Published in final edited form as:

J Memb Sci. 2010 April 15; 352(1-2): 41–49. doi:10.1016/j.memsci.2010.01.058.

Novel Perfluorinated Polymer-Based Pervaporation Membranes for Separation of Solvent/Water Mixtures

V. Smuleac¹, J. Wu¹, S. Nemser², S. Majumdar², and D. Bhattacharyya^{1,*}

¹Department of Chemical and Materials Engineering, University of Kentucky, Lexington, KY 40506

²Compact Membrane Systems Inc., Wilmington, DE 19804

Abstract

Traditionally, the pervaporation of water-solvent mixtures where the solvent is the major component is performed using hydrophilic membranes (such as PVA or zeolites). In the present paper a new type of pervaporation membrane (amorphous perfluorinated polymer, hydrophobic) was studied for separation of water-solvent mixtures. This membrane has high free volume and is inert for all solvents, and has a remarkable mechanical, chemical and thermal stability. The water is transported by solution diffusion model and the separation of solvent is primarily based on molecular sieving (size exclusion) principles. The membrane shows a high stability for operation over a broad range of feed concentrations without swelling; the operating temperature does not have a significant effect on membrane separation performance. Separation factors as high as 349 and 500 for water-ethanol and water-IPA mixtures (2-98 % wt water-solvent) and fluxes of 0.15 and 0.05 kg/m²h, respectively were obtained at 22 °C. The permeance-based selectivities were also calculated, and the selectivity is approximately constant for a wide range of feed concentrations. The pervaporation of more complex (ternary) mixtures of water-ethanol-ethyl acetate showed that this system could be successfully applied for solute separation based on size exclusion.

1. Introduction

Solvent dehydration is of a great importance in pharmaceutical and other industries. Among the available techniques, pervaporation is attractive due to its relative simplicity and lower costs, as compared to traditional methods. In addition it can be used even in azeotropic systems, which is difficult to achieve using traditional processes, such as distillation. Usually in the pervaporation mixture the minor component is preferentially transported through the membrane; thus for high solvent concentration in mixtures to be separated (such as solvent dehydration application), hydrophilic membranes are used (for example PVA). For the opposite case, high water content in mixture (such as separation of volatile organics from water or fermentation broth), hydrophobic membranes (polydimethyl siloxane, silicone rubber etc.) would be preferred to remove organics (in low concentration) from water. An

© 2010 Elsevier B.V. All rights reserved.

* Corresponding Author: D. Bhattacharyya University Alumni Professor Dept. of Chemical and Materials Engineering University of Kentucky 177 Anderson Hall Lexington, KY 40506-0046 Phone: 859-257-2794 Fax: 859-323-1929 db@engr.uky.edu.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

extensive review on this topic (water-solvent pervaporation for low solvent concentration area) can be found in literature [1].

Traditionally, the separation of components in pervaporation is based on a difference in transport rate of individual components through the membrane. The transport of species in pervaporation is composed of several steps: 1) transport from bulk to the membrane interface, 2) preferential sorption on the membrane, 3) diffusion through the membrane 4) desorption from the membrane (permeate side). Steps 1 and 4 can be controlled by changing the operating conditions; in addition step 4 is very rapid if the pressure at the permeate side of the membrane is kept low. Steps 2 and 3 are described most often using solution diffusion model. The diffusion of species through the membrane is a very complex process. It usually implies that there is a coupling effect; i.e. the transport of species *i* (flux) through the membrane depends on all species present and it can be modeled using irreversible thermodynamics.

For the case of solvent dehydration in particular, a variety of materials have been reported in literature, such as polymeric [2-5], inorganic [6-8] or mixed matrix [9-12] as being suitable to be used in pervaporation. An interesting approach is to use layer-by-layer polyelectrolyte assemblies, these ultrathin films can be used in pervaporation and show high fluxes and high separation factors for a variety of water-solvent mixtures [13-17]. A comprehensive list of pervaporation membranes can be found in recent reviews [18-20] and their performances (both flux and separation factor) vary greatly.

Another approach in pervaporation is to use a membrane which is porous with pore sizes around 0.4 to 0.5 nm, large enough to let water molecules pass through and retain any other solvent molecules that have a larger molecular size (size exclusion mechanism). This type of membranes, which separate species by molecular sieving mechanism, was reported in literature for silica [21], titania [22] silica-zirconia [6] or composite membranes of aluminophosphate/sodium alginate [23,24] and it was shown that narrow pore size distribution is critical in obtaining high separations.

In the present study, a novel membrane based on fluoropolymer, a material with a high free volume and an exceptional mechanical, chemical and thermal stability is studied for water/solvent separation by pervaporation. These membranes have been used commercially to separate water vapor and air from gasoline vapor mixture in underground storage tank application [25]. They have also been very effective in removing free, emulsified and dissolved water from industrial lubricant fluids [26]. Although this membrane is hydrophobic, it has small pores and transports preferentially water from water-solvent mixture. The hypothesis is that the solvent species are separated from the mixture based on size exclusion and not chemical affinity as in conventional pervaporation. The vapor permeation and pervaporation of organic mixtures through perfluoropolymer membranes is reported in literature [27-29]. These are made of perfluoro-2,2-dimethyl-1,1,3-dioxole copolymerized with tetrafluoro ethylene with variable copolymer ratios (such as AF2400 and AF 1600), and are commercially available from DuPont. However our paper is the first study dealing with the separation of aqueous-solvent mixtures using perfluoropolymer membranes. The pervaporation performances were evaluated in terms of both productivity (flux) and separation performance. The effect of various parameters (feed composition, temperature etc.) and the ability to operate these membrane systems over a broad range of water activities were also examined. The following systems were studied: water-ethanol, water-isopropanol, water-ethyl acetate and water-ethanol-ethyl acetate.

2. Materials and methods

The solvents used in pervaporation experiments, ethanol (EtOH, 99.5% purity, ACS reagent) and isopropanol (IPA, 99.9% HPLC grade) were purchased from Acros Organics and ethyl acetate (EA, 99.9% HPLC grade) from Fisher Scientific. Hydrophilic microfiltration membrane from Millipore (polyvinylidene fluoride, 650 nm pore diameter and 125 μm thickness), was also used for diffusion experiments.

Two membranes were used in the pervaporation experiments and they were supplied by Compact Membrane Systems (CMS). Both membranes were made of amorphous perfluorinated polymer, CMS-3 on e-PTFE and the other consisted of CMS-3 (dense, selective layer) on polyacrylonitrile (PAN)/ polyester fabric as a support. The permeation through an amorphous polymer is controlled by diffusion and smaller molecules permeate more rapidly. Therefore, small molecules (e.g., water vapor, oxygen, nitrogen) rapidly permeate through CMS membranes but larger molecules such as solvent permeate at a much lower rate. CMS membranes have 33 to 36% free volume compared to 15-20% for other membranes, so they have much higher flux. As these membranes are made of perfluoropolymers, they are chemically stable.

The two membranes were examined (cross section and membrane surface) by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM), respectively. The membrane samples for TEM were prepared by sectioning with a diamond knife (slices of about 50 nm thickness). The TEM images for CMS-3 on e-PTFE are shown in Figure 1A (cross-section) and 1B (dense layer). It can be seen that the dense layer has an approximate thickness of 0.5 to 1 μm while the whole membrane thickness including the porous layer is about 10.5 μm . The e-PTFE support, with a nominal pore size of 50 nm was obtained from Pall Corporation. For the second membrane, CMS-3 on PAN, Figures 2 A, B, C and D show the SEM images of the entire membrane, dense layer (for two batches) and highly porous support. The thickness of the dense layer can be estimated in the range from 1.5 to 2.5 μm , whereas the PAN/polyester fabric supplied by Sepro (pore size in a range from 40 to 80 nm), has a thickness of approximately 300 μm .

The pervaporation experimental setup is shown in Figure 3. A water bath was used to heat the feed solution to the desired temperature (the heater had a thermostat and a thermometer immersed in the feed solution) and a centrifugal pump ensured the recirculation of the feed solution (about 5 cm^3/sec , laminar flow) through the cross flow membrane cell, and back in the feed container. At the feed side atmospheric pressure was kept and the pressure at the permeate side of the membrane cell was measured with a vacuum gauge. The collector tube was immersed in a salt and ice mixture (temperature was approximately -6°C) to condense the permeate, and a vacuum pump created low pressure at the permeate side of the membrane cell (typically 0.03-0.04 bar).

The membrane used in these experiments, had an external area (the membrane area in direct contact with the feed solution) of 65 cm^2 . Pervaporation runs varied for each experiment, depending on the membrane, feed temperature or water content in feed. Typically, at least 1 hour runs were conducted for CMS-3 on e PTFE and 30 minutes for CMS-3 on PAN. Material balance was applied for the volume of the liquid in feed and permeate before and after the pervaporation experiment; and the agreement was within 2%. Refractive index was used to determine the concentration of EtOH, IPA and ethyl acetate in water for both feed and permeate samples, using a Bausch and Lomb refractometer. The error in measurement with refractive index instrument was less than 1% (discrepancies occurred at the 3rd decimal).

Diffusion cell experiments were also conducted with the CMS-3 membranes, to determine solvent diffusivity coefficients through the membrane. The CMS-3 on PAN membrane (external area 4.5 cm²) was mounted in the tube connecting two chambers. The experimental setup is shown in Figure 4. A 1% wt. IPA or EtOH solution was put in one chamber (A) while an equal volume of pure water (B) was put in the other. Continuous stirring was applied in each chamber. Concentrations were taken every hour periodically and a TOC analysis was performed to measure solvent concentration on the (water) dilute side. The total length of these experiments was 5 hours. Because the solvent solutions are dilute, the permeate concentration of ethyl acetate as well as ethanol and IPA concentrations in diffusion experiments were measured by total organic carbon (TOC) analysis, using a TOC-5000A Shimadzu analyzer. Three replicates were taken for each measurement, and the error was <3%.

3. Results and Discussion

3.1. Solvent diffusion through the dense membrane

As mentioned previously, diffusion cell experiments were conducted to determine solvent diffusivity coefficients through the CMS-3 membrane. Diffusion rate from the diffusion cell was calculated using the steady diffusion across a thin film model:

$$D = \frac{1}{\beta t} \ln \left(\frac{C_{right}^0 - C_{left}^0}{C_{right} - C_{left}} \right) \quad (1)$$

where β is equal to: $\frac{A}{l} \left(\frac{1}{V_{right}} + \frac{1}{V_{left}} \right)$ and A , l , V and t are the area available to diffusion, film thickness, cell volume and time, respectively. C_{right}^0 , C_{left}^0 and C_{right} , C_{left} are the initial concentrations and the concentrations at the time t , in each chamber. The values for diffusivity coefficients for both solvents are shown in Table 1. It can be observed that the values are four orders of magnitude lower than the diffusivity in bulk solution at infinite dilution, and it is consistent with the diffusion coefficients dense membranes reported in literature [30,31]. For comparison, identical experiments were conducted using a very open (650 nm pore diameter) PVDF microfiltration membrane, and the diffusivity coefficients were close (same order of magnitude) to the values in bulk solution.

3.2. Pervaporation of binary water-alcohol mixtures

The parameters that are used to characterize a pervaporation process are the flux and separation characteristics. The most common way to define membrane separation characteristics in pervaporation is the separation factor, α and can be calculated by:

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

where y_A , y_B are the permeate and x_A , x_B are the feed concentrations of the components A and B in the mixture, A being the faster permeant (water). The flux for each component in the mixture is expressed in terms of kg/(m²)(h).

As mentioned previously, two membranes were used in pervaporation experiments, CMS-3 on e-PTFE and CMS-3 on PAN support and the membrane material is inert to either alcohol or solvent. The membrane is dense, as it can be seen from SEM and TEM imaging and based on diffusion coefficients for ethanol and IPA through the membrane. This membrane was also mounted in a steel cell, normally used for nanofiltration and reverse osmosis, filled

with deionized ultrafiltered water in the feed side and no water was permeated through the membrane even when applying a pressure of 13 bar.

It is believed that the water transport is based on solution-diffusion mechanism while the separation of the other species (solvent molecules) occurs primarily due to size exclusion, as the membrane material is inert to both water and solvent. The molecular size for the species used in the pervaporation experiments, water, EtOH, IPA and ethyl acetate are shown in Table 2. These values for the solvent molecular diameters are approximate, assuming the molecules as hard spheres, but are often used in literature.

3.2.1. CMS 3 on e-PTFE support—The pervaporation experiments for water-EtOH and water-IPA were conducted on this membrane at different temperatures and various feed compositions. The values for solvent and water fluxes as well as water/solvent separation factors for different systems are shown in Figures 5 and 6. As mentioned previously, the separation of species (in water/solvent mixtures) in this membrane (CMS-3) is based on high water transport rate and solvent exclusion primarily by size. The molecular size of IPA is greater than that of EtOH, as a consequence the flux of IPA is lower than the latter one. The flux of IPA is independent of the water flux, and for ethanol there is a slight flux increase with decreasing water flux. This shows no coupling for water-IPA system, otherwise the permeate IPA concentration (flux) would be significantly affected as the water activity is varied. For the case of EtOH, it is possible to form hydrogen bonding between ethanol and water and thus EtOH could be co-transported to the permeate side; anyway there is a small variation of EtOH flux over a broad range of water activities.

A small amount of alcohol could permeate through the membrane due to pore size distribution (or defects in the membrane). For both binary water-alcohol systems, this has a more significant impact on separation factor for the high water content in the feed solution. As a consequence for both water-EtOH and water-IPA mixtures, the separation factor decreases by an order of magnitude; from 34 to 4 and 81 to 10, respectively, when the water content is increased from 12 to 96 (92 for IPA) % wt. For an intermediate water concentration (56 % wt), the separation factor lies in between for both systems. This is also in agreement with the size exclusion principles and the separation factor for water-IPA is consistently greater than that for ethanol/water systems, under similar feed concentrations.

For simplicity, pervaporation can be described as two separate processes, vapor liquid equilibrium at the membrane interface, followed by vapor permeation through the membrane [35]. Thus a simple equation for the transport of species through the membrane can be derived, assuming no coupling between species and constant diffusion coefficient. This is very similar to gas permeation equations, the driving force being the difference in partial pressures at the feed and permeate sides of the membrane:

$$J_i = k_i (x_i \gamma_i p_{\text{vap},i}^s - p_{\text{perm},i}) \quad (3)$$

Where J_i , k_i , x_i , γ_i are the flux, permeance, molar fraction and activity coefficient respectively and $p_{\text{vap},i}^s$, $p_{\text{perm},i}$ are the saturated vapor pressure and the permeate side pressure for the species i . The permeance is defined as the permeability divided by the membrane thickness.

In order to determine the driving force, activities for both water-alcohol systems were calculated using UNIFAC method. The partial pressure at the permeate side was kept low (0.03-0.04 bar) and was considered negligible. From equation (3), there should be a linear relationship between water flux and driving force. The linear dependence of the water flux on driving force was observed for both solvent/water systems studied (only the data for

EtOH shown in Figure 7). The flux was normalized (dividing the water flux in water alcohol mixture by pure water flux at the corresponding temperature) in order to account for variations in thickness. For the data in Figure 7, the driving force (and the water flux) was changed by varying the feed composition (lower 3 points, x_{water} varied from 0.996 to 0.12 at 65 °C) and the temperature (85 and 90 °C, respectively and x_{water} of 0.56 for the upper two data points). The coefficient of the fit was 0.976 and thus, the correlation obtained can be used to predict the flux under different operating conditions (temperature, molar fraction in feed). For the water-IPA system the trend was also linear, but the slope was smaller, showing a lower permeance.

The permeance coefficients can be used to determine the membrane separation performance in terms of selectivity, defined as the ratio of the water and alcohol permeances (in the water-alcohol mixtures). The variation of the selectivity with the water-alcohol fraction in feed is shown in Figure 8. It can be observed that there is a little change in selectivity (as compared to separation factors, α) with increasing water fraction for each mixture and it is higher for the water-IPA than water-EtOH system. The permeance-based selectivity depends only on the intrinsic membrane properties and does not depend on the operating conditions, thus clarifying the contribution of the membrane on the separation performance. In order to distinguish between the effect of the membrane nature and operating conditions, it is preferred to report the membrane performance in terms of permeance (or permeability) and permeance-based selectivity over the flux and separation factor [36-38].

The effect of temperature on membrane performances in terms of flux and permeance was studied for water-EtOH (4:96 % wt) system. Consistent with the results published in literature, there is an Arrhenius type relationship between flux and temperature for both water and EtOH (Figure 9). The semi-log of flux vs. reciprocal temperature is linear and the slope was used to calculate the apparent activation energy for water and EtOH permeation flux through the membrane. The values were 11.6 and 15.0 kcal/mol, respectively. The activation energy for water, 11.6 kcal/mol, agrees well with the literature results for the pervaporation of the water-ethanol mixtures on other membranes such as ceramic [31] and lower than for many polymeric membranes (reported in the range from 20 to 56 kcal/mol) [39-41].

Similarly to the flux, there is an Arrhenius-type relationship between the permeance and temperature and using the semi-log plot (Figure 10) it is possible to calculate the apparent activation energy of the membrane permeance. Unlike the $\ln(\text{flux})$ vs. $1/T$ plot, there are 5 points (three different temperatures and three compositions for 65°C), and r^2 values of 0.93 and 0.91 for water and alcohol, respectively. It can be observed that there is a smaller variation of $\ln(\text{permeance})$ vs. $1/T$ as compared to $\ln(\text{flux})$ vs. $1/T$ and also that $\ln(\text{permeance})$ is not much affected by composition. As expected, the activation energies obtained from permeance are lower than those obtained from the flux data; for ethanol, the value is 5.4 kcal/mol and for water 0.6 kcal/mol, respectively. This trend is very similar with data published using polyvinyl alcohol (PVA) and zeolite-embedded composite PVA membranes, used for separation of water-ethanol mixtures [42]. In that study, it was shown that for the unmodified PVA membrane the apparent activation energies of the membrane permeance were 3.0 kcal/mol for water and 11.4 kcal/mol for EtOH. For various zeolite/PVA composite membranes these values were in range from 0.5 to 2.0 kcal/mol for water and 8.3 to 11.8 kcal/mol for EtOH, respectively.

Also, an insignificant dependence of permeance on temperature was observed also on other systems such as water-butanol [36]. It was suggested that this is due to both negative and positive effects of temperature on the activity coefficient (γ) and saturated vapor pressure which cancel each other's effect on permeance. Thermodynamically, the effect of

temperature is positive on diffusion and negative on sorption; this again minimizes its influence on permeance. To summarize, both selectivity and permeance are less dependent on the feed temperature (as compared to flux and separation factor), because these depend on the membrane intrinsic properties and not on the operating conditions.

A comparison of the permeate water concentration obtained in pervaporation of the water-ethanol mixture and VLE [43] is shown in Figure 11. There is a high water concentration in permeate for the entire feed composition range studied, showing the high selectivity of the membrane toward water permeation.

3.2.2. CMS-3 on PAN support—The membrane performance in terms of separation capability and flux were studied for water-EtOH and water-IPA binary mixtures, at different feed concentrations (in solvent dehydration range, solvent concentration greater than 88% wt.). The results for the pervaporation of the both water-alcohol mixtures on the CMS-3 on PAN membrane are shown in Figures 12 and 13. For 88% wt solvent, the separation factor is lower for both EtOH and IPA than for the membrane studied previously; however it should be observed that the flux is higher even at lower operating temperature (22 vs. 65-90 °C or higher).

Unlike previous membrane, these 1.5 μm membranes are supported on a backing made of PAN (polyacrylonitrile). The hydrophilic support may enhance the water transport. Due to high permeability, the majority of the pervaporation with CMS-3 on PAN membrane were conducted at room temperature.

As in the case of the previous membrane, according to size exclusion principles, the separation factor for water-IPA system is higher than for water-EtOH. It increases dramatically as the solvent concentration increases (water activity is reduced) and this also causes a significant reduction in flux. It can be observed that the solvent flux varies very little from 88% to 94% wt alcohol in feed (especially for IPA) and is significantly decreased at higher solvent concentration. As mentioned already, the water is mostly transported through the membrane so at high solvent concentration (low water content) the feed composition is changing and consists mostly of solvent.

The separation factor vs. total flux plot for the pervaporation of the ethanol/water mixture on two membrane batches, the same casting procedure was applied but the thickness varied (1.5 and 2.5 μm , respectively), shows an exponential relationship with a coefficient of fit of 0.97 (Figure 14). An increase in the membrane thickness will decrease the flux; as a consequence the pervaporation experiments for the thicker membrane (batch 2) were conducted at a higher temperature (60°C). At constant feed concentration, the separation factor was not significantly affected by temperature; thus for temperatures between 22 and 60 °C, the separation factor for the water-EtOH mixture (99% wt ethanol) had an average value of 349 with a standard deviation of 12%. This is different from other membrane systems where there is a solvent-membrane interaction (preferential transport). Thus, in the case where there is no swelling such as for ceramic membranes [44], the trend is that increasing the temperature also increases the separation factor (the fluxes of both components increase, but not to the same extent). For most polymeric membranes the trend is opposite (mainly due to swelling and plasticization of the membrane material) [10, 45]. For our case, the membrane is inert to both solutes and the trend is in between the 2 cases.

It is known that one major problem in pervaporation processes (such as in solvent dehydration) using hydrophilic membranes is swelling at high water concentration. As a consequence, the flux (and permeance) increases while the membrane separation performance decreases. For example, it was reported in literature [37] that the permeance for

a hydrophilic membrane (cross-linked polyvinyl alcohol) increased by an order of magnitude as the water content in feed (for various water-solvent mixtures) increased from 0.3 to 0.6 wt; this was associated with a severe decrease in selectivity. The swelling can be reduced by using supported polymeric membranes (such as PVA on ceramic support), where the swelling is suppressed by substrate matrix [11] or increasing the degree of cross-linking between polymer chains. However for the latter case, the flux is dramatically reduced [45], although it was shown that the incorporation of the hydrophilic moieties can increase the water flux [5].

For our case, due to hydrophobic nature of the CMS-3 membranes, the variation of the water activity does not affect the membrane properties (no swelling). As shown for IPA in Figure 15, the membrane permeance (obtained by dividing the membrane flux by the driving force) is constant over the entire range of water activities (inset shows the permeance at low water activities, dehydration area for EtOH/water systems). The last point in the graph for both ethanol and IPA shows a lower value for water permeance; as aforementioned, at this high solvent concentration, the feed composition is changing rapidly and no longer constant for higher water concentrations as the water is transported through the membrane. Permeances were used to calculate the membrane selectivity (the same way as for CMS 3 on e-PTFE). The selectivity was found to be independent on the feed concentration (0.88 to 0.96 wt fraction range) for both water-EtOH and water-IPA systems (plots not shown here), except for highest alcohol concentration (0.98 wt fraction) where the feed concentration changes rapidly as mentioned above. As a consequence, the selectivity is considerably higher (approx. 60) than that observed for 0.88 to 0.96 wt fraction range (approx. 15).

Similar to CMS 3 on e-PTFE membrane (Figure 7), there is a linear dependence of water flux on water driving force for water- EtOH systems (shown as normalized to the pure water flux) in Figure 16. Unlike previous case (broad concentration range), the water mole fraction varied from 0.03 to 0.26 (high solvent concentration only) for 22° C experiments. The driving force was also varied by changing the operating temperature 50° C and 60° C (at a water mole fraction of 0.03). A linear relationship is also obtained for water-IPA system (not shown here) and exhibited a lower permeance than the one for water-EtOH system.

To summarize, a comparison of the separation performance for CMS-3 membranes with selected literature values for various membrane systems (polymeric, polyelectrolyte, mixed matrix or zeolite) is shown in Table 3. It can be observed that CMS-3 has a higher flux (at room temperature) than most membranes at higher operating temperatures, although some of these membranes exhibit higher separation factors.

3.3. Pervaporation in ternary water-alcohol- ethyl acetate mixtures

In pharmaceutical industry and solvent dehydration area in particular, complex mixtures are often encountered, which may contain: water, alcohols, organic solvents, salt etc. In this study we investigated the effect of a tertiary component, ethyl acetate (EA) - an organic solvent very often used in pharmaceutical industry, on separation performances for water-EtOH and water-IPA systems.

Ethyl acetate is a larger molecule than both IPA and ethanol and has a solubility in water as high as 8.3 % wt. The pervaporation experiments were conducted on CMS-3 membrane, supported on PAN. Firstly, the pervaporation performances (temperature of 22 °C) for binary mixtures containing 4% and 8% wt EA in water were investigated. No EA was detected by refractive index measurements in the permeate side. A very small amount of organic compound in the permeate side was detected by TOC measurements (61 mg/L), however this amount is insignificant compared to the feed solution (40000 mg/L, corresponding to 8% wt EA in water) and it was considered negligible. This also shows that

the membrane pore size for CMS-3on PAN is about 0.49 nm (corresponding to the size of EA, completely rejected).

Next, the pervaporation results (at 22 °C) for ternary mixtures containing water-EtOH-EA (5% wt. EA and 10% wt. EtOH) and water-IPA-EA (5% wt. EA and 10% wt. IPA) were compared with binary water-ethanol and water-IPA. The separation factor for water-alcohol in presence of EA was close (within 13%) compared to that for binary water-ethanol and water-IPA mixtures. The total flux for ternary mixtures during pervaporation was also within 10% as compared to their corresponding binary mixtures (no EA). These results show that the presence of EA does not affect the water-alcohol separation and confirm once again that the primary mechanism for solvent separation is molecular sieving (size exclusion). Thus, these membranes constitute an interesting approach for purification of water-solvent mixtures based on their size, and high water transport rate.

Conclusions

A novel pervaporation membrane with high free volume for water transport and solvent exclusion was studied for water-solvent separations. The membrane shows a high mechanical, thermal and chemical stability and it can be operated at broad water/solvent compositions without swelling like in traditional polymeric membranes. The nature of the support plays an important role in membrane productivity (flux). These membranes have higher fluxes at the room temperature than most membranes reported in literature and operated at higher temperatures, and can be applied for separation of more complex mixtures based on differences in molecular size. The constant water permeance over a broad concentration range is a very important aspect of these types of membranes. The permeance-based selectivity for both water-EtOH, and water-IPA was found to be independent of composition.

Acknowledgments

This project has been supported by the NIH-SBIR program. Jason Wu (one of the co-authors) is a B.S. Chemical Engineering student at Purdue University.

References

1. Vane LM. A review of pervaporation for product recovery from biomass fermentation processes. *J. Chem. Technol. Biotechnol.* 2005; 80:603–629.
2. Slater CS, Schurmann T, McMillian J, Zimarowski A. Separation of diacetone alcohol-water mixtures by membrane pervaporation. *Sep. Sci. Technol.* 2006; 41:2733–2753.
3. Li G, Zhang W, Yang J, Wang X. Time-dependence of pervaporation performance for the separation of ethanol/water mixtures through poly(vinyl alcohol) membrane. *J. Colloid. Interf. Sci.* 2007; 306:337–344.
4. Yu YH, Kusumawardhana I, Lai JY, Liu YL. PTFE/polyamide thin-film composite membranes using PTFE films modified with ethylene diamine polymer and interfacial polymerization: Preparation and pervaporation application. *J. Coll. Interface Sci.* 2009; 336:260–267.
5. Zhang QG, Liu QL, Zhu AM, Xiong Y, Ren L. Pervaporation performance of quaternized poly(vinyl alcohol) and its crosslinked membranes for the dehydration of ethanol. *J. Membr. Sci.* 2009; 335:68–75.
6. Yang J, Yoshioka T, Tsuru T, M. Asaeda Pervaporation characteristics of aqueous-organic solutions with microporous SiO₂-ZrO₂ membranes: Experimental study on separation mechanism. *J. Membr. Sci.* 2006; 286:205–213.
7. Asghari M, Mohammadi T, Alamdari RF, Agend F. Thin-layer template-free polycrystalline modernite membranes on cylindrical mullite supports. *Micropor. Mesopor. Mat.* 2008; 114:148–154.

8. Ma Y, Wang JH, Tsuru T. Pervaporation of water/ethanol mixtures through microporous silica membranes. *Sep. Purific. Technol.* 2009; 66:479–485.
9. Yoshida W, Cohen Y. Ceramic-supported polymer membranes for pervaporation of binary organic/organic mixtures. *J. Membr. Sci.* 2003; 213:145–157.
10. Peters TA, Poeth CHS, Benes NE, Buijs HCWM, Vercauteren FF, Keurentjes JTF. Ceramic-supported thin PVA pervaporation membranes combining high flux and high selectivity; contradicting the flux-selectivity paradigm. *J. Membr. Sci.* 2006; 276:42–50.
11. Cao X, Zhang T, Nguyen QT, Zhang Y, Ping Z. A novel hydrophilic polymer-ceramic composite membrane 1 Acrylic acid grafting membrane. *J. Membr. Sci.* 2008; 312:15–22.
12. Kariduraganavar MY, Varghese JG, Choudhari SK, Olley RH. Organic-inorganic hybrid membranes: solving the trade-off phenomenon between permeation flux and selectivity. *Ind. Eng. Chem. Res.* 2009; 48:4002–4013.
13. Sullivan DM, Bruening ML. Ultrathin, cross-linked polyimide pervaporation membranes prepared from polyelectrolyte multilayers. *J. Membr. Sci.* 2005; 248:161–170.
14. Zhu Z, Feng X, Penlidis A. Layer-by-layer self-assembled polyelectrolyte membranes for solvent dehydration by pervaporation. *Mat. Sci. Eng., C: Biomimetic and Supramolecular Systems.* 2007; 27:612–619.
15. Chen Y, Xiangli F, Jin W, Xu N. Organic-inorganic composite pervaporation membranes prepared by self-assembly of polyelectrolyte multilayers on macroporous ceramic supports. *J. Membr. Sci.* 2007; 302:78–86.
16. Zhang G, Yan H, Ji S, Liu Z. Self-assembly of polyelectrolyte multilayer pervaporation membranes by a dynamic layer-by layer technique on a hydrolyzed polyacrylonitrile ultrafiltration membrane. *J. Membr. Sci.* 2007; 292:1–8.
17. Zhao Q, Qian JW, An QF, Yang Q, Zhang P. A facile route for fabricating novel polyelectrolyte complex membrane with high pervaporation performance in isopropanol dehydration. *J. Membr. Sci.* 2008; 320:8–12.
18. Shao P, Huang RYM. Polymeric membrane pervaporation. *J. Membr. Sci.* 2007; 287:162–179.
19. Chapman PD, Oliveira T, Livingston AG, Li K. Membranes for the dehydration of solvents by pervaporation. *J. Membr. Sci.* 2008; 318:5–37.
20. Wee SL, Tye CT, Bhatia S. Membrane separation process-Pervaporation through zeolite membrane. *Sep. Purific. Technol.* 2008; 63:500–516.
21. De Vos RM, Verweji H. High-selectivity, high-flux silica membranes for gas separation. *Science.* 1998; 279:1710–1711. [PubMed: 9497287]
22. Sekulic J, ten Elshof JE, Blank DHA. Selective pervaporation of water through a nonselective microporous titania membrane by a dynamically induced molecular sieving mechanism. *Langmuir.* 2005; 21:508–510. [PubMed: 15641814]
23. Bhat SD, Naidu BVK, Shanbhag GV, Halligudi GV, Sairam SB, Aminabhavi TM. Mesoporous molecular sieve (MCM-41)-filled sodium alginate hybrid nanocomposite membranes for pervaporation separation of water-isopropanol mixtures. *Sep. Purif. Technol.* 2006; 49:56–63.
24. Bhat SD, Mallikarjuna NN, Aminabhavi TM. Microporous alumino-phosphate (AlPO4-5) molecular sieve-loaded novel sodium alginate composite membranes for pervaporation dehydration of aqueous-organic mixtures near their azeotropic compositions. *J. Membr. Sci.* 2006; 282:473–483.
25. Bowser, J.; Majumdar, S. Perfluoropolymer membranes for gasoline vapor emissions reduction. Paper presented at the International Congress on Membranes and Membrane Processes; Honolulu, Hawaii, USA. July 2008;
26. Majumdar, S.; Kosaraju, P.; Nemser, S.; Farooq, K. Perfluorinated membrane dehydrator for industrial lubricant fluids. Paper presented at the Annual Meeting of the North American Membrane Society; Charleston, South Carolina, USA. June 2009;
27. Polyakov AM, Starannikova LE, Yampolskii Yu. P. Amorphous Teflons AF as organophilic pervaporation materials Transport of individual components. *J. Membr. Sci.* 2003; 216:241–256.
28. Polyakov AM, Starannikova LE, Yampolskii Yu. P. Amorphous Teflons AF as organophilic pervaporation materials Separation of mixtures of chloromethanes. *J. Membr. Sci.* 2004; 238:21–32.

29. Polyakov M, Bondarenko G, Tokarev A, Yampolskii Yu. P. Intermolecular interactions on target organophilic pervaporation through the films of amorphous Teflon AF2400. *J. Membr. Sci.* 2006; 277:108–119.
30. Shah D, Bhattacharyya DB, Ghorpade A, Magnum W. Pervaporation of pharmaceutical waste streams and synthetic mixtures using water selective membranes. *Environ. Progress.* 1999; 18:21–29.
31. Shah D, Kissick K, Ghorpade A, Hannah R, Bhattacharyya DB. Pervaporation of alcohol-water and formamide-water mixtures using hydrophilic zeolite NaA membranes: mechanisms and experimental results. *J. Membr. Sci.* 2000; 179:185–205.
32. Bowen TC, Noble RD, Falconer JL. Fundamentals and applications of pervaporation through zeolite membranes. *J. Membr. Sci.* 2004; 245:1–33.
33. Manjare SD, Ghoshal AK. Comparison of adsorption of ethyl acetate on activated carbon and molecular sieves 5A and 13X. *J. Chem. Eng. Data.* 2006; 51:1185–1189.
34. Van der Bruggen B, Schaep J, Wilms D, Vandecasteele C. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci.* 1999; 156:29–41.
35. Wijmans JG, Baker RW. The solution-diffusion model: a review. *J. Membr. Sci.* 1995; 107:1–21.
36. Guo WF, Chung TS, Matsuura T. Pervaporation study on the dehydration of aqueous butanol solutions: a comparison of flux vs. permeance, separation flux vs. selectivity. *J. Membr. Sci.* 2004; 245:199–210.
37. Delgado P, Sanz MT, Betran S. Pervaporation of the quaternary mixture present during esterification of lactic acid with ethanol. *J. Membr. Sci.* 2009; 332:113–120.
38. Baker RW, Wijmans JG, Huang Y. Permeability, permeance and selectivity: A preferred way of reporting pervaporation performance data. *J. Membr. Sci.* 2010; 348:346–352.
39. Burshe MC, Sawant SB, Joshi JB, Pangarkar VG. Sorption and permeation of binary water-alcohol systems through PVA membranes crosslinked with multifunctional crosslinking agents. *Sep. Purif. Technol.* 1997; 12:145–156.
40. Tu C-Y, Liu Y-L, Lee K-R, Lai J-Y. Hydrophilic surface-grafted poly (tetrafluoroethylene) membranes using in pervaporation dehydration process. *J. Membr. Sci.* 2006; 274:47–55.
41. Zhang W, Li GW, Fang YJ, Wang XP. Maleic anhydride surface-modification of crosslinked chitosan membrane and its pervaporation performance. *J. Membr. Sci.* 2007; 295:130.
42. Huang Z, Guan H-M, Tan WI, Qiao X-Y, Kulprathipanja S. Pervaporation study of aqueous ethanol solution through zeolite-incorporated multilayer poly(vinyl alcohol) membranes: Effect of zeolites. *J. Membr. Sci.* 2006; 276:260–271.
43. Al-Rub FAA, Banat FA, Jumah R. Vapor-liquid equilibrium of ethanol-water system in the presence of molecular sieves. *Sep. Sci. Technol.* 1999; 34:2355–2368.
44. Verkerk AW, van Male P, Vorstman MAG, Keurentjes JTF. Description of dehydration performance of amorphous silica pervaporation membranes. *J. Membr. Sci.* 2001; 193:227–238.
45. Shen J, Wu L, Qiu J, Gao C. Pervaporation separation of water/isopropanol mixtures through crosslinked carboxymethyl chitosan/polysulfone hollow-fiber composite membranes. *J. Appl. Pol. Sci.* 2007; 103:1959–1965.
46. Ruckenstein E, Liang L. Poly(acrylic acid)-poly(vinyl alcohol) semi- and interpenetrating polymer network pervaporation membranes. *J. Appl. Polym. Sci.* 1996; 62:973.
47. Gimenes ML, Liu L, Feng XS. Sericin/poly(vinyl alcohol) blend membranes for pervaporation separation of ethanol/water mixtures. *J. Membr. Sci.* 2007; 295:71.
48. Liu YL, Yu CH, Lee KR, Lai JY. Chitosan/poly(tetrafluoroethylene) composite membranes using in pervaporation dehydration processes. *J. Membr. Sci.* 2007; 287:230.
49. Huang RYM, Pal R, Moon GY. Pervaporation dehydration of aqueous ethanol and isopropanol mixtures through alginate/chitosan two plycompositemembranes supported by poly(vinylidene fluoride) porous membrane. *J. Membr. Sci.* 2000; 167:275.
50. Kurkuri MD, Toti US, Aminabhavi TM. Syntheses and characterization of blend membranes of sodium alginate and poly(vinyl alcohol) for the pervaporation separation of water + isopropanol mixtures. *J. Appl. Polym. Sci.* 2002; 86:3642.

51. Lee KR, Chen RY, Lai JY. Plasma deposition of vinyl acetate onto Nylon-4 membrane for pervaporation and evaporation separation of aqueous alcohol mixtures. *J. Membr. Sci.* 1992; 75:171.
52. Xu ZK, Dai QW, Liu ZM, Kou RQ, Xu YY. Microporous polypropylene hollow fiber membrane. Part 2. Pervaporation separation of water/ethanol mixtures by the poly(acrylic acid) grafted membranes. *J. Membr. Sci.* 2003; 214:71.
53. Sekulic J, Luiten MWJ, ten Elshof JE, Benes NE, Keizer K. Microporous silica and doped silica membrane for alcohol dehydration by pervaporation. *Desalination.* 2002; 148:19.
54. van Gemert RW, Cuperus FP. Newly developed ceramic membranes for dehydration and separation of organic mixtures by pervaporation. *J. Membr. Sci.* 1995; 105:287–291.
55. Tanaka K, Yoshikawa R, Ying C, Kita H, Okamoto KI. Application of zeolite membranes to esterification reactions. *Catal. Today.* 2001; 67:121–125.
56. Okumus E, Urkan TG, Yilmaz L. Effect of fabrication and process parameters on the morphology and performance of a PAN-based zeolite-filled pervaporation membrane. *J. Membr. Sci.* 2003; 223:23.

A) **B)**

Figure 1.
TEM imaging: A) cross-section and B) dense layer for CMS-3 on e-PTFE membrane

Figure 2.
SEM imaging: A) cross-section B) dense layer and C) back side of CMS-3/PAN membrane showing polyester support

- 1 – heating bath
- 2 – feed container
- 3 – thermometer
- 4 – centrifuge pump
- 5 – membrane cell
- 6 – vacuum gauge
- 7 – collecting tube
- 8 – cooling bath

Figure 3.
Experimental setup for the pervaporation system

Figure 4. Experimental setup for the solvent diffusion through the membranes A) 1% wt alcohol (IPA or EtOH) B) water

Figure 5.

Flux and separation factor variation with feed composition for the pervaporation of a water-EtOH mixture on CMS-3 on e-PTFE membrane (65 °C)

Figure 6.

Flux and separation factor variation with feed composition for the pervaporation of a water-IPA mixture on CMS-3 on e-PTFE membrane (75 °C)

Figure 7. Normalized water flux dependence on driving force for water-EtOH systems at various temperatures. (water wt. fraction varying from 0.12 to 0.96)

Figure 8.
Selectivity variation with feed composition for the pervaporation of water-IPA and water-EtOH mixtures on CMS-3 on e-PTFE membrane

Figure 9.
Semi-log plot of flux variation with reciprocal temperature for water-EtOH mixture separation

Figure 10. Semi-log plot of permeance variation with reciprocal temperature for water-EtOH mixture separation (0.04 wt. fraction EtOH)

Figure 11.
Comparison of the pervaporation performance and VLE for water-ethanol system at 1 atm

Figure 12. Flux and separation factor variation with feed composition for the pervaporation of a water-EtOH mixture on CMS-3 on PAN membrane (22 °C)

Figure 13.

Flux and separation factor variation with feed composition for the pervaporation of a water-IPA mixture on CMS-3 on PAN membrane (22 °C)

Figure 14. Variation of the separation factor vs. total flux for the pervaporation of water-EtOH mixtures, using two membrane batches (Inset: selectivity vs. temperature for water-ethanol mixture, 99% wt EtOH)

Figure 15.

Water permeance as a function of the feed composition for water-IPA and water-EtOH mixtures (flux divided by the driving force, expressed in bars)

Figure 16.

Normalized water flux dependence on driving force for water-EtOH systems at various temperatures. (x_{water} varying from 0.03 to 0.12)

Table 1

Solvent diffusivity coefficients in bulk and membrane media

System	Diffusivity Ethanol (cm ² /s)	Diffusivity IPA (cm ² /s)
bulk, infinite dilution	8.40×10^{-6}	8.70×10^{-6}
CMS-3	4.72×10^{-10}	1.05×10^{-10}
PVDF *	---	1.96×10^{-6}

* microfiltration membrane, 650 nm pore diameter, 125 μ m thickness

Table 2

Molecular size of the species used in pervaporation experiments (reference number in brackets)

Molecule	Molecular size (nm)
Water	0.296 [32]
EtOH	0.43 [32], 0.52 [34]
IPA	0.47 [32], 0.58 [34]
Ethyl Acetate	0.495 [33], 0.69 [34]

Table 3
Pervaporation performance in terms of total flux and separation factor (α) for various membrane systems

Membrane	Membrane Support	Binary Mixture (wt. % H ₂ O)	α	Flux (kg/m ² h)	T °C	Reference
PAA, PVA	PAA, PVA	EtOH/H ₂ O (5)	50	0.26	50	[46]
Sericin	Sericin	EtOH/H ₂ O (10)	90	0.07	60	[47]
PVA	PVA	EtOH/H ₂ O (10)	115	0.12	60	[47]
Sericin/PVA (50:50)	Sericin/PVA 50:50)	EtOH/H ₂ O (10)	130	0.07	60	[47]
Chitosan	Chitosan	EtOH/H ₂ O (10)	127	0.201	50	[41]
PAN	Layer by layer assembly	IPA/H ₂ O (9)	495	1.8	70	[14]
Alumina	Layer by layer assembly	IPA/H ₂ O (10)	6100	2.0	50	[13]
PSSA-g-PTFE/Chitosan	PTFE	IPA/H ₂ O (10)	1490	0.409	25	[48]
Alginate	PVDF, Chitosan	EtOH/H ₂ O (4)	90	0.172	50	[49]
Na-Alg	Na-Alg	IPA/H ₂ O (10)	356	0.012	30	[50]
Nylon-4/PVA	Nylon-4	EtOH/H ₂ O (10)	13.5	0.42	25	[51]
PAA	Polypropylene	EtOH/H ₂ O (10)	4.9	0.175	24	[52]
Silica	α -Alumina	IPA/H ₂ O (10)	73	0.65	80	[53]
Zeolite	γ -Alumina	EtOH/H ₂ O (5)	1633	0.2	79	[54]
Zeolite-X	α -Alumina	EtOH/H ₂ O (10)	360	0.89	75	[55]
PAN	PAN	EtOH/H ₂ O (8)	281	0.007	50	[56]
CMS-3	PAN	EtOH/H ₂ O (9.4)	33	0.92	22	This Work
CMS-3	PAN	IPA/H ₂ O (9.4)	51	0.66	22	This Work
CMS-3	PAN	EtOH/H ₂ O (1.3)	319	0.15	22	This Work
CMS-3	PAN	EtOH/H ₂ O (1.3)	387	1.65	50	This Work
CMS-3	PAN	IPA/H ₂ O (1.3)	500	0.05	22	This Work
CMS-3	e-PTFE	IPA/H ₂ O (12.4)	81	0.111	70	This Work