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Separation of Tetrahydrofuran from Aqueous Mixtures by Pervaporation

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ABSTRACT

Studies on the separation of tetrahydrofuran (THF) and water by pervaporation were conducted. A silicalite-filled silicone composite membrane was used for organic permeation and a polyvinyl alcohol composite membrane for dehydration. Effects of feed concentration, feed temperature, permeate-side pressure, and type of membrane were studied. The silicone composite membrane yielded a selectivity of 205 and a THF flux of $1.1 \text{ kg/m}^2 \cdot \text{h}$ at benchmark conditions of 50°C feed temperature, 2 torr permeate-side pressure, and a feed concentration of 4.4% w/w THF. An increase in temperature increased the flux exponentially in an Arrhenius-type manner, but had little effect on selectivity. These data show that the trend agrees with an Arrhenius-type relationship. An increase in feed concentration increased the flux, but the selectivity for THF decreased. As the permeate-side pressure increased, the flux decreased in a sigmoidal fashion, but the selectivity for THF increased. Some initial studies on dehydration were also performed. Use of pervaporation in a solvent recovery/reuse system in industry has also been examined.

INTRODUCTION

The separation of tetrahydrofuran–water solutions by pervaporation has been examined. This separation, either by organic permeation or by dehydration, can be accomplished by pervaporation. The research goals were to study organic permeation and dehydration, and analyze the effects

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of process parameters on the separation. With the results obtained, the potential of using pervaporation in the recovery of tetrahydrofuran from process streams, and in wastewater treatment, can be seen. This paper focuses on the separation of tetrahydrofuran and water under varying process conditions with the primary emphasis on organic permeation from dilute aqueous process mixtures. Further considerations on modeling and process utilization of a hybrid system will be the subject of a subsequent paper.

Pervaporation typically uses a nonporous polymeric membrane to selectively separate one or more components from a liquid feed mixture. The traditionally accepted mechanism for this separation is solution-diffusion. The membrane acts as a mass separating agent, or additional phase. Preferentially permeated components are first sorbed into the membrane on the feed side. The components then diffuse through the membrane due to a concentration gradient. The components then desorb nonselectively from the membrane on the permeate side as a vapor due to the partial pressure being lower than the saturation pressure on the downstream side. This low pressure is obtained by continuous pumping (vacuum pervaporation), although other methods such as sweeping gas pervaporation can be performed. As different species pass through the membrane at different rates, a component at low concentration in the feed can be highly enriched in the permeate.

The driving force for this separation is a difference in chemical potential, $\Delta\mu_i$, across the membrane. The activity of the permeating components in the liquid state (feed side) is greater than the activity of the permeating components in the vapor state (permeate side). The standard phenomenological expression relating the driving force, $\Delta\mu_i$, and the thickness of the membrane, l , to transport rate, J_i , is

$$J_i = L_i \frac{\Delta\mu_i}{l} \quad (1)$$

where L_i is a phenomenological transport coefficient.

The permeability of a component is a function of diffusivity and solubility in the membrane. Diffusivity and solubility are not constant values, but are highly dependent on concentration, swelling of the membrane, and interactions of components in the mixture. Due to the interactions of permeating components, coupling phenomena occur, and linear relations cannot be employed. Experimental studies are therefore essential to determine separation performance and to evaluate process parameters for scale-up and design.

The flux of the components, and the selectivity of the membrane to one component over another, determine the effectiveness of pervaporation.

The flux of a component is a rate of permeation per membrane area. The typical units are $\text{kg}/(\text{m}^2 \cdot \text{h})$. Flux can be expressed as the total flux, J_T , or for an individual permeating component, J_i . The flux is measured by knowing the mass of the permeate, membrane area used, and duration of the collection.

Selectivity is a measure of a membrane's separation efficiency. It is a ratio of the mass fractions of the components in the permeate and in the feed. The selectivity of component A over B is given as:

$$\alpha^A = \frac{y_A/y_B}{x_A/x_B} \quad (2)$$

where y_A = mass fraction of component A in the permeate

y_B = mass fraction of component B in the permeate

x_A = mass fraction of component A in the feed

x_B = mass fraction of component B in the feed

The concentration of the collected permeate vapor does not depend on the relative volatilities of the components, like distillation, but is based on the relative permeation rates through the membrane. Therefore, the separation is not limited by the vapor-liquid equilibrium of the mixture. This advantage is very beneficial in the separation of azeotropic mixtures.

A full discussion of the theory, design, and applications of pervaporation processes is beyond the scope of this paper. The reader is referred to several other publications to obtain a better understanding of the underlying principles, system design, and commercial applications (1–6).

The two main applications of pervaporation discussed here are organic permeation and dehydration. Organic permeation involves using an organicophilic/hydrophobic membrane, such as silicone-based polymers, to selectively separate organics from an aqueous mixture. The permeate produced has a high concentration of organic, while the retentate is depleted of that species. An application for organic permeation is the selective removal of organics from wastewater streams and dilute biochemical processing streams (7–9). Additionally, costly organic solvents can be recovered, purified, and reused. The reasons for removal of organics from wastewater streams is environmentally driven, and recent environmental regulations have hastened the use of this technology in many industries.

Use of pervaporation to selectively permeate solvents such as ethanol, butanol isomers, acetone, and ethyl acetate from dilute aqueous mixtures has been previously investigated by the authors (10–13). These studies have examined separating solvents common to the pharmaceutical and other industries.

Dehydration involves using a hydrophilic membrane, such as polyvinyl alcohol (PVA) composite membranes, to selectively remove water from an organic–water mixture. Dehydration applications have been commercially utilized in many industries (1). Pharmaceutical processes use organic solvents in the synthesis of certain drugs. Organic solvents are used for separations operations, such as extraction, precipitation, crystallization, washing, adsorption, ion exchange, and chromatography. Some water dissolves in these organic solvents during use, and it must be removed so that the solvents can be recovered and reused. Organic solvents are also used in the specialty chemicals industry and in a variety of other areas such as microelectronics production.

A solvent used in many of these applications is tetrahydrofuran (THF). Recovery of THF by means of distillation may be very expensive due to the azeotrope formed by THF–water (94.1% w/w at 760 torr). Pervaporation breaks these azeotropes and is therefore suggested as an alternative method for recovering THF. This paper focuses on the organic permeation of THF from aqueous mixtures and also presents some limited data on the dehydration of THF–water mixtures. A “hybrid” system of these two processes has the potential for use in the recovery/reuse of THF and in the purification of wastewater streams. This type of system has been investigated for other wastewater treatment applications (14). The most immediate use of pervaporation is the direct integration with traditional existing distillation operations for cost reduction and capacity improvement.

There is a minimal amount of information available on THF separation by pervaporation in the open literature. Most literature accounts on this separation briefly mention dehydration using both commercially available membranes and novel membranes in basic laboratory studies. The use of pervaporation to successfully remove small quantities of water from THF mixtures has been generally mentioned in several sources although no specifics on the experimental conditions were given. A feed THF mixture of 0.4% w/w water is reduced to 0.22% w/w water (220 ppm) using a commercially available PVA composite membrane (1). Another study with a PVA composite membrane dehydrated THF feeds of 97% w/w to less than 0.01% w/w water (15). These values come from several commercial sources and no specifics on process conditions are given. This would therefore indicate that further study is warranted before any conclusions can be drawn.

Inoue and Mikake (16) looked at pervaporation for solvent recovery as used in the chemical industry. They used commercially available dehydration membranes (most likely PVA composite membranes). Actual mixtures from various industries were employed, and successful solvent dehy-

dratration was accomplished. In one trial a feed mixture consisting of 85.6% THF, 3.5% water, and 10.9% benzene was dehydrated, producing a retentate with a water content of 0.1%. A second study with a more complex mixture of 68.6% THF, 0.9% water, and 30.5% "unknowns" was dehydrated to 0.05% water by pervaporation.

These tests were done on a lab-scale system with temperatures in the range of 80 to 95°C. No information was given on the other process parameters or flux values. It appears that the unknowns do not adversely affect the dehydration process for the THF, but do have some effect. Inoue and Mikake stated in previous studies with dehydrating alcohols and chlorinated hydrocarbons that these "unknowns" had an effect on selectivity. This does suggest the need to test the actual process stream in question.

Nguyen et al. (17) investigated the preparation of novel pervaporation membranes for dehydrating various solvents. Their studies focused on preparing membranes from polyacrylonitrile–polyvinylpyrrolidone (PAN–PVPD) blends. The studies were done at a temperature of 20°C and a permeate-side pressure of 1 torr.

These studies were done on a lab scale, so only membrane selectivities and fluxes were determined. The best membrane in their study appears to be a PAN–PVPD blend which is selective to water and exhibits reasonable fluxes. The membrane had a water selectivity of 10.7 and a flux of 0.4 kg/m²·h with a feed concentration of 5.9% water. Another variation of this membrane yielded higher fluxes but lower selectivities. Experiments with a porous version of the membrane produced no separation although the flux was extremely high.

Additional studies by the group showed the effect of water content on flux and selectivity. These experiments indicated that as the water content of the feed increased from 0 to 25%, flux increased linearly. This is due to the effects of swelling of the polymer. Selectivity decreases as the water concentration of the feed increases.

An earlier dehydration study by Neel et al. (18) describes the results with a polytetrafluoroethylene–polyvinylpyrrolidone (PTFE–PVPD) membrane. Their studies at 25°C investigated dewatering an azeotropic mixture (5.7% H₂O, 94.3% THF). The membrane exhibited a β -selectivity of 9.24 (permeate water concentration/feed water concentration = 9.24) and a flux of 0.94 kg/m²·h. The authors discuss influences of external parameters on flux and selectivity in general terms. They qualitatively mention the effects of temperature, pressure, concentration polarization, and temperature polarization on separation. They mention some work on modeling a continuous pervaporation system for binary separation.

Neel et al. (19) have continued to work on dehydration of THF mixtures using regenerated cellulose (Cuprophan) membranes. They studied the

effect of downstream, permeate-side pressure on flux and selectivity. The researchers stated that it is important to investigate each type of system (solvent mixture and membrane) to understand the effect of permeate-side pressure on the selectivity and flux. The effect of this process parameter on selectivity may depend on the thermodynamic properties of the constituents being separated. Various feed mixtures (water content ranging from 9.7 to 25% w/w) were separated at 20°C and showed flux to decrease gradually with increasing permeate-side pressure. Selectivity remains relatively constant up to around 15 mbar (11.25 torr), then decreases at this apparent "critical" value. When feed temperature is increased, this "critical" pressure is increased. Nguyen (20) continues to study the earlier efforts at understanding the effect of downstream pressure on pervaporative performance. He has developed a model to predict the performance of the water-THF Cuprophan system.

The selective permeation of THF from dilute solution was only mentioned briefly in the paper by Nagase et al. (21). They mention a study in which a feed solution of 6.53% THF is increased in the permeate to 84.3%. The membrane used was a copolymer of poly(1-trimethylsilyl-1-propyne) and 1-(3,3,3-trifluoropropylidemethylsilyl-1-propyne), PTMSP/FPDSP. The process conditions were 50°C and a permeate-side pressure of 0.5 torr. The permeability of the membrane to the THF feed solution was $1.63 \times 10^{-1} \text{ g} \cdot \text{m} / \text{m}^2 \cdot \text{h}$. The thickness of the membrane is given as 30–50 μm , so the flux is in the range of 3.26 to 5.43 $\text{kg} / \text{m}^2 \cdot \text{h}$.

EXPERIMENTAL MATERIALS AND METHODS

The pervaporation system used in the research is a bench-scale test unit from Zenon Environmental Systems, Inc. (Burlington, Ontario), which is shown schematically in Fig. 1. The feed solution is passed through a heat exchanger to keep the feed at a constant temperature. The feed is continuously pumped through the membrane module, which houses flat sheet membranes with an area of 79.1 cm^2 , and back to the feed tank. A second heat exchanger on the retentate line is used for cooling or heating of the solution. A rotameter and control valve allows for regulation of feed flow rate.

The system has three impingers that can be used to collect the permeate, which is condensed by liquid nitrogen held in dewars. Two of the impingers are used in a rotating fashion for permeate collection; the third trap is used as an extra measure to condense permeate before the vacuum pump. There are two pressure gauges, one for feed pressure and the other for permeate-side pressure. A vacuum pump provides the low pressure on the permeate side. The materials of construction of the system are

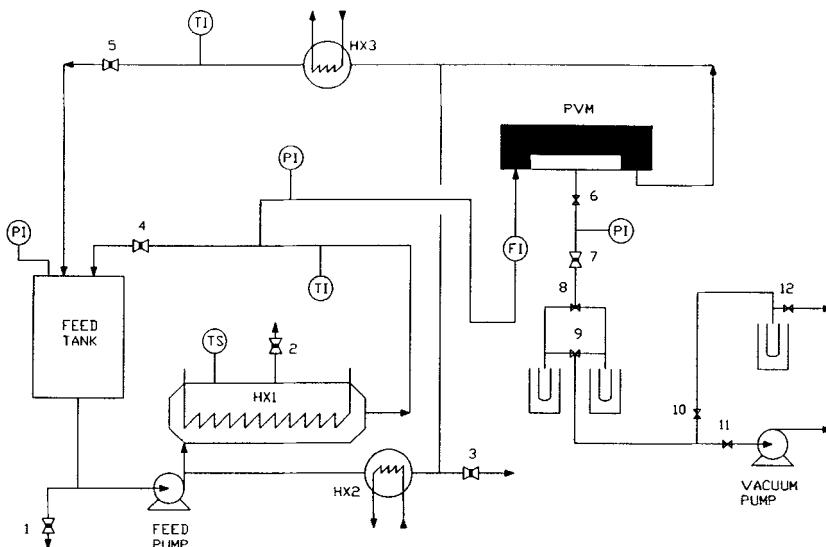


FIG. 1 Schematic of bench-scale pervaporation system (Zenon Environmental Systems, Inc., Burlington, Ontario, Canada) utilized in research. Pressure indicator, PI; temperature indicator/sensor, TI/TS; flow indicator, FI; pervaporation module, PVM; heat exchangers, HX1, 2, 3; valves, 1–12.

compatible with various process applications. Stainless steel construction is used throughout, and gasket material depends on the particular solvent being processed. For THF, an acceptable material is EPDM (ethylene-propylene-diene monomer). Permeate flux is measured gravimetrically, and a refractometer is used to determine the feed and permeate concentrations of the THF.

The Zenon unit is a compact and economical bench-top unit that can be utilized to perform runs separating various feed mixtures using different membranes (22). The experimental system has the ability to accurately control process parameters and yield meaningful data to examine process feasibility for both organic permeation and dehydration applications. The unit can be utilized in a research or teaching setting.

The experimental studies utilized various membranes, with the results of two being reported. The first membrane examined was an organophilic, silicalite-filled, silicone composite membrane (designation: Pervap 1170) obtained from the GFT Division of Carbone of America Corp. (Parsippany, New Jersey). The second membrane examined was a hydrophilic polyvinyl alcohol (PVA) composite membrane (designation: Pervap 1000), also obtained from Carbone.

The benchmark conditions for the organic permeation and dehydration runs were used to test the stability of the membranes. The benchmark process conditions for organic permeation were a feed temperature of 50°C, feed flow rate of 11 L/min, feed concentrations of 4.4% w/w THF, and a permeate-side pressure of approximately 2 torr. The benchmark conditions for dehydration were a feed temperature of 50°C, feed flow rate of 11 L/min, feed concentration of 10% w/w water, and a permeate-side pressure of 2 torr. Runs at benchmark conditions were occasionally repeated to evaluate any change in membrane characteristics over time.

RESULTS AND DISCUSSION

Organic Permeation

An initial analysis of permeate concentration vs feed concentration was performed to see the difference between separation by pervaporation and by more conventional processes like distillation that separate based on relative volatilities (vapor-liquid equilibrium). Figure 2 shows that permeate produced using pervaporation has a higher THF concentration than

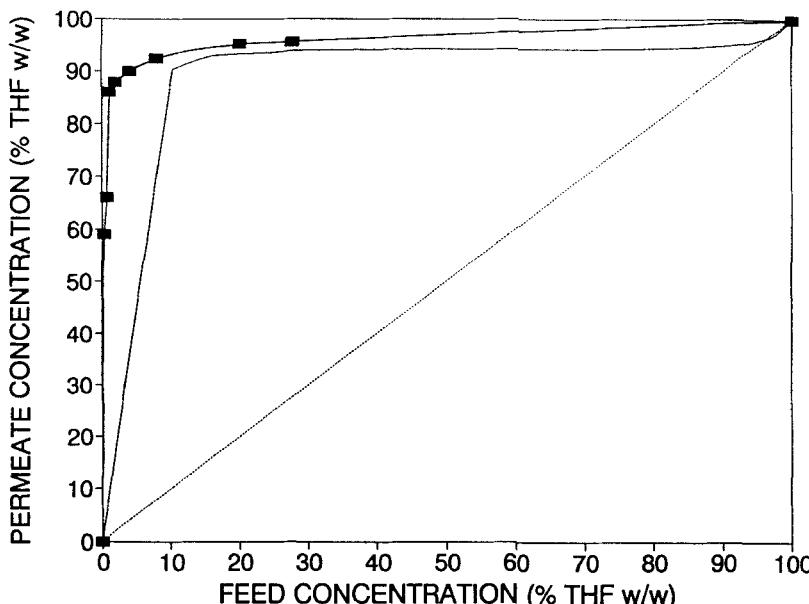


FIG. 2 Permeate THF concentration vs feed THF concentration at 2 torr permeate-side pressure and 50°C. Organic permeation studies with silicone composite membrane. Vapor-liquid equilibrium (VLE) of tetrahydrofuran and water mixture (at 50°C). Experimental pervaporation data (■), VLE (—), and $x = y$ line (— - -).

would a vapor product using distillation. A much greater difference in enrichment between these two types of separation is more evident at lower THF feed concentrations using pervaporation.

It was found that there are limitations on THF feed concentration and feed temperature when using these membranes. For organic permeation, specifications from Carbone indicate a temperature limitation of 80°C and an organic feed concentration of 10–40% for the organophilic membrane. With the use of THF as the solvent, if the THF feed concentration exceeds ~30%, the membrane deteriorates quickly. This is attributed to the aggressiveness of THF toward the membrane. The temperature limitation is further enhanced by the vapor pressure of THF. Since THF's boiling point is low, significant vaporization of THF at temperatures greater than 80°C leads to an unstable feed concentration.

An analysis of the effect of feed concentration on flux and selectivity was performed with a feed temperature of 50°C and a permeate side pressure of approximately 2 torr. As the feed concentration was increased from 0.33 to 27.6% w/w THF, the permeate flux increased from 0.172 to 4.21 kg/m²·h (Fig. 3). The fluxes of the individual components are also

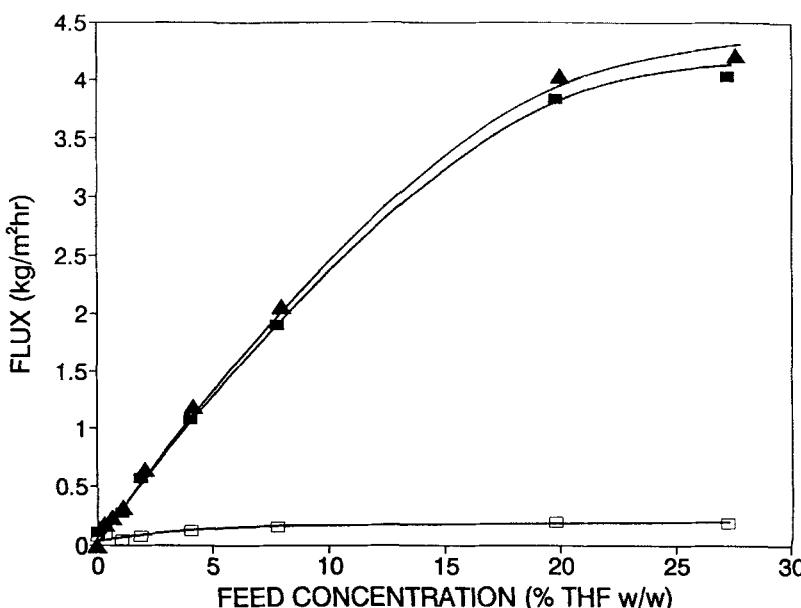


FIG. 3 Flux (total, THF and water) vs feed THF concentration for the silicone composite membrane operating at 50°C and ~2 torr permeate-side pressure. Total flux (▲), tetrahydrofuran flux (■), and water flux (□).

shown. The flux of the THF increases with the total flux, but the flux of the water increased only slightly.

The effect of increasing feed concentration on selectivity of tetrahydrofuran is seen in Fig. 4. As the concentration of the feed was increased from 0.33 to 27.6% w/w THF, the selectivity of THF decreased from 550 to 60. Similar trends for flux and selectivity are seen in the permeation of other organics studied by our group (10–13).

An analysis of the effect of feed temperature on flux and selectivity was performed with a feed concentration of 4.4% w/w THF and a permeate-side pressure of 2 torr. As the feed temperature increased from 30 to 80°C, the flux increased exponentially from 0.702 to 2.56 kg/m²·h (Fig. 5). The flux of THF increased with the total flux, but the flux of water increased only slightly.

When the natural log (ln) of the flux was graphed versus the reciprocal absolute temperature (Kelvin), the results agreed with the Arrhenius effect of temperature on rate (Fig. 6). The equation found for the total flux using these axes is

$$J_T = 992e^{-2175/T} \quad (3)$$

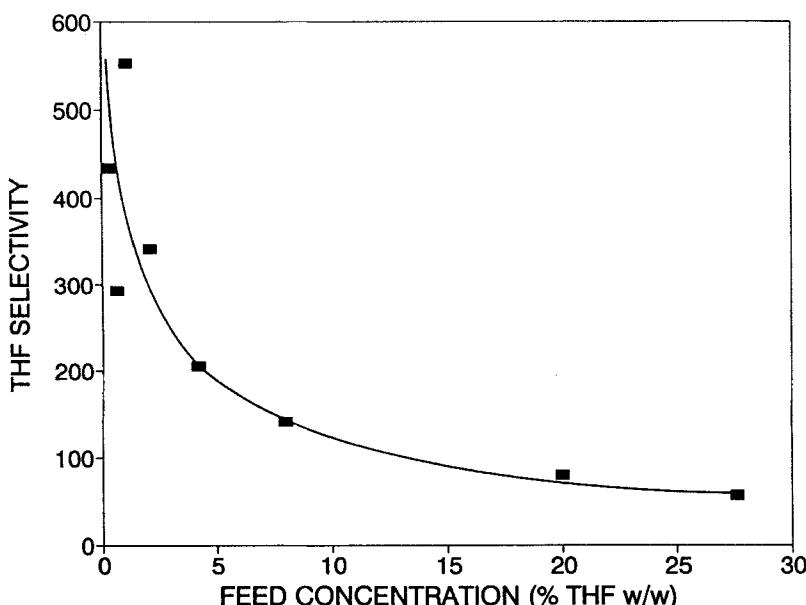


FIG. 4 THF selectivity vs feed THF concentration for the silicone composite membrane at 50°C and 2 torr permeate-side pressure.

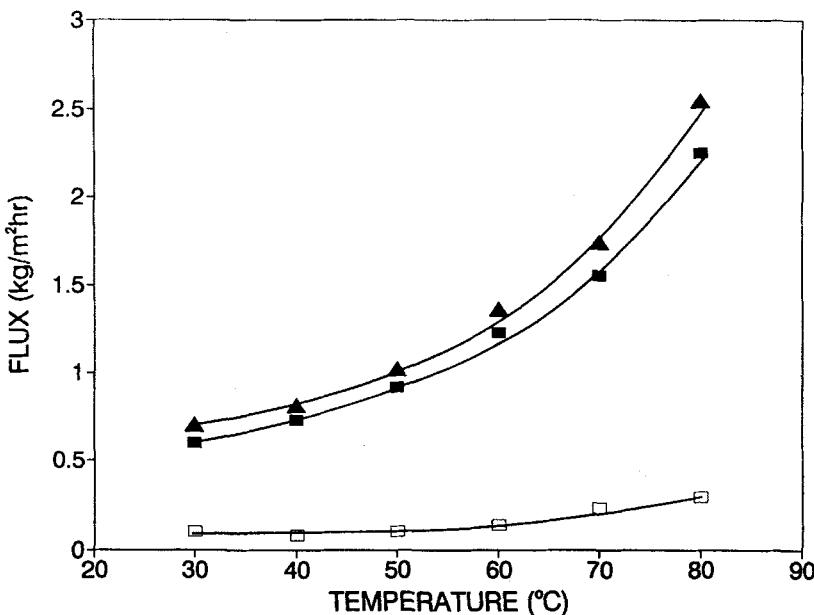


FIG. 5 Flux vs temperature for a 4.4% w/w tetrahydrofuran feed mixture and 2 torr permeate-side pressure using the silicone composite membrane. Total flux (▲), tetrahydrofuran flux (■), and water flux (□).

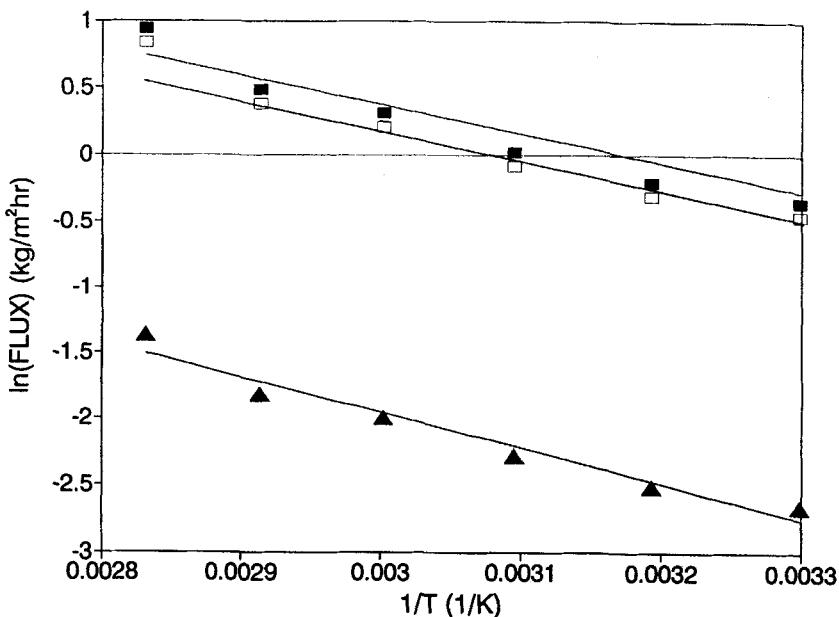


FIG. 6 Natural log, \ln , of flux vs reciprocal absolute temperature for a 4.4% w/w tetrahydrofuran feed mixture and 2 torr permeate-side pressure using the silicone composite membrane. Total flux (■), tetrahydrofuran flux (□), and water flux (▲).

An activation (separation) energy of 4.3 kcal/mol was calculated. Similar exponential increases of flux due to a temperature increase were seen for other solvents previously studied, although the exact nature of the curve depends on the mixture being separated and the membrane employed.

There does not seem to be much of an effect of temperature on permeate concentration over the range studied (30 to 80°C). The permeate concentration of THF decreased slightly from 91 to 88% w/w, although this result may not be statistically significant. Pervaporation using ethanol and acetone in water showed little effect of temperature on permeate concentration as well (10, 12). This shows that pervaporation processes can be enhanced commercially by increasing the feed temperature. This increase yields higher fluxes without adversely affecting selectivity.

An analysis of the effect of permeate-side pressure on flux was performed with a feed concentration of 4.4% w/w THF and a feed temperature of 50°C. As the permeate-side pressure was increased from 2 to 120 torr, the flux decreased sigmoidally from 1.02 to 0.433 kg/m²·h (Fig. 7). The component fluxes are also shown. The THF flux followed the same decrease as the total flux, but the decrease in the flux of water was only

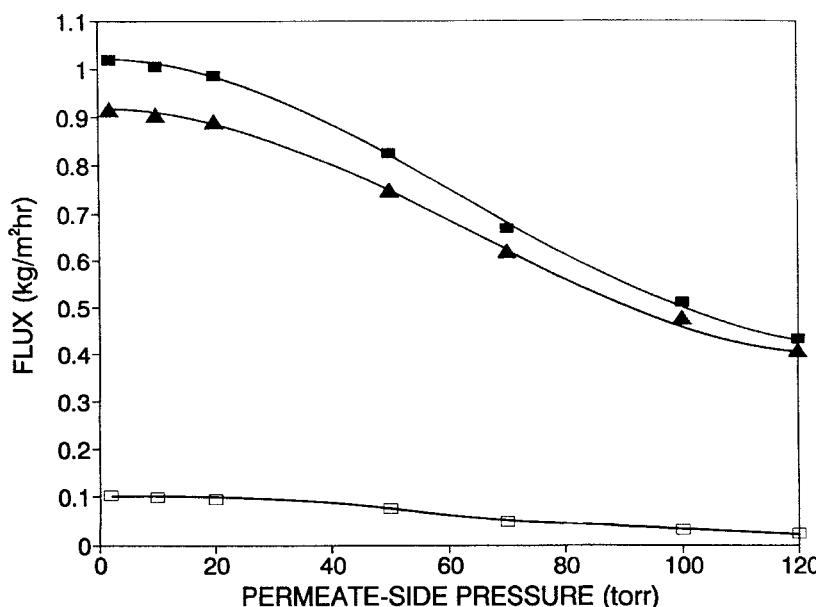


FIG. 7 Flux vs permeate-side pressure for a 4.4% tetrahydrofuran feed mixture at 50°C using the silicone composite membrane. Total flux (■), tetrahydrofuran flux (▲), and water flux (□).

small. The flux appears to decrease slowly at low pressures, and then decreases more rapidly as permeate-side pressure increases. At permeate-side pressures <20 torr, no major effect on flux is apparent. A similar decrease in flux was also observed in previous studies with acetone (12).

The decrease in flux with increasing permeate-side pressure is due to a decrease of the driving force. As the pressure increases, it approaches the saturated vapor pressures of THF and water. The difference between these pressures therefore decreases, and the driving force decreases. Since the saturated vapor pressure of water is much lower than that of THF, the flux of water decreases more quickly than the flux of THF, and therefore the concentration of THF in the permeate will rise. The limiting pressure of the permeate is therefore the vapor pressure of THF at the operating temperature. Beyond this pressure, the driving force is zero. For the benchmark temperature of 50°C, the saturated vapor pressure, the limiting pressure, for THF is 440 mmHg.

The permeate concentration of THF changes over the range studied (2 to 120 torr). Over this range, permeate concentration increases from 90 to 94.3% w/w THF. Due to the increase in the concentration of THF in the permeate, the selectivity increases. Over the pressure range studied (2 to 120 torr), the selectivity of THF increased from 195 to 355.

The membrane cell allows for crossflow of the feed past the membrane surface, so the effects of feed flow rate on pervaporative performance were examined. The results showed that as the feed flow rate was decreased, there was very little, if any, effect on flux or permeate concentration. For the flow rates studied, the Reynolds number ranged from 19,970 to 109,800. This calculation indicates that for both the minimum and maximum flow rates used, the turbulent regime was maintained. Therefore, the mass transfer coefficient is not significantly changed, and the product will not be greatly affected, as the results show. The effects of concentration might have been observed if runs were conducted at much lower Reynolds numbers with a more dilute feed mixture.

Dehydration

The evaluation of pervaporation for the dehydration of THF mixtures was also studied, although not as thoroughly as the organic permeation case. These studies used a PVA composite dehydration membrane to remove water from THF. Dehydration was carried out at two permeate-side pressures: 2 and 20 torr. The 20 torr run was used to match a more industrially utilized process pressure. The effects of feed concentration on permeate concentration and flux were examined.

At permeate-side pressures of 2 and 20 torr and a feed temperature 50°C, the effect of feed concentration on permeate concentration was ob-

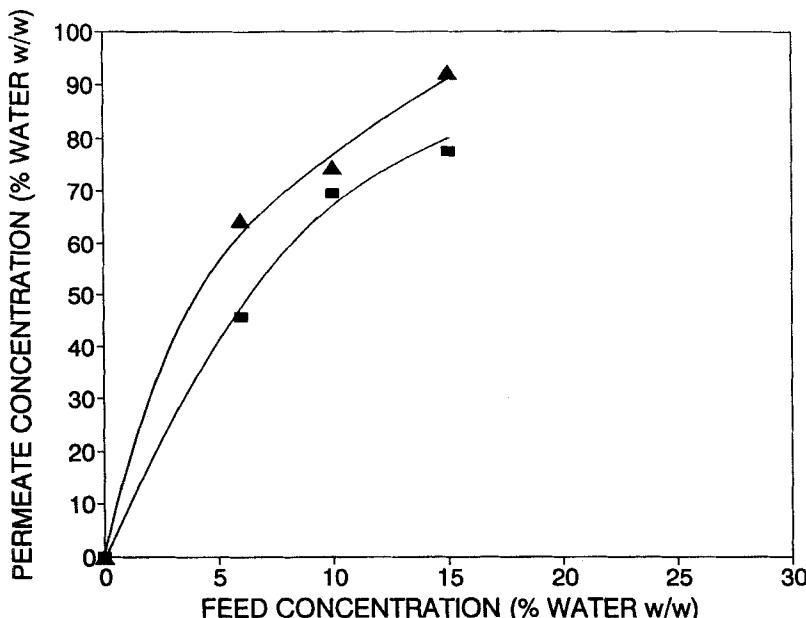


FIG. 8 Permeate water concentration vs feed water concentration for dehydration using the PVA composite membrane at 2 and 20 torr and 50°C. Pressures utilized: 2 torr (▲) and 20 torr (■).

served. As the feed concentration increased from 6 to 15% w/w water, the permeate concentration increased from 64.5 to 92.2% w/w water for 2 torr and from 45.7 to 77.5% w/w water for 20 torr (Fig. 8). These results indicate good selectivity for water for this membrane.

The effect of feed concentration on flux was also studied. As the feed concentration increased from 6 to 15% w/w water, the total flux increased exponentially from 0.155 to 1.584 kg/m²·h for 2 torr (Fig. 9), and 0.0681 to 0.714 kg/m²·h for 20 torr (Fig. 10). For both pressures, the water flux followed the total flux, and the THF flux increased slightly, then leveled off (Figs. 9 and 10). Similar trends of increasing flux with increasing feed concentration are obtained with ethanol and THF in water mixtures using a PVP (polyvinylpyrrolidone) membrane (17).

Long-term stability tests on using the aforementioned membranes for dehydration were not performed. Organic permeation runs showed excellent stability of a silicone composite membrane over long periods of operation at benchmark conditions. The data for dehydration were not performed under extensive long-term operation. Unfortunately, some problems were encountered with the PVA dehydration membrane which will require further investigation.

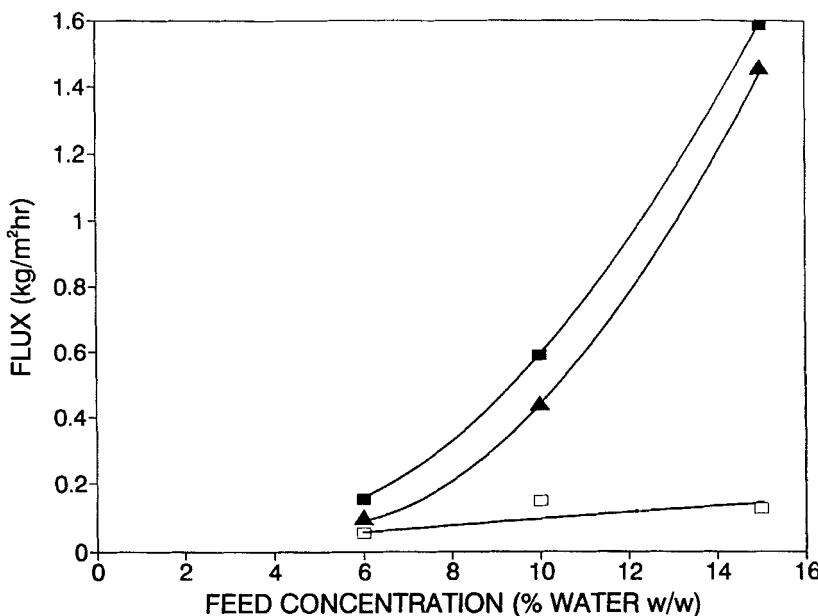


FIG. 9 Flux (total, THF and water) vs feed water concentration for dehydration using the PVA composite membrane operating at 50°C and 2 torr permeate-side pressure. Total flux (■), tetrahydrofuran flux (□), and water flux (▲).

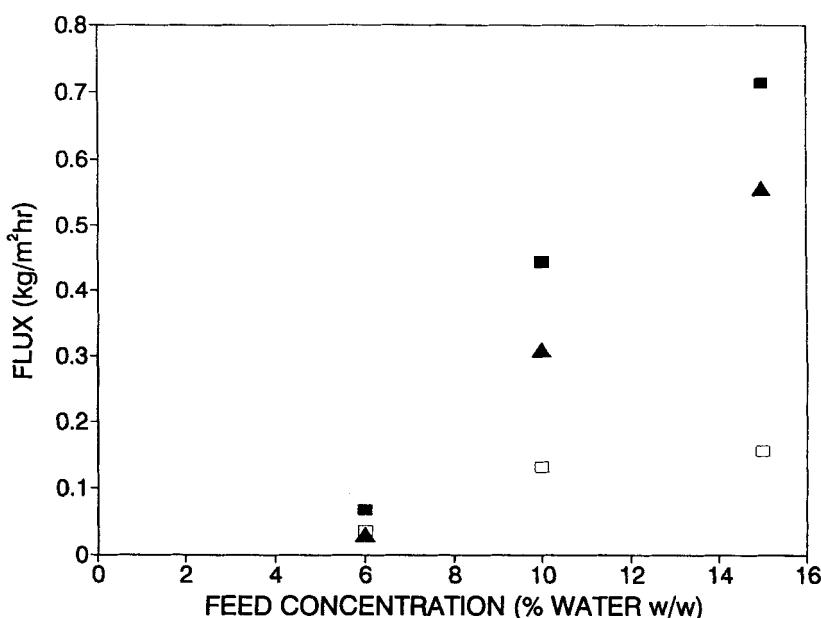


FIG. 10 Flux (total, THF and water) vs feed water concentration for the PVA composite membrane operating at 50°C and 20 torr permeate-side pressure. Total flux (■), tetrahydrofuran flux (□), and water flux (▲).

These test results can be utilized to determine the degree of dehydration in actual practice. By knowing the permeate concentration and flux through the membrane, the retentate concentration can be found. For a given size membrane, the permeate flow rate can be measured, as well as its concentration. A mass balance on the membrane system will then yield the retentate concentration. However, if the retentate concentration is specified, the membrane area required can be found from the mass balance.

CONCLUSIONS

Pervaporation is an effective type of separation that has great potential in the treatment of wastewater, chemical/biochemical processing stream separation, as well as solvent purification and recovery. As can be seen in these results, the tetrahydrofuran–water azeotrope is effectively broken, which yields a greatly enriched THF permeate in a single step. Using a hydrophilic membrane, water is effectively removed from high concentration solvent streams. Pervaporation using dehydration can be used with existing distillation columns, whereas water can be removed from the high solvent concentration distillate stream to obtain a highly pure solvent stream.

The process parameters studied included feed temperature, feed concentration, and permeate-side pressure. As the feed concentration increased, flux increased and permeate concentration increased. As the feed temperature increased, the flux increased exponentially, and selectivity remained relatively constant. As the permeate-side pressure was increased, the flux decreased sigmoidally, while the selectivity increased. The optimal flux occurred at high feed temperature and low permeate-side pressure. The results obtained with the system are reliable, and translation of results to commercial-scale operation is possible.

With the ability of pervaporation to preferentially permeate both water and THF (depending on the membrane employed), a hybrid system of staged membranes is feasible for producing purified water from a waste stream and purified solvent for recovery/reuse. A second paper is being prepared that will investigate system modeling and design. It is hoped that with the optimum process parameters, a system can be used to economically treat wastewater and recover the solvents.

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