/water solutions and two 30-min washes in distilled water. The membranes were then dried *in vacua* and allowed to equilibrate in the feed solution for at least 4 h prior to use in pervaporation experiments.

Pervaporation Apparatus

Figure 1 shows a schematic diagram of the apparatus used for the pervaporation experiments. The pervaporation apparatus consisted of a permeation cell made of stainless steel equipped with a magnetic stirrer, glass tubes for condensing and collecting the permeate vapor, a pressure controller, an air dryer, and a vacuum pump. The permeation area of the membrane in contact with the feed solution was 10.2 cm^2 . The *n*-butanol/water feed mixtures used in this study contained 0.81, 2.44, and 4.09 wt % *n*-butanol.

Pervaporation Procedure

A filter paper was placed on top of the porous metal plate on the lower part the pervaporation

cell, and the membrane was mounted over the filter paper and secured with tape. After assembling the upper and lower parts of the pervaporation cell, the feed solution was poured into the cell which was then placed on the stirrer. The membrane was allowed to equilibrate with the feed for at least 4 h prior to starting the experiment. At the beginning of an experiment, values 1, 3, 4, 5, and 6 (refer to Fig. 1) were closed and the vacuum pump was turned on. The waste trap was placed in a liquid nitrogen bath and valves 4 and 5 were opened in order to collect any liquid present in the lines up to the pervaporation cell until the pressure reading showed 0.3 Torr on the pressure indicator. The valve from the permeation cell (valve 1) was then opened and the permeate was collected in the waste trap for 30 min to 1 h depending on the type of membrane used (for membranes treated with tetraoctylammonium bromide salt, 1 h was required, whereas for membranes treated with tetrabutylammonium salt, 30 min was required). After collection in the waste trap was over, the permeate was switched to the collection trap. Valves 4 and 5 were quickly closed, valve 6 was opened, the waste trap was removed, and a nitrogen bath was placed under the collection trap. A timer was started in order to later calculate the permeate flux. The vapor that permeated through the membrane was collected by condensation with the liquid nitrogen for 30 min to 2 h, again depending on type of membrane. During the experiment, the pressure on the permeate side was maintained between 1.2 and 2.1 Torr. All experiments were performed at room temperature.

Performance Parameters

The performance of membranes in a pervaporation process can be described by two parameters:



Figure 2 Separation factors versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes treated with various quaternary ammonium salts: (\blacklozenge) tetraoc-tylammonium bromide; (\blacksquare) tetraheptylammonium bromide; (\blacktriangle) tetrahexylammonium bromide; (\bigstar) tetrahexylammonium bromide; tetrahexylammo

the flux and the separation factor. The total permeate flux, J, is the permeate flow per unit membrane area per unit time:

$$J = \frac{(\text{mass of permeate collected}}{(\text{membrane area in contact}}$$

with feed)(collection time)

If the composition of the permeate is known, then the component fluxes can be calculated by multiplying the weight fraction of each component by the total permeate flux. The separation factor describes the ability of the process to separate two substances in the liquid feed. The separation factor of n-butanol in water is defined as

$$lpha = rac{Y_{
m ButOH}/Y_{
m H_2O}}{X_{
m ButOH}/X_{
m H_2O}}$$

where $Y_{\rm ButOH}$ and $Y_{\rm H_2}O$ are the butanol and water concentrations (wt %) in the permeate and $X_{\rm ButOH}$ and $X_{\rm H_2}O$ are the butanol and water concentrations (wt %) in the feed. If no separation

occurs, the separation factor will be 1.0. If there is an enrichment in n-butanol from the feed to the permeate, the separation factor will be greater than unity, and if there is an enrichment in water from the feed to the permeate, the separation factor will be less than unity, and if there is an enrichment in water from the feed to the permeate, the separation factor will be less than unity.

Analysis

The permeate and feed compositions were analyzed using a Millipore–Waters high-pressure liquid chromatograph (HPLC) with water as the moving phase at a flow rate of 1.0 mL/min. For each analysis, three injections in the HPLC were done. An average of the three areas, A, were obtained and the following percent errors were calculated:

$$\%E_{\max} = rac{A_{\max} - A_{avg}}{A_{avg}} imes 100$$

 $\%E_{\min} = rac{A_{\min} - A_{avg}}{A_{avg}} imes 100$



Figure 3 Total permeate flux versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes treated with various quaternary ammonium salts: (\blacklozenge) tetraoc-tylammonium bromide; (\blacksquare) tetraheptylammonium bromide; (\bigstar) tetrahexylammonium bromide; (bm brom) tetrahexylammonium bromide; (bm brom) tetrahexylammonium brom) tetrahexylammonium brom) tetrahexylammonium brom)

If either of the percent errors was greater than 2%, the highest and lowest areas were canceled, two more injections were performed, and the percent errors were calculated once more. This procedure was repeated until the percent errors were less than 2%. The average area obtained was then converted to a weight percent of *n*-butanol through the use of a calibration curve, which was prepared in the same way from solutions of known *n*-butanol concentrations.

The measurement of the degree of swelling was carried out as follows: A TFC membrane sample was weighed after being dried *in vacua*. The sample was then immersed in a *n*-butanol-water mixture at room temperature and left to equilibrate for 4 h. The swollen membrane was then removed from the solution, quickly wiped with low lint kimwipes to remove droplets adhering on the surface, and then weighed.

The degree of swelling can sometimes provide insight into the transport phenomena because it is often linked to the polymer–solvent interactions. The degree of swelling for the membrane is defined as

Degree of swelling (%) =
$$\frac{W_s - W_d}{W_d} \times 100$$

where W_d and W_s are the weight of the dry membrane and that of membranes swollen in a *n*butanol/water mixture, respectively.

RESULTS

For each *n*-butanol/water feed solution, two pervaporation runs were performed on two individual membranes of the same type (e.g., PVDF/ SPPO membrane treated with tetraheptylammonium bromide salt). For composite SPPOH membranes without treatment and those treated with tetraoctylammonium bromide, a pervaporation experiment was done only once when solutions containing 0.81, 2.44, and 4.09 wt % *n*-butanol were used as the feed. The separation and flux data obtained are reported in Figures 2–8 and in Figure 10. The results obtained from the swelling experiments are displayed in Figure 9.



Figure 4 Partial fluxes versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes treated with tetraoctylammonium bromide: (\blacklozenge) total; (\blacksquare) *n*-butanol; (\blacktriangle) water.

DISCUSSION

Figure 2 shows the data for the pervaporation of aqueous solutions of different concentrations us-

ing PVDF/SPPO membranes loaded without and with quaternary ammonium cations of various aliphatic substituents. In every case, the separation factor was higher than unity, indicating that



Figure 5 Partial fluxes versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes treated with tetraheptylammonium bromide: (\blacklozenge) total; (\blacksquare) *n*-butanol; (\blacktriangle) water.



Figure 6 Partial fluxes versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes treated with tetrapentylammonium bromide: (\blacklozenge) total; (\blacksquare) *n*-butanol; (\blacktriangle) water.



Figure 7 Partial fluxes versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes treated with tetrabutylammonium bromide: (\blacklozenge) total; (\blacksquare) *n*-butanol; (\blacktriangle) water.



Figure 8 Separation factor versus weight percent of *n*-butanol in the feed for PVDF/SPPO membrane.

these membranes were alcohol-selective. The highest separation factor obtained was 3.73 for the PVDF/SPPO/N⁺(octyl)₄ membrane (PVDF/ SPPO membrane treated with tetraoctylammonium bromide salt). There is a trend that the membranes loaded with longer aliphatic chain substituents demonstrate higher separation factors, although the trend is not very obvious. The membranes with longer aliphatic chain substituents have a greater affinity toward the alcohol in the feed. Consequently, the permeation of *n*-butanol relative to the permeation of water is enhanced and the separation factor becomes greater. The separation factors were in the range of 2.0–3.7. The separation factor was the highest when the n-butanol concentration in the feed was in the intermediate range (2.28–2.54 wt %) except in the case of the PVDF/SPPO/ $N^+(octyl)_4$ membrane. The decrease in the separation factor from the intermediate to high concentration range may be the result of membrane swelling at higher n-butanol concentrations in the feed and is discussed later in greater detail.

Figure 3 shows the flux data for the pervaporation of aqueous solutions of n-butanol of varied concentrations for the PVDF/SPPO membranes

loaded with quaternary ammonium cations with aliphatic substituents of various chain lengths. As expected, the total permeates flux of the membrane increases as the aliphatic substituent chain length decreases. These data along with those shown in Figure 2 indicate that the membranes demonstrating higher separation factors have lower permeate fluxes. The permeate fluxes remain constant over the tested concentration range with the exception of the PVDF/SPPO/ N^+ (pentyl)₄ membrane, which can be treated as an anomaly. The total pervaporation fluxes provide little insight into the transport mechanism. However, they may be rationalized by separating them into their respective *n*-butanol and water components.

Figures 4–7 present the partial *n*-butanol flux, partial water flux, and total flux for the PVDF/ SPPO membranes loaded with quaternary ammonium cations with various aliphatic substituent chain lengths. It is observed that the *n*-butanol flux is small relative to the total flux throughout the considered concentration range. The water flux, on the other hand, dominates the total permeate flux. This may be the reason why the total permeate fluxes are not a strong function of *n*-



Figure 9 Degree of swelling in *n*-butanol solutions for PVDF/SPPO membranes treated with various quaternary ammonium salts: (\blacklozenge) tetraoctylammonium bromide; (\blacksquare) tetraheptylammonium bromide; (\bigstar) tetrahexylammonium bromide; (\times) tetrapentylammonium bromide; (\blacklozenge) tetrabutylammonium bromide; (\ast) SPPO alone.

butanol concentration. Moreover, the concentration of water is in the narrow range of 94.1-99.0%.

Figure 8 also shows the separation data obtained for the pervaporation of aqueous n-butanol solutions using a PVDF/SPPO membrane. Due to the sulfonated groups, the membrane is expected to be hydrophilic. The results confirm this expectation, as can be observed by the separation factors being below 1.0, indicating that the membrane was preferentially permeable to water. The separation factor approaches unity as n-butanol concentration in the feed increases. This means that there is less n-butanol/water separation at higher n-butanol concentrations. This result may be due to the higher swelling of SPPO polymer at higher n-butanol concentrations as indicated in Figure 9.

Figure 10 presents the flux data for the pervaporation of aqueous *n*-butanol solutions by the PVDF/SPPO membrane. The results indicate that the total permeate flux was practically constant over the *n*-butanol feed concentration range. Again, the water flux dominates the total flux.

The variation in the degree of swelling with increase in the *n*-butanol content can be observed in Figure 9 for all membranes under study. It may be observed that membrane swelling increases dramatically with increase in the *n*-butanol concentration. This increase is more evident for the PVDF/ SPPO membranes treated with N^+ (heptyl)₄, N⁺(hexyl)₄, N⁺(pentyl)₄, and N⁺(butyl)₄. However, the PVDF/SPPO/N⁺(octyl)₄ membrane also shows an increase in swelling with an increase in the nbutanol content. Assuming that the swelling is caused by the incorporation of alcohol molecules in the membrane in preference to water molecules because of the hydrophobic character of the membrane, the separation factor should drop as the nbutanol concentration increases. The swelling phenomena could also explain the low butanol fluxes. In the case of the PVDF/SPPO membrane, however, the assumption is that the membrane swelling is caused by the incorporation of water molecules in the membrane because of hydrophilic sulfonated sites. The swelling of this membrane also increases with the *n*-butanol content. This explains why the PVDF/SPPO membrane is water-selective and why



Figure 10 Partial fluxes versus weight percent of *n*-butanol in the feed for PVDF/SPPO membranes: (\blacklozenge) total; (\blacksquare) *n*-butanol; (\blacktriangle) water.



Figure 11 Comparison of results obtained using PVDF/SPPO membrane treated with tetraoctylammonium bromide salt to the vapor-liquid equilibrium data: (\blacktriangle) pervaporation; (—) vapor-liquid equilibrium; (- - -) *x*-*y* diagonal.

Permeating Molecule	Molar Volume (cm ³ /mol)	Solubility Parameter, δ (MPa ^{1/2})	$(\delta_{\rm butyl} - \delta)^{\rm a}$	$(\delta_{octvl} - \delta)^b$
Water	18.0	47.9	17.9	26.0
Butanol	92.8	23.3	6.7	1.4

 Table I
 Molar Volume and Solubility Parameter of the Permeating

 Molecule
 Parameter of the Permeating

^a Solubility parameter for tetrabutylammonium bromide⁷ is 30.0 MPa^{1/2}

^b Solubility parameter for tetraoctylammonium bromide⁷ is 21.9 MPa^{1/2}.

the separation factor is lowered with increase in the n-butanol concentration.

The results obtained for the PVDF/SPPO/ $N(octyl)_4$ membranes were compared to the vapor-liquid equilibrium data of the butanol-water system since they demonstrated the highest separation factors. As can be seen in Figure 11, the pervaporation results are found between the diagonal and the vapor-liquid equilibrium line. They are, however, closer to the diagonal line. Table I includes the solubility parameters of water and *n*-butanol along with solubility parameter differences between water and two tetraalkylammonium bromides and those between *n*-butanol and two tetraalkylammonium bromides. It is clear that the former differences are much greater than are the latter differences, indicating that tetraalkylammonium bromides have greater affinity to *n*-butanol. Thus, the TFC membranes used in this study are *n*-butanol-selective. Moreover, differences between n-butanol and tetrabutylammonium bromide is greater than that between butanol and tetraoctylammonium bromide. This indicates that *n*-butanol has greater affinity to tetraoctylammonium bromide than to tetrabutylammonium bromide. Thus, the separation factor of membranes with tetraoctylammonium bromide is greater than that of membranes with tetrabutylammonium bromide.

It should be emphasized, however, that many parameters contribute to the preferential permeation of a specific component. Size exclusion is another possibility. The molecular sizes of the permeating molecules are also given in Table I. The molecular size of butanol is rather large in comparison to the water molecule, allowing higher mobility of water than that of *n*-butanol. This explains the relatively low selectivity of the TFC membrane regardless of the strong preferential sorption of *n*-butanol.

As was previously mentioned in the Materials and Membrane Preparation section, the ion-exchange capacity of the coating layer polymer was 2.0 meq/g, which corresponds to approximately 29% degree of substitution. Therefore, most of the active layer surface remains uncovered by the alkyl chains of the quarternary ammonium ions. The water molecules can thus penetrate through the neutral areas of the membrane surface. This would explain why the water fluxes are so high compared to the butanol fluxes.

CONCLUSIONS

The pervaporation of aqueous *n*-butanol solutions using PVDF/SPPO/N⁺R₄ membranes resulted in a permeate which contained a higher concentration of *n*-butanol than did the feed solution, indicating that the membranes were alcohol-selective. Increasing the *n*-butanol content from 0.8 to 2.4 wt % caused the separation factor to increase. The separation factor increased as the aliphatic substituent chain length increased. The total permeate flux increased as the aliphatic substituent chain length decreased. Increasing the *n*-butanol content in the aqueous solution resulted in a stronger swelling effect of the membrane. High membrane swelling caused the reduction in the separation factor when the feed *n*-butanol concentration was increased from 2.5 to 4.0%. The total permeate flux was dominated by the water flux.

The pervaporation of aqueous *n*-butanol solutions using PVDF/SPPO membranes resulted in a permeate which contained a higher concentration of water than did the feed solution, indicating that they were water-selective. The separation factor for the PVDF/SPPO membranes approached unity as the *n*-butanol concentration in the feed was increased.

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