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The Effect of Process Parameters on the Pervaporation of Alcohols through Organophilic Membranes

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Abstract

Several organophilic membranes were utilized to selectively permeate ethanol, *n*-butanol, and *t*-butanol from dilute aqueous mixtures using pervaporation (PV). Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membranes were utilized to investigate the effect of temperature, pressure, and start-up/transient time on the separation of aqueous ethanol mixtures. Results indicate optimal ethanol selectivity and flux at the lowest permeate-side pressure. Increased temperature significantly enhanced the productivity of PTMSP, but extended operation of the PTMSP membranes at high temperatures resulted in flux degradation. Two other hydrophobic membranes, poly(dimethyl siloxane) (PDMS) and a poly(methoxy siloxane) (PMS) composite, were used to separate *n*-butanol and *t*-butanol from dilute aqueous mixtures. The effect of feed concentration on the flux and selectivity was investigated. Both membranes were found to be more permeable to *n*-butanol than *t*-butanol. The PDMS membrane was found to be more effective than the PMS membrane in terms of flux and selectivity. The effect of membrane thickness on water permeation and on organic selectivity was also studied using the PDMS membrane.

INTRODUCTION

Pervaporation is a membrane process that uses a semipermeable barrier to selectively separate the components of a liquid feed mixture producing a vapor-phase permeate and a liquid retentate. Therefore, pervaporation differs from the other members of the membrane family in that a phase change occurs during separation. Due to the permselective nature of the membrane, a substance at low concentration in the feed stream can become enriched in the permeate. The membrane in this process is the mass sep-

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arating agent, and its characteristics are important in determining the effectiveness of the separation desired. The separation is not based on the relative volatilities like distillation, but on the relative rate of permeation in the membrane.

The accepted mechanism for pervaporative transport through nonporous membranes is solution-diffusion (*1*). The transport theory and models have been presented elsewhere (*2–6*), and a summary of some important concepts is presented here. The permeating component goes into solution with the membrane at its surface, then diffuses through. A vacuum or sweeping gas is typically applied on the permeate side of the membrane. The permeating component desorbs from the membrane as a vapor and can be condensed. The chemical potential difference across the membrane from the feed (liquid) side to the permeate (vapor) side is the driving force for separation. As each component of the feed dissolves in the membrane, then diffuses across the membrane to the permeate side, the flux of each component is given by

$$J_i = D_i c_i \left[\frac{d(\mu_i / RT)}{dz} \right] \tag{1}$$

where J_i is the component flux, c_i is the component concentration, D_i is the diffusion coefficient, μ_i is the chemical potential, R is the universal gas constant, T is temperature, and z is a position coordinate in the membrane normal to its surface. For pervaporation the activity gradient across the membrane far exceeds the pressure gradient so the previous equation can be written as

$$J_i = D_i c_i \left[\frac{d(\ln a_i)}{dz} \right] \tag{2}$$

where a_i is the component activity. The diffusion coefficient and activity are important aspects in analyzing the transport.

The separation effectiveness of pervaporation is quantified by two parameters, flux and selectivity. In the case of a binary feed mixture of components A and B, the following expressions apply. Selectivity is the term utilized in pervaporation to denote the degree of separation achieved. It is a ratio of the concentrations of Components A and B in the permeate and feed. The membrane's selectivity for Component A can be expressed as

$$\alpha_{\mathrm{B}}^{\mathrm{A}} = \frac{y_{\mathrm{A}}/y_{\mathrm{B}}}{x_{\mathrm{A}}/x_{\mathrm{B}}} \tag{3}$$

where x and y represent mass fractions of Components A and B in the feed and permeate, respectively. A selectivity value greater than unity indicates the selective permeation of A over B, and a value less than unity indicates selective permeation of B over A. Some researchers prefer to use an enrichment factor that is a ratio of a component's concentration in the permeate to its concentration in the feed.

$$\beta_A = y_A/x_A \tag{4}$$

There are several variations of the pervaporation process that have been described by Neel et al. (*7*). The most common pervaporation operations use a vacuum imposed on the permeate side of the membrane. Sweeping gas pervaporation systems use an inert gas stream on the permeate side of the membrane to continuously remove the permeate being produced. Other process variants and hybrids include thermopervaporation, saturated vapor permeation, extractive pervaporation, and perstraction.

Pervaporation research has been rapidly expanding this past decade with a significant increase in academic and industrial research (*8*, *9*). Slater and Hickey (*8*) have presented a thorough chronological review of this subject and have analyzed the worldwide distribution of research activity.

The one application area that pervaporation has been most commercially developed, and therefore most published information exists, is selective permeation of water from aqueous–organic mixtures. Examples of this are solvent dehydration and dehydration of aqueous solutions at their azeotrope. Commercial systems using poly(vinyl alcohol) (PVA) composite membranes for dehydrating aqueous mixtures of ethanol, isopropanol, and acetone are now in use (*10–13*). Due to the commercial interest in this area, the majority of information in the open literature on modeling and on the effect of process parameters is in this category of pervaporation separations.

Not as much effort has been directed at selective organic permeation either from anhydrous or aqueous mixtures. The use of pervaporation for the separation of anhydrous mixtures is relevant to traditional petrochemical processing (*10*, *14*), but is not commercially viable with currently available membranes. The use of organophilic pervaporation membranes for organic removal from aqueous systems has commercial potential for biochemical processing, hazardous waste treatment, water purification, and beverage processing (*10*). There is a need to create a base of information and disseminate data so confidence can be gained and developments will proceed in this type of pervaporation application.

Our research group's interests are in the area of selective organic permeation from aqueous mixtures. In particular, we hope to integrate pervaporation with biological processing in our Biochemical Engineering Laboratory. Pervaporation processes can be integrated into an alcohol fermentation scheme (*15*). As a first step in that direction, we have been investigating the selective permeation of ethanol, butanol isomers, acetone, and acetic acid, through poly(dimethyl siloxane), poly[1-(trimethylsilyl)-1-propyne], and other organophilic/hydrophobic membranes. The studies are aimed at understanding the effects of process parameters on flux and selectivity. The authors have published the results of research on pervaporation of ethanol from aqueous mixtures using symmetric poly(dimethyl siloxane) membranes (*16*). The work presented herein is the next step in this research: investigating other membrane materials and process conditions for ethanol–water separations and the permeation behavior of other alcohols such as the butanol isomers.

The separation of ethanol from water by pervaporation has been widely studied. The major benefit of this separation is the enhancement of the production of ethanol from fermentation operations. Since the concentration of ethanol in fermentation broths is usually in the order of a few percent by weight, it is an excellent candidate for separations research. Hickey and Slater (*15*) reviewed the use of pervaporation for the selective permeation of ethanol from dilute solutions and fermentation operations. The majority of the published results address potential applications in the biotechnology area, and several report actual findings with fermentation process systems. References to some recent papers on ethanol–water separations not mentioned in the prior review article (*15*) will be cited here. Most researchers have worked with silicone-based polymers, such as poly(dimethyl siloxane), surface-modified and composite forms (*17–23*). Substituted poly(acetylene) polymers, such as poly[1-(trimethylsilyl)-1-propyne] membranes, and fluorinated polymers, such as poly(tertafluoro ethylene), have also been the focus of investigations (*23–25*).

The utilization of pervaporation for butanol–water separation from dilute mixtures is another challenging subject for investigation. When *n*-butanol is created by acetone–butanol fermentation, its concentration in the broth is in the order of 0.5 wt%. The potential savings in separation costs are therefore even greater than that of ethanol fermentation.

The study of butanol separation has other benefits as well. Butanols exist in dilute concentration in by-product streams that result from the production of various organic chemicals. Pervaporation is useful in recovering butanols for recycle or end product use. This results in an overall increase in productivity and yield. Unlike ethanol, butanol has four isomers, each with different properties: vapor pressure, shape (steric), miscibility in water, etc. The nature of the butanol/water vapor–liquid equilibrium curves is quite unique. The investigation of butanol pervaporation, as well as other isomers, may help to determine what effects these chemical properties have on the separation.

The pervaporation of *n*-butanol has been the focus of much of the research done with butanol isomers. Boddeker and coworkers investigated the separation of all four butanol isomers (*26*, *27*) using the polyether-*block*-polyamide (PEBA) membrane. Rautenbach et al. separated the *n*-butanol–water binary mixture with a PVA composite membrane (*28*). Silicone rubber membranes have been used to separate butanol by many groups. Research has been done on actual butanol fermentation broths (*29–34*) and with simple binary mixtures as well (*35–38*). Hennepe et al. enhanced the performance of the silicone rubber membrane by adding zeolites to the structure (*36*, *37*). Matsumura and coworkers examined butanol separations with an oleyl alcohol liquid membrane (*35*). Tanigaki et al. (*39*, *40*) used a poly(methyl methacrylate-*co*-styrene) membrane in their studies.

EXPERIMENTAL METHODS

The experimental system used in these studies employed a flat sheet membrane cell which is discussed in detail in a previous paper (*16*) and shown in Fig. 1. Feed solution is continuously pumped to the feed port of the membrane test cell, flows across the membrane surface, and is removed from the cell via the retentate port. The active membrane area for permeation is 28.74 cm^2. Permeate is collected as product by using two cold finger condensers placed in series and chilled by liquid nitrogen. The concentration of the retentate is not that different from the feed, since the

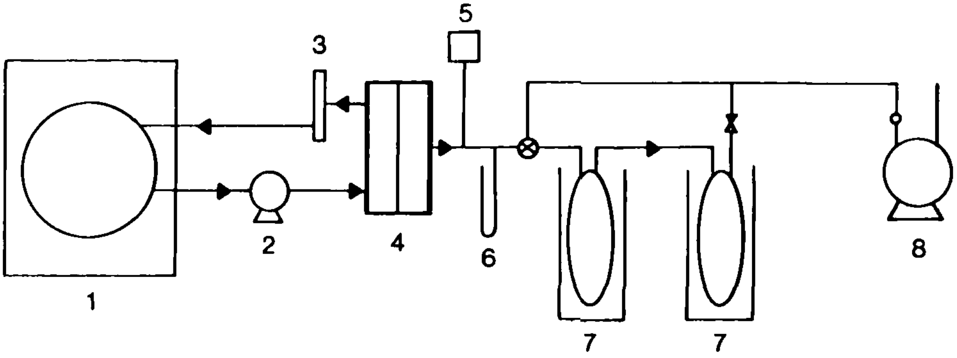

FIG. 1. Membrane pervaporation system process diagram. System components: temperature-controlled feed tank (1), feed pump (2), flowmeter (3), membrane cell (4), pressure meter (5), pressure manometer (6), permeate condensers (7), vacuum pump and pressure regulator (8).

single-pass recovery of the membrane module is very low. Feed temperature, flow rate, and permeate-side downstream pressure can all be measured and controlled.

The experiments recorded in this paper were performed with various types of organophilic membranes. Two silicone-based membranes, a symmetric poly(dimethyl siloxane) (PDMS) membrane from the General Electric Company and a poly(methoxy siloxane) (PMS) composite membrane from the GFT Corporation, were used. Symmetric, asymmetric, and composite forms of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) membrane were also utilized.

RESULTS AND DISCUSSION

Ethanol–Water Separations with PTMSP Membranes

Initial studies of the poly[1-(trimethylsilyl)-1-propyne] (PTMSP) polymer encompassed its symmetric, asymmetric, and composite forms. Symmetric films were ~13 μm thick, and the asymmetric membranes consisted of a dense "skin" of approximately 2 μm. A composite membrane with a 200-Å PTMSP selective layer on a poly(acrylonitrile) (PAN) support was utilized. Ethanol–water mixtures of 1 and 5% w/w were used to evaluate membrane separation performance.

The optimization of flux and selectivity is affected by the type of polymer (and the modifications on it) and its thickness. Not much information exists on the effects of process parameters, i.e., temperature, pressure, and transient time, on pervaporative separations with organophilic membranes. Models developed based on the wealth of data on dehydration separations using hydrophilic membranes are not that useful here. The initial screening of the PTMSP membranes involved the same polymeric film, but prepared in such a way as to modify the membrane structure.

An initial screening of the three PTMSP membrane candidates indicated that the asymmetric PTMSP membrane was the one for use in the process parameter studies. Some of the operating concerns with the symmetric and composite types will be summarized. The symmetric polymer gave acceptable selectivities but lacked a reasonable flux to make further studies warranted. The composite membrane had a higher flux but had little or no selectivity to ethanol.

The asymmetric PTMSP studies evaluated the effects of feed temperature, transient start-up time, and permeate-side pressure on flux and selectivity. All pervaporation experiments with this membrane utilized a benchmark condition to evaluate any change in membrane characteristics over processing time. Although the research group has performed some of the process variable studies at both 1.0 and 5.0% w/w ethanol, the 5%

concentration is much closer to actual concentrations in fermentation operations.

An analysis of the effect of feed temperature on flux and selectivity with the PTMSP membrane was performed with feed concentrations of 1.0 and 5.0% w/w ethanol and a permeate-side pressure of ~1 mmHg (torr). As the feed temperature was varied from 20 to 90°C, the permeate flux increased exponentially from 272 to 7580 g/m^2·h (Fig. 2). The benchmark permeate flux at 30°C was 394 g/m^2·h. The same trend is observed with the 1% feed concentration, although the total flux is much less. At 30°C the total flux was 317 g/m^2·h, and at 90°C it was 6410 g/m^2·h. Figure 2 also shows the individual component flux of ethanol vs feed temperature. Again, an exponential increase in ethanol flux is seen as temperature increases. For the 5% feed study, the ethanol flux increased from 85 to 2650 g/m^2·h as the temperature was increased from 20 to 90°C. The results agree with the Arrhenius effect of temperature on the permeation of the components in the membrane.

The effect of feed temperature on the permeate ethanol concentration is shown in Fig. 3. In the 5% feed study, the ethanol permeate concen-

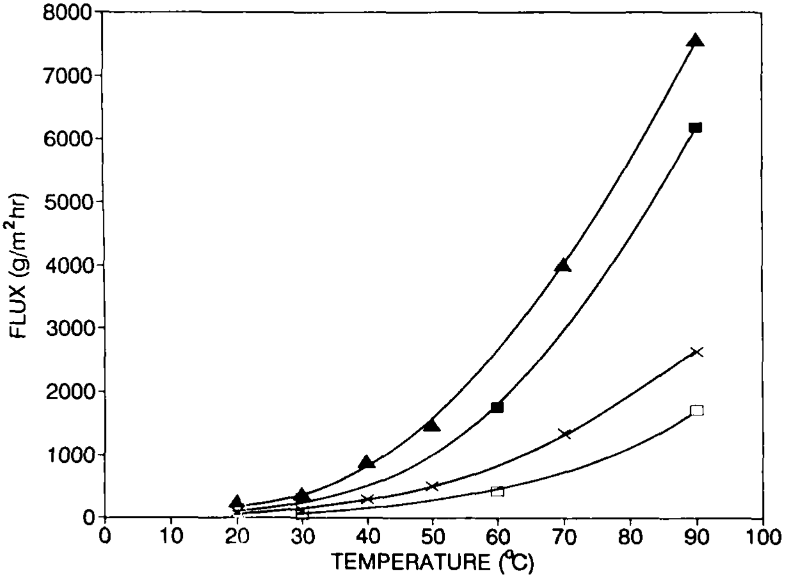

FIG. 2. Flux (total and ethanol) vs temperature for the PTMSP membrane separating 1 and 5% w/w ethanol–water mixtures: total flux (■) and ethanol flux (□) for the 1% w/w ethanol feed; total flux (▲) and ethanol flux (×) for the 5% w/w feed. Permeate-side pressure of ~1 mmHg used.

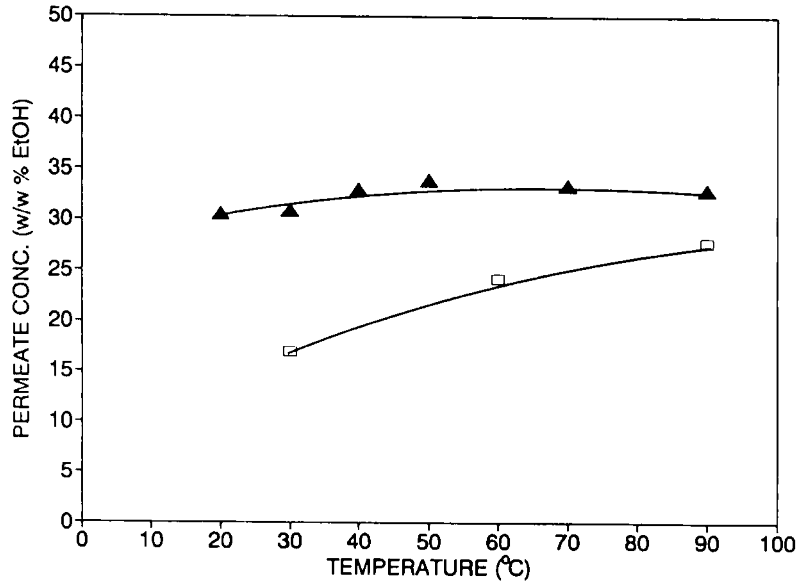

FIG. 3. Permeate concentration vs temperature for the PTMSP membrane: ethanol feed mixture of 1% (□) and 5% (▲). A permeate-side pressure of ~1 mmHg used.

tration only changed slightly from 30.6 to 33% as the feed temperature increased from 20 to 90°C. Results obtained with the 1% feed study suggest that the feed temperature has a greater effect at lower concentrations, with selectivity increasing as temperature increases. Permeate concentration increased from 17.0 to 27.8% over the temperature range evaluated. The membrane's permeability of ethanol to water seems to increase slightly as the temperature is increased. Therefore, as the temperature is increased, the diffusivity and/or solubility of the ethanol in the membrane increases more than that of water.

Extended high temperature operation was detrimental to the PTMSP membrane. The high temperature, 90°C, data point reported above was obtained after several hours of operation. It was observed that after operating the membrane at the 90°C condition, benchmark values decreased slightly, although selectivity remained relatively constant. A long-term study indicated that the high temperature stability of the PTMSP membrane was quite poor. The membrane's flux declines severely after long-term exposure. Interestingly enough, the selectivity of the membrane was not greatly affected.

The effect of the permeate-side pressure on pervaporation performance was examined using the 5% ethanol feed concentration at a temperature of 30°C. As the permeate-side pressure was increased from 1 to 40 mmHg, the permeate flux decreased from 389 to 39.4 g/m^2·h (Fig. 4). Flux appears to decrease slowly at low pressures and decrease more rapidly as pressure increases. It does appear that there is not a major effect of permeate-side pressure on flux for conditions <10 mmHg; this finding agrees with the work of Masuda et al. (*41*). The ethanol flux decreases from 128 to 12.4 g/m^2·h as the permeate-side pressure is increased from 1 to 40 mmHg.

There does not seem to be any effect of pressure on the permeate concentration over the range studied (1 to 40 mmHg). Permeate concentration of ethanol fluctuated slightly over the range 29.5 to 33.5%, representing selectivities of 7.95 and 9.57, respectively. There is no apparent trend or significant difference among the values reported.

Start-up transient permeation behavior was examined with a new (virgin) membrane. Process conditions were the same as before: 5.0% w/w ethanol, 30°C, and a permeate-side pressure of 1 mmHg. The results shown in Fig. 5 show that the initial permeation rate is quite high and that the flux reaches steady-state within several hours. The flux at the first hour of processing is 747 g/m^2·h and the selectivity is 7.0, which is slightly lower than the steady-state values reported previously.

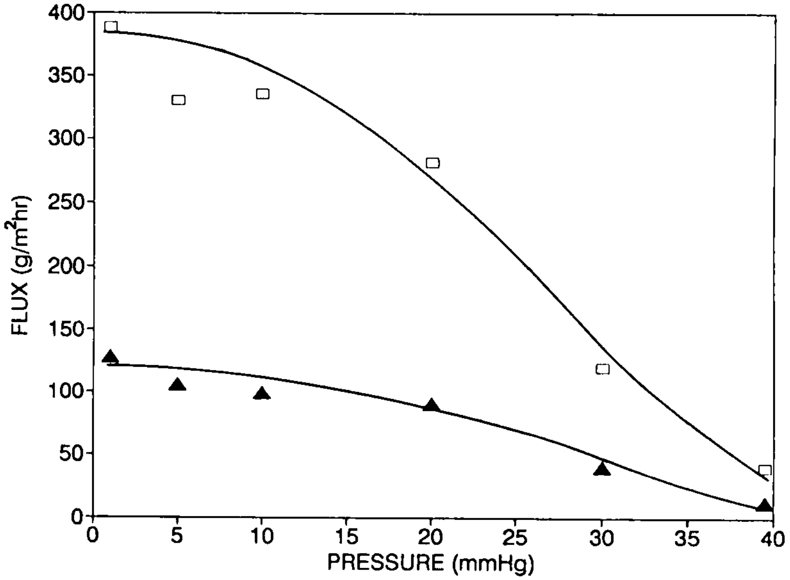

FIG. 4. Flux vs pressure for the PTMSP membrane: total flux (□) and ethanol flux (▲). Feed conditions of 5% w/w ethanol and a temperature of 30°C.

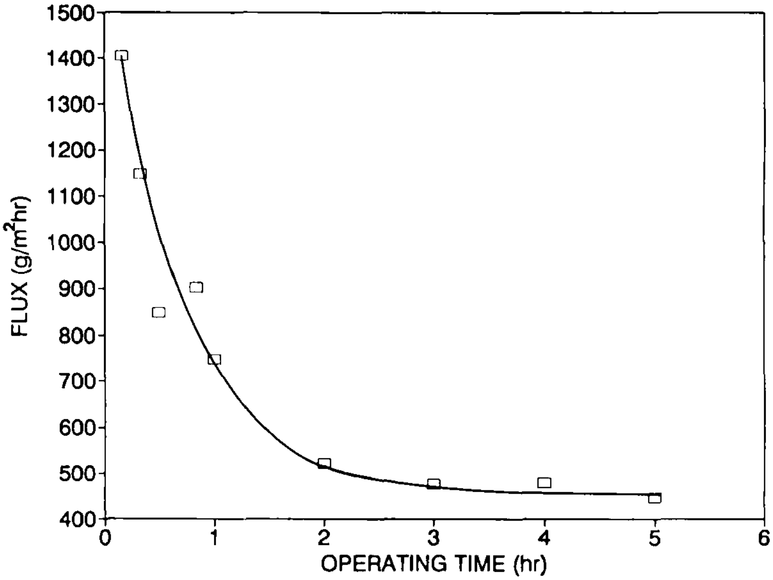

FIG. 5. Flux vs operating time using a new/virgin PTMSP membrane: total flux (☐). Feed conditions of 5% w/w ethanol, a permeate-side pressure of ~1 mmHg, and a temperature of 30°C.

Butanol–Water Separations with Silicone-Based Membranes

The first group of studies on butanol–water separation utilized a symmetric poly(dimethyl siloxane) (PDMS) membrane to gain a general understanding of separation performance. The PDMS membrane, supplied by General Electric Corporation, had a thickness of ~25 μm and was symmetric in nature. The second set of experiments utilized a poly(methoxy siloxane) (PMS) composite membrane. The composite silicone membrane used in this investigation was supplied by the GFT Corporation. It is composed of a PMS permselective layer on a polysulfone support. The membrane is recommended for separating liquid feeds at or below 10 wt% organic.

The studies performed with the PDMS membrane were done to evaluate the effect of butanol feed concentration on the permeate flux and selectivity. An additional study was performed with the PDMS membrane to determine the effect of membrane thickness on separation. Two butanol isomers, *n*-butanol (*n*-butyl alcohol) and *t*-butanol (*t*-butyl alcohol), were used for this investigation. All runs were conducted at a permeate-side pressure of ~1 mmHg and a feed temperature of 50°C, unless otherwise indicated.

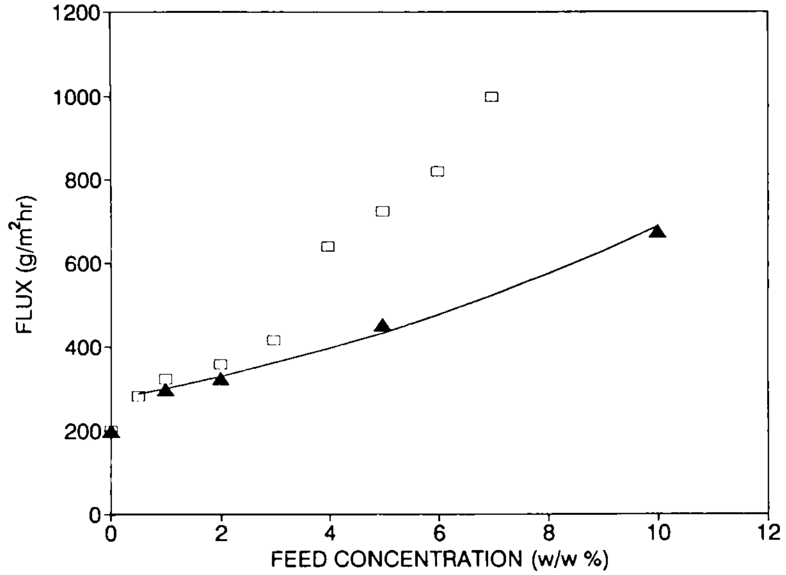

FIG. 6. Total flux vs feed concentration for the PDMS membrane separating a butanol–water mixture: *n*-butanol feed mixture (□) and *t*-butanol feed mixture (▲). Feed temperature of 50°C and a permeate-side pressure of 1 mmHg.

The results of the total flux vs the feed concentration differed between *n*-butanol and *t*-butanol (Fig. 6). As the feed concentration of *n*-butanol increased from 0.5 to 7% w/w, the total flux increased from 282 to 1000 g/m^2·h. Between 3 and 4% w/w there was an anomalous jump in flux and each segment of the curve was nonlinear, tending up at higher concentrations. The total flux for the *t*-butanol solution increased from 297 g/m^2·h at 1% w/w to 677.5 g/m^2·h at 10% w/w, also in a nonlinear fashion. The same type of weakly exponential flux behavior was observed for ethanol with the same membrane (*16*).

A graph of the total flux versus the feed concentration (Fig. 7) was constructed on a log scale to linearize the data. The slopes for the two *n*-butanol data sets are nearly equal; however, they have different intercepts due to the jump that occurred between 3 to 4% w/w *n*-butanol. The *t*-butanol data fall on a single line.

Figure 8 is a graph of the component butanol flux versus feed concentration. The curve for *n*-butanol is similar to the total flux behavior, but the *t*-butanol flux versus feed concentration is nearly linear. The same relationship that existed for the total flux for each study prevailed for the component flux as well. A comparison of the selectivity versus the feed

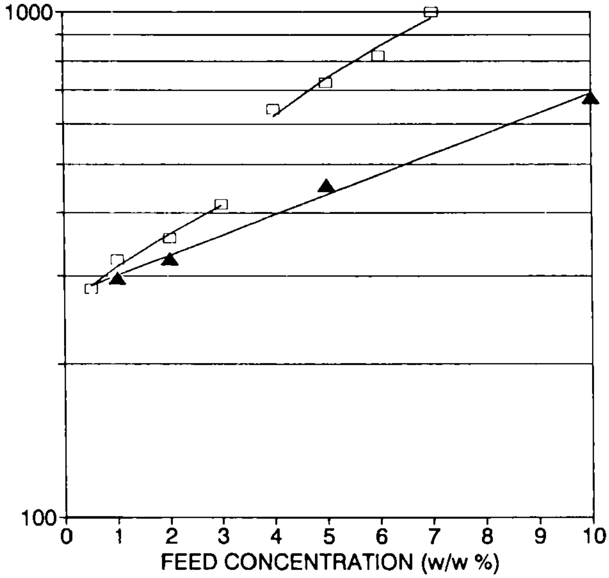

FIG. 7. Total flux vs feed concentration for the PDMS membrane separating a butanol–water mixture: *n*-butanol feed mixture (□) and *t*-butanol feed mixture (▲). Feed temperature of 50°C and a permeate-side pressure of 1 mmHg.

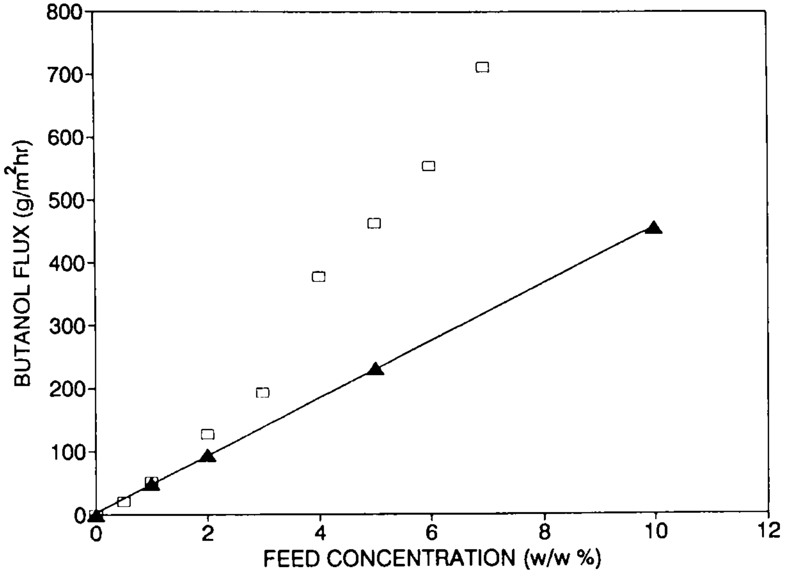

FIG. 8. Butanol flux vs feed concentration for the PDMS membrane: *n*-butanol feed mixture (□) and *t*-butanol feed mixture (▲). Feed temperature of 50°C and a permeate-side pressure of 1 mmHg.

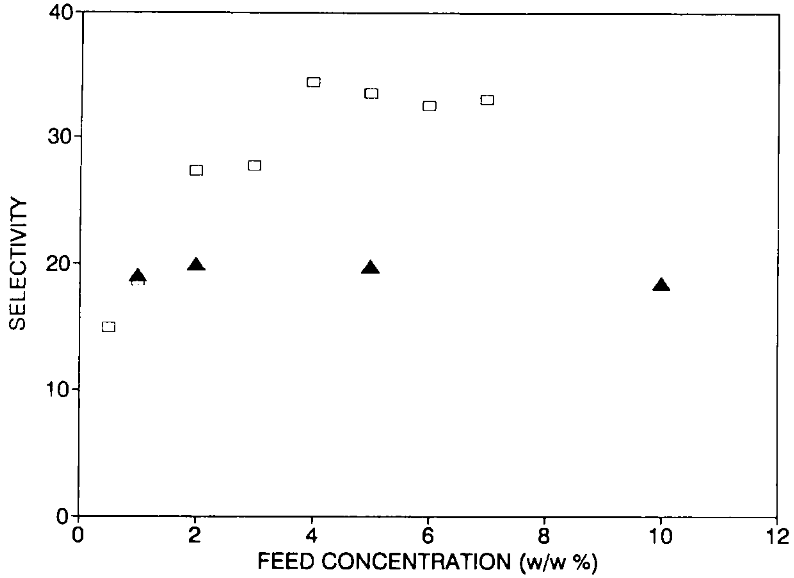

FIG. 9. Selectivity vs teed concentration for the PDMS membrane: *n*-butanol feed mixture (□) and *t*-butanol feed mixture. (▲). Feed temperature of 50°C and a permeate-side pressure of 1 mmHg.

concentration is shown in Fig. 9. The *t*-butanol selectivity showed little variation with the feed concentration. Values between 18.5 and 20 were seen for feed concentrations between 1 and 10% w/w. The *n*-butanol selectivity increased between the feed concentration of 0.5 to 4% w/w and then leveled off. The selectivity ranged from a low of 15 at 0.5% w/w to 34.4 at 4% w/w.

An explanation of the sudden increase in total flux of the *n*-butanol–water/PDMS system has not been determined. Boddeker et al. (*27*), using the PEBA membrane, observed only one exponential relationship between total *n*-butanol flux and feed concentration in a similar study.

The experimental studies with the PMS membrane were identical to the studies done with the PDMS membrane. A constant permeate-side pressure of ~1 mmHg and a feed temperature of 50°C were again used. Figure 10 presents the data on the effects of feed concentration on the total flux for both *n*-butanol and *t*-butanol with the PMS membrane. The relationship for both butanol fluxes was linear with respect to feed concentration in the range studied. At 1% w/w the total flux of *n*-butanol was 138 g/m^2·h and increased linearly to 380 g/m^2·h at 7% w/w. The total flux of the *t*-butanol solution increased from 116 g/m^2·h at 1% w/w to 256 g/m^2·h at 10%

w/w. In both cases the flux for pure water through the membrane, 199 g/m^2·h, was higher than the flux of the 1% w/w solutions.

The component butanol flux versus the feed concentration is also shown in Fig. 10. The component *t*-butanol flux was linear with feed concentration as was the total flux. The *t*-butanol flux was 14 g/m^2·h for a 1% w/w feed and 149 g/m^2·h for a 10% w/w feed. As the *n*-butanol feed concentration increased from 1 to 7% w/w, the total flux increased from 15 to 197 g/m^2·h. The component *n*-butanol flux is linear between feed concentrations of 1 and 2% w/w, but then deviates at higher concentrations.

The results of selectivity versus feed concentration are shown in Fig. 11. The selectivities for the PMS membrane do not vary much for either *n*-butanol or *t*-butanol in the feed concentration ranges studied. For *n*-butanol the selectivities ranged between 11.0 and 14.3, and for *t*-butanol the selectivities extended from 12.4 to 14.3. The PMS membrane was slightly more selective to *t*-butanol as compared to *n*-butanol.

The effect of butanol feed concentration on the water flux is shown in Fig. 12. Both membranes permeate pure water at the same rate, ~200 g/

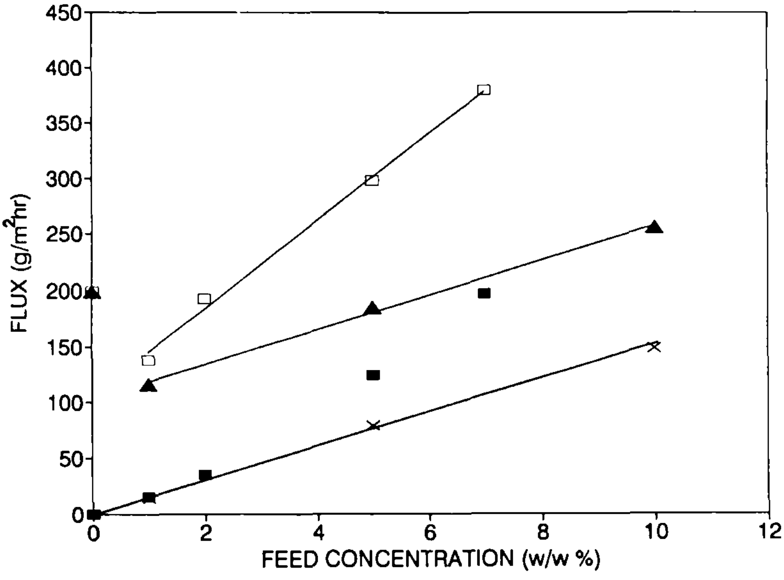

FIG. 10. Flux (total and butanol) vs feed concentration for the PMS membrane separating a butanol–water mixture: *n*-butanol feed mixture total flux (□) and butanol flux (■); *t*-butanol feed mixture total flux (▲) and butanol flux (×). Feed temperature of 50°C and a premeate-side pressure of 1 mmHg.

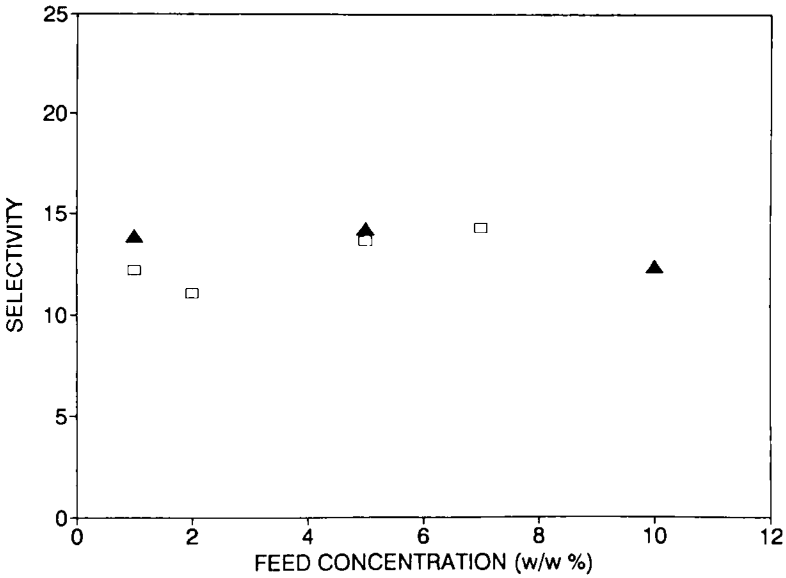

FIG. 11. Selectivity vs feed concentration for the PMS membrane: *n*-butanol feed mixture (□) and *t*-butanol feed mixture (▲). Feed temperature of 50°C and a permeate-side pressure of 1 mmHg.

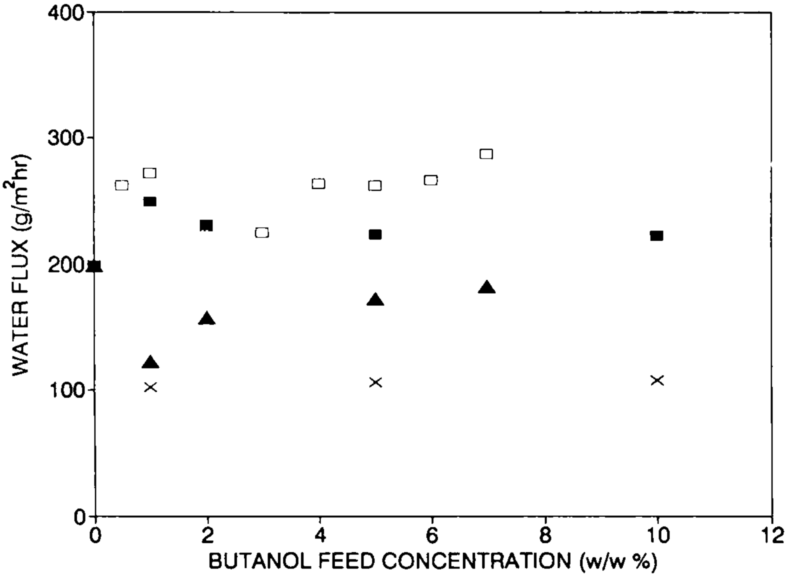

FIG. 12. Water flux vs feed concentration for the PDMS and PMS membrane: PDMS membrane with *n*-butanol feed mixture (□) and *t*-butanol feed mixture (■); PMS membrane with *n*-butanol feed mixture (▲) and *t*-butanol feed mixture (×). Feed temperature of 50°C and a permeate-side pressure of 1 mmHg.

$m^2 \cdot h$. The presence of either butanol tends to enhance water flux through the PDMS membrane but to suppress water flux through the PMS membrane.

The effect of PDMS thickness on the water permeation and the selectivity on a 1% w/w *t*-butanol solution was investigated. The membrane thickness was increased by using additional layers of the homogeneous, symmetric PDMS membranes (~25 μm). Figure 13 shows the relationship of water flux to the inverse of the membrane thickness. The relationship was linear, which agrees with the work of other researchers (*26*, *42–44*).

A 1% w/w *t*-butanol feed was separated using the PDMS membrane at three different membrane thicknesses. The membrane thickness showed no effect on selectivity over the range studied, as predicted by several models (*42*, *45*, *46*). Permeate concentrations ranged between 15.3 and 16.6% w/w. In cases in which this behavior is observed, membrane performance can be optimized by reducing the membrane thickness. The thinner membrane will provide an enhanced flux at the same selectivity, unless conditions are reached in which the organic flux becomes dependent on feed-side mass transfer (*45*).

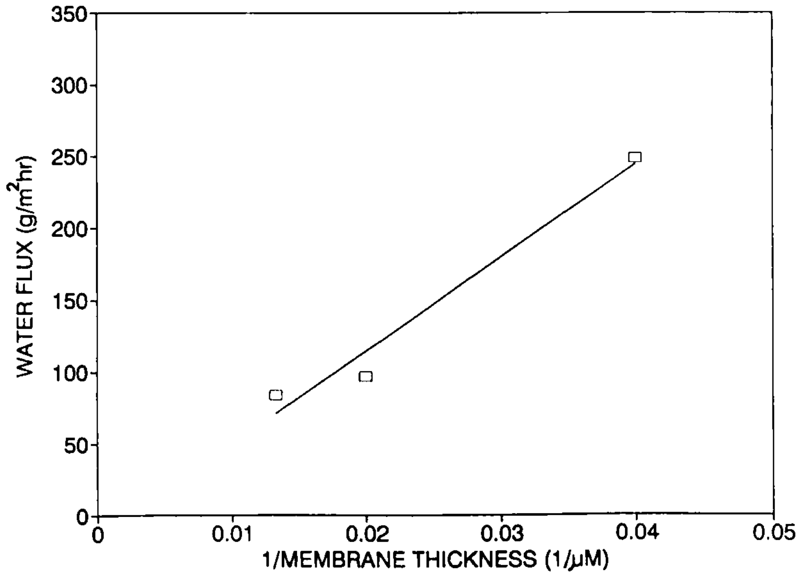

FIG. 13. Water flux vs the inverse membrane thickness for the PDMS membrane using feed conditions of 50°C and 1% w/w *t*-butanol and a permeate-side pressure of 1 mmHg.

CONCLUSIONS

The pervaporative performance of several organophilic membranes for the separation of dilute aqueous binary mixtures of ethanol, *n*-butanol, and *t*-butanol has been studied. Ethanol–water separation studies focused on analyzing the effects of feed temperature and permeate-side pressure on flux and selectivity using an asymmetric PTMSP membrane. The effects of feed temperature were studied with dilute ethanol feed solutions and showed that the flux increased exponentially with temperature. Selectivities did not seem to be greatly affected by operating temperature, although it appears to increase slightly. The PTMSP membrane did not have good flux stability for operations at high temperature for long periods of time. When the permeate-side pressure was increased, it was seen that flux decreased and selectivity remained relatively constant. The transient start-up behavior was studied with a new (virgin) membrane. The flux was initially higher, then reached steady-state after several hours of processing. Selectivities were initially lower, but approached steady-state quickly.

Two silicone-based membranes were compared for separating dilute aqueous mixtures of *n*-butanol and *t*-butanol. A PDMS membrane was found to be more effective in terms of flux and selectivity than a PMS composite membrane. Both membranes were more permeable to *n*-butanol than to *t*-butanol. However, the PDMS membrane had a much higher separation selectivity for *n*-butanol whereas the PMS composite membrane showed approximately the same selectivities for the two butanols. An unusual jump in flux was observed as the feed concentration of *n*-butanol was increased. The cause of this increase has not yet been determined and will be the focus of further research. The relationship of the permeation of water to the membrane thickness was observed. The linear trend of flux versus the inverse membrane thickness matched the behavior reported by several other sources. A study of the effect of membrane thickness on the membrane's selectivity was performed on the water–*t*-butanol/PDMS system. For this system, the membrane thickness had no effect on the selectivity.

SYMBOLS

a	activity
c	concentration
D	diffusion coefficient
J	flux
R	universal gas constant
T	temperature
y	permeate composition

x	feed composition
z	position coordinate normal to membrane surface
α_B^A	selectivity of Component A to B
β_A	enrichment factor

Subscripts

A	Component A
B	Component B
i	Component i

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