Ethanol Dehydration Using Hydrophobic and Hydrophilic Polymer Membranes

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This paper describes the development of membranes based on perfluoro polymers for the separation of aqueous ethanol mixtures in pervaporation or vapor permeation mode. Hydrophobic perfluoro polymers were selected because their chemical and thermal stability allows them to be used at temperatures up to 130 °C in hot ethanol/water vapors. The permeance and selectivity of membranes made from these polymers are quite different from the properties of the cross-linked hydrophilic membranes that are commonly used to separate water/ethanol mixtures. Perfluoro polymers absorb less than 1% liquid in mixtures ranging from pure water to pure ethanol. As a result, the water permeance and water/ethanol selectivity of the membranes are essentially independent of feed water/ethanol composition. However, the water permeances of perfluoro membranes are low for commercial applications. Multilayer composite membranes, consisting of a perfluoro protective layer and a selective hydrophilic polymer underlayer, have the stability of hydrophobic perfluoro membranes combined with the high permeances and good selectivities of hydrophilic membranes.

1. Introduction

In an earlier paper, we described a low-energy distillation-membrane permeation process for separating aqueous mixtures.[1] The process is expected to be particularly useful for the separation of bioethanol in the next generation of cellulose-to-biofuels plants. More than 500 of these plants will be built if the U.S. Department of Energy Biofuels Program is to meet its 2022 production targets.[2]

In this process, illustrated in Figure 1 for cellulose-to-ethanol production, a low concentration ethanol beer stream (①) is sent to a stripper column operated at 0.5 bar. This stripper produces an ethanol-free bottoms and an overhead vapor (②) at a pressure of 0.5 bar containing 50 wt % ethanol. This vapor is then compressed to 3 bar. Compression increases the temperature of the vapor and a heat exchanger (not shown) integrated with the reboiler is used to cool this vapor to about 130 °C (about 5 °C above the dew point). The compressed gas is then sent to a two-step membrane separation unit. The first membrane unit lowers the water content of the overhead vapor from 50 wt % (②) to ~10 wt % water in the residue stream (③). The permeate vapor from this unit (④) has a high water concentration (91 wt % water) and contains the bulk of the water content of the overhead vapor. This water vapor is recycled back to the stripping column, recovering all of its latent heat content. The remaining water in the residue stream of the first membrane unit (③) is removed by a second membrane unit. This unit lowers the water concentration from ~10 wt % to 0.3 wt % water. Because the vapor being treated by this unit has a lower average water concentration, the permeate (⑤) contains less water and more ethanol. This stream is condensed and remixed with the feed stream (①). The dry ethanol residue vapor stream produced by the second membrane unit (⑥) is condensed in the stripper column reboiler to recover its latent heat content. The total energy used is less than half the energy required for a conventional distillation-molecular sieve process.

This paper describes the development of membranes suitable for the process shown in Figure 1. To be successful in this application, membranes must meet several requirements.
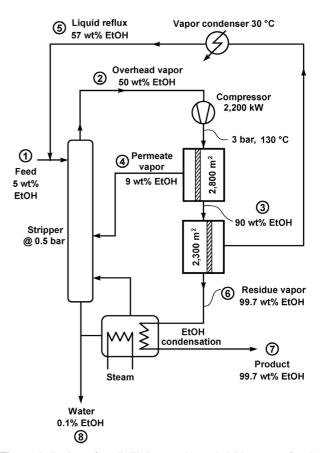

Figure 1. Design of a distillation-membrane hybrid process for the separation of a 220 000 kg/h ethanol/water mixture from cellulose fermentation broth (equivalent to 30 million gal/y of ethanol production). The membrane used has a water permeance of 2000 gpu and an ethanol permeance of 50 gpu. The assumed efficiency of the compressor is 75%. A simple stripper column is used in this design (no rectification section).

- The membranes should be stable in ethanol/water mixtures at the operating temperature of the process; that is, temperatures up to 130 °C.
- The membranes should have useful permeances *and* selectivities over the full range of feed water vapor concentration expected; that is, 50 wt % water to <1 wt % water.

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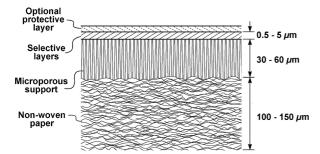
Figure 2. Schematic cross-section of the multilayer composite membrane.

- Economical methods of packaging membranes into membrane modules must be developed. Even when high permeance membranes are used, several thousand m² of membrane will be needed for a full scale bioethanol plant.

Only the first two issues will be discussed in this paper. The third requirement is related to the membrane module design and will be described in a later paper, together with the field test results.

A number of existing membranes could be considered for this application; each has its own benefits and disadvantages.[3]

- Composite membranes with hydrophilic selective layers made from cross-linked cellulose esters or poly(vinyl alcohol).[3−7] Such membranes have been used for commercial dehydration applications and have good selectivities and high permeances. They suffer from two problems: (i) swelling of the membrane at high water concentrations, which reduces membrane selectivity; and (ii) slow degradation at temperatures above ∼100 °C.
- Ceramic and zeolite membranes.[8,9] When first introduced, these membranes had stability problems, but they are now reported to have excellent water/ethanol selectivities and high permeances at temperatures of 130 °C or more. The remaining issue is the high cost; significant cost reductions will be needed to bring these membranes into commercial use.
- Polyimide integral asymmetric (Loeb−Sourirajan)-type membranes, usually formed into hollow fine fibers.[10,11] These membranes are reported to have good temperature stability, adequate permeances, and good water/ethanol selectivities. However, condensation of vapor onto the membrane surface must be avoided to prevent membrane degradation; such condensation is difficult to avoid in industrial systems.

In our work, we tried to combine and improve performance and stability benefits without introducing new disadvantages. The approach, as described in this paper, was to develop multilayer composites of the type shown schematically in Figure 2. Composite membranes have the advantage that each layer can be separately selected to satisfy the function it must perform. The nonwoven paper provides the mechanical strength of the membrane. This paper is too coarse to be directly coated with the thin selective layer, so the paper is overcoated with a microporous ultrafiltration support membrane. The top surface of this membrane is finely microporous with pore diameters in the range of 100−500 Å. One or more selective layers can then be coated onto this support. For this application, all of these membrane components must be stable in hot ethanol/water mixtures at 130 °C.

The need for chemical stability was an important driver in our search for an appropriate selective material. Our company has been developing perfluoropolymer (PFP) membranes for separation of natural gas and petrochemical hydrocarbon-

containing gas streams for a number of years.[12,13] The structures of some of these Teflon-like polymers are shown in Figure 3. These polymers are inert and completely stable at temperatures up to 130 °C or more. They are amorphous glassy materials with glass transition temperatures in the range of 100−250 °C. The polymers have a combination of good mechanical properties, superior thermal stability (thermal decomposition temperatures: 300−400 °C), and robust chemical resistance. Perfluorinated polymers are insoluble in all solvents except a few perfluoro compounds and are unaffected by acids and alkalis; fuels and oils; low-molecular-weight esters, ethers, and ketones; aliphatic and aromatic amines; strong oxidizing substances; and other chemicals. Because of their perfluoro nature, the PFP membranes do not swell in water or ethanol. Nonetheless, PFP membranes are surprisingly permeable to water.

2. Membrane Characterization

2.1. Theoretical Basis. In this paper, membrane performance is quantified in terms of membrane permeance and selectivity using the solution-diffusion equation.[14,15]

$$j_i = \frac{P_i}{L}(p_{i_o} - p_{i_L}) \tag{1}$$

where j_i is the molar flux (cm³(STP)/cm²·s), L is the membrane thickness, p_{i_o} and p_{i_L} are the partial vapor pressures of component i on either side of the membrane, and P_i is the permeability of the membrane material, usually expressed in Barrer (1×10^{-10} cm³(STP)·cm/cm²·s·cmHg). This equation describes both gas permeation (where p_{i_o} and p_{i_L} are the gas phase partial pressures) and pervaporation (where p_{i_o} is the feed vapor pressure of component i in equilibrium with the feed liquid).

Because the thickness of the selective layer in composite membranes is difficult to measure, membrane permeation rates are normally reported as permeances (pressure-normalized fluxes) expressed as

$$\frac{P_i}{L} = \frac{j_i}{p_{i_o} - p_{i_L}} \tag{2}$$

where the permeance P_i/L is expressed in gas permeation units or gpu (1×10^{-6} cm³(STP)/cm²·s·cmHg).

The membrane separation performance is given as the ratio of the permeances of components i and j:

$$\alpha_{ij} = \frac{P_i/L}{P_j/L} = \frac{P_i}{P_j} \tag{3}$$

where α_{ij} is the selectivity of the membrane for component i over component j.

The permeance and selectivity as described above are intrinsic properties of the separation membranes and are universally used to describe permeation through gas separation membranes. This paper reports pervaporation and vapor permeation separation measurement in this form. We prefer to report data as permeances and selectivities because these terms are normalized for driving force, and so results obtained at different conditions or driving forces can be compared. This procedure also allows pervaporation and vapor permeation data to be compared from different studies.

The membrane application shown in Figure 1 uses vapor permeation. Nonetheless, in the early portion of our membrane development program, membranes were characterized by their pervaporation performance. We did this because pervaporation
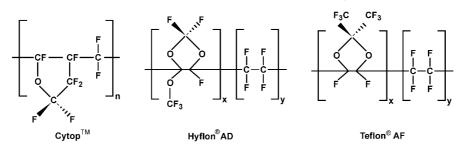
Figure 3. Chemical structures of the perfluoro polymers Cytop, Hyflon AD, and Teflon AF.
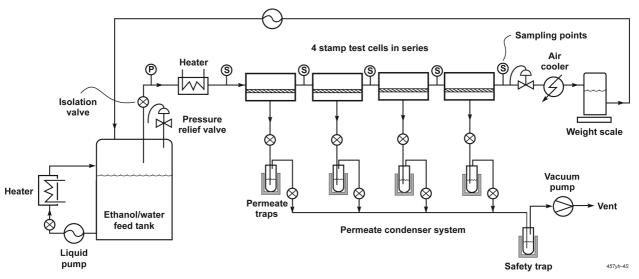

Figure 4. Diagram of the test apparatus for measuring ethanol/water vapor permeation performance through thin composite membranes.

experiments are much easier to perform than vapor permeation experiments and the results are generally more reliable. In principle, there should be no difference in permeability data obtained using the two techniques.[14] We found this was true for membrane stamp data, as the results reported in Section 3.3. show.

2.2. Experimental Measurements: Pervaporation and Vapor Permeation. 2.2.1. Pervaporation. Laboratory pervaporation stamp measurements were performed using a flow-through test cell and a liquid nitrogen-cooled permeate collection system using two switchable traps. This apparatus has been described in many papers[5,7,16,17] and is not covered again here.
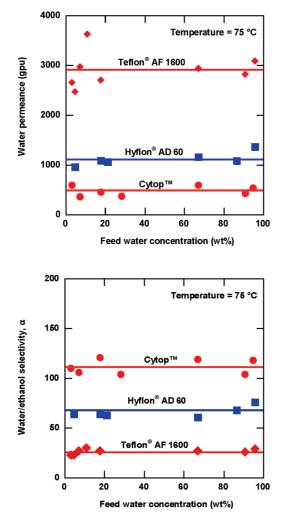
2.2.2. Vapor Permeation. The apparatus we used for vapor permeation membrane stamp tests is shown schematically in Figure 4. Four test cells were connected in series. The feed tank containing 10−15 L of solution was heated to 100−120 °C with a circulation pump and heater. The pressurized feed vapor produced then passed through the test cells. The feed vapor flow rate was controlled by the energy delivered to the heater which determined how much liquid was evaporated. The temperature of the boiling liquid and hence the vapor pressure of the vapors leaving the tank was regulated by the pressure control valve on the residue stream leaving the last test cell. A superheater was installed just before the first membrane test cell to provide 5−10 °C superheating of the feed vapor. As this superheated vapor passed through the test cells, its temperature was maintained by heat tracing the test cells. A vacuum pump was used to create a vacuum of less than 1 Torr on the permeate side of the membrane samples.
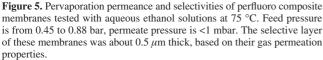
At the start of each membrane test, the feed tank was isolated from the test cells and was preheated to the desired temperature through a liquid circulation pump and a heater. The isolation valve was then opened and hot feed vapor began to pass through

the four test cells. During startup, liquid nitrogen was only added to the safety trap in front of the vacuum pump. It generally took 2−3 h to bring the test system to a uniform temperature. When the system was judged to have reached steady state, liquid nitrogen was added to the four permeate traps and permeate collection began. The mass of permeate collected over 30−120 min was measured and the permeate composition was determined by gas chromatography. At the same time, the residue vapor stream was condensed and its flow rate was calculated from the residue condensate weight per unit time. The condensed residue was recirculated back to the feed tank at the end of the experiment. Five sampling points (shown in the figure) were used for taking samples of the feed vapor with a syringe to measure the feed composition of each membrane sample. The vapor samples condensed inside the cold syringe and were analyzed using gas chromatography.

Using the feed composition measured for each membrane sample, the measured saturation vapor pressure, permeate composition and permeate flow rate, membrane permeance, and membrane selectivity were calculated using eqs 2 and 3.

3. Results

3.1. Pervaporation Tests. 3.1.1. Hydrophobic Perfluoro Membranes. An initial series of tests was used to characterize the three perfluoro polymers shown in Figure 3. Composite membranes were prepared from each polymer in the same way and nitrogen permeation measurements showed the perfluoro layer of each membrane to be about 0.5 μm thick. A systematic set of pervaporation experiments with ethanol/water mixtures was performed with all three PFP membranes. The experiments were conducted at 75 °C with ethanol/water mixtures varying over the full range of water concentration from 0 to 100%. The

Figure 5. Pervaporation permeance and selectivities of perfluoro composite membranes tested with aqueous ethanol solutions at 75 °C. Feed pressure is from 0.45 to 0.88 bar, permeate pressure is <1 mbar. The selective layer of these membranes was about 0.5 μm thick, based on their gas permeation properties.

Figure 6. Effect of feed water concentration on pervaporation permeance and selectivity of a commercial hydrophilic cellulose ester membrane with water/ethanol mixtures (75 °C, permeate pressure of 5 mbar).

data in Figure 5 show that the pervaporation performance is independent of the feed water concentration over the entire test range. This is probably due to the very low water and ethanol sorption (<1%) of the perfluoro materials. Nonetheless, the membranes are surprisingly water permeable. At 75 °C, the average water permeances for Cytop, Hyflon AD, and Teflon AF membranes are 500, 1100, and 2900 gpu, respectively, with corresponding average water/ethanol selectivity of 110, 70, and 27. This pervaporation performance mirrors what we have seen with gas mixtures.[13] Cytop (Asahi Glass, $T_g - \sim 105$ °C) is the most selective but least permeable material. Teflon AF (DuPont, $T_g - 160-240$ °C) has the highest free volume and highest permeability, but the lowest selectivity. Hyflon AD (Solvay Solexis, $T_g - 130$ °C) is somewhere in between. Based on these separation performance and the T_g values, we focused most of our perfluoro membrane development work on Hyflon AD membranes.

The permeance and selectivity data in Figure 5 are in sharp contrast to the data usually reported for hydrophilic membranes in the literature. By way of example, Figure 6 shows water/ethanol pervaporation data for a commercial cellulose ester membrane measured in our laboratory under the same conditions. The cellulose ester membrane permeance and selectivity are very concentration dependent. At low water concentrations in the feed, the membrane is extremely selective. As the water
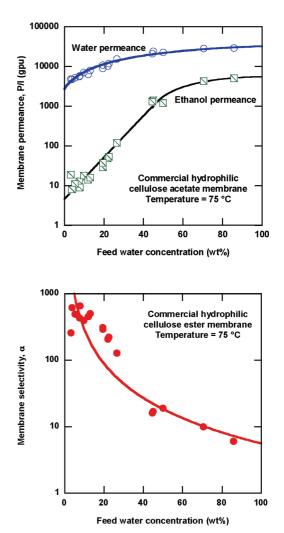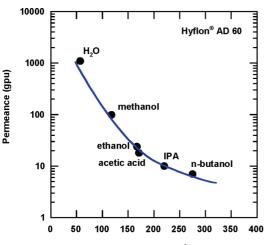
concentration increases, the ethanol and water permeances both increase. This increase is probably due to swelling of the membrane by water, leading to plasticization. Plasticization increases the water permeance from 5000 gpu at less than 5 wt % water to 32 000 gpu at 100 wt % water, a 6-fold increase, but has a much larger effect on ethanol permeance, which increases from less than 10 gpu at less than 5 wt % water to more than 6000 gpu at 100 wt % water, an almost 600-fold increase. As a consequence, the water/ethanol selectivity falls to only 5 at very high water concentrations.

The PFP membranes can also be used for separation of other water/solvent mixtures, such as water/isopropanol, water/butanol, and water/acetic acid. Figure 7 shows data obtained in screening pervaporation experiments at 75 °C with composite Hyflon AD membranes for various water/solvent binary mixtures. Solvent permeance decreases as the critical volume (a measure of molecular size) of the penetrant increases. This indicates that permeation of these compounds through the Hyflon AD membrane is largely diffusion controlled. Based on these results, the water/solvent selectivity of the Hyflon AD membrane for all mixtures except water/methanol is more than 40. This selectivity is low compared to that of hydrophilic membranes, but the ability of the Hyflon AD membrane to separate the mixtures over the entire range of water concentrations is remarkable. This makes PFP membranes an ideal choice for separating hot, dilute aqueous solutions. The ability of PFP membranes to handle harsh chemical environments, for example

Figure 7. Permeance of a Hyflon AD 60 composite membrane when tested with 5−10 wt % organic solvent/water mixtures in pervaporation experiments at 75 °C.
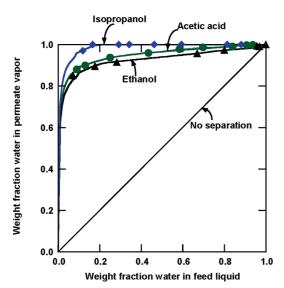

Figure 8. Pervaporation performance of Hyflon AD 60 membranes with water/isopropanol, water/ethanol/ and water/acetic acid mixtures. The water permeances were in the range of 1000−2000 gpu at all feed water concentrations (75 °C, permeate pressure of <5 mbar).

Figure 9. Water/ethanol pervaporation performance of a pure hydrophilic cellulose ester membrane, a perfluoro (Hyflon AD 60) membrane, and a multilayer perfluoro-coated cellulose ester membrane (75 °C, permeate pressure <1 mbar).

mixtures containing 80−100% acetic acid, also opens up the possibility of a number of other applications.

Figure 8 plots the permeate water concentration versus feed water concentration for ethanol, isopropanol, and acetic acid dehydration experiments with the Hyflon AD membranes. For these three solvents, the order of selectivity is water/isopropanol selectivity > water/acetic acid selectivity > water/ethanol selectivity. As a consequence, membranes produce the most water in the permeate from a water/isopropanol mixture, and the least water in the permeate from a water/ethanol mixture, regardless of the feed water concentration. In all cases, however, the permeate water concentrations are higher than 80 wt % at feed water concentrations more than 10 wt %, further demonstrating the ability of the membranes to function well in water-rich environments.

3.1.2. Perfluoro-Coated Hydrophilic Membranes. Neither the PFP membranes (data shown in Figure 5) nor the hydrophilic cellulose ester membranes (data shown in Figure 6) had all the permeation properties required for our process. The hydrophilic membranes had high permeances, but selectivity dropped to unacceptable levels at feed water concentrations above 20 wt
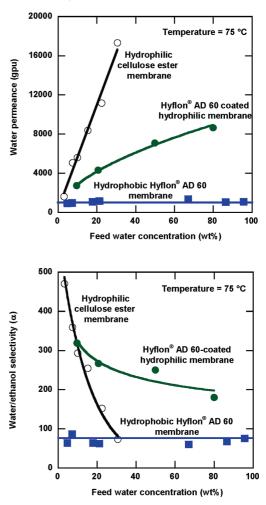
%. The perfluoro membranes maintained constant selectivities and permeances at all feed water concentrations, but the permeances were on the low end of what is needed for a commercial process. To combine the positive attributes of each membrane, we prepared multilayer membranes in which a very thin perfluoro polymer protective coating was applied as a top coat to the hydrophilic cellulose ester membrane. This combination gives performance that is improved over both individual membranes, as shown in Figure 9.

The perfluoro coating layer could be made extremely thin because the cellulose ester membrane provided a smooth, defect-free support surface. As a consequence, the water permeance of the coated membranes was lower than that of the uncoated hydrophilic membrane, but much higher than that of the thicker pure PFP membrane. More importantly, the coated membrane maintained a high selectivity at all feed water concentrations. At high feed water concentrations, the membrane had a higher selectivity than either of the component layers alone. The perfluoro layer protects the hydrophilic layer from direct contact with high concentrations of water, thereby controlling plasticization of the hydrophilic layer by sorbed water and enabling the selective properties of the layer to be maintained.

3.2. Vapor Permeation Tests. We attempted to use the best membranes from the pervaporation tests in vapor permeation experiments, but a number of problems developed. Our pervaporation tests were run at temperatures of 75−100 °C. Vapor permeation operating temperatures were higher, generally
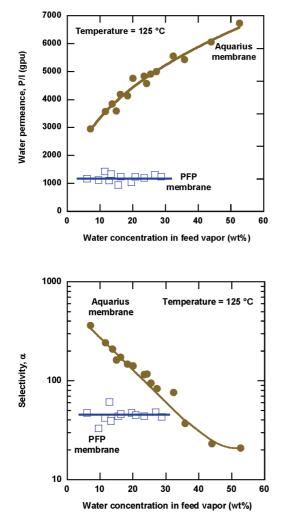
Figure 10. Comparison of ethanol/water membrane vapor permeation separation data obtained at 125 °C with an Aquarius membrane (•) and a PFP membrane (□). Feed pressure is from 3.1 to 3.6 bar, permeate pressure is <50 mbar.

Figure 11. Experimental pervaporation and vapor permeation stamp test data obtained with water/ethanol mixtures. Membrane stamps cut from the same membrane roll were tested at 110 °C. The membrane selectivity was in the 100−200 range for all the experiments shown.

110−130 °C. The extra 30 °C surfaced a number of membrane stability and permeance issues, and considerable reformulation was required to make a stable membrane. The resulting membrane is now designated Aquarius. Data comparing the properties of an Aquarius membrane and a Hyflon AD membrane are shown in Figure 10. The Aquarius membrane shows the higher water permeance: about 2000 gpu at water concentrations below 10 wt % and more than 6000 gpu at water concentrations above 50 wt %. These permeance values are high compared to values reported in the literature for other membranes. With the increase in feed water concentration, the permeance of the Aquarius membrane increases, but the water/ethanol selectivity decreases. Nonetheless, the selectivity is adequate for the separations needed, even when the membrane is operating at temperatures up to 120−130 °C with feed vapors containing up to 50 wt % water.

The vapor permeation results shown in Figure 10 were measured on the same membranes using the apparatus shown in Figure 4; these tests were conducted from low water concentrations to high water concentrations lasting for about three weeks. At the end of these tests, the membranes were retested at low water concentrations; no significant changes in permeance or selectivity had occurred. In subsequent tests, the same membranes were repeatedly tested at the same conditions (125 °C, ~20 wt % water feed vapor) over a period of three weeks. Again, no significant change in performance from the
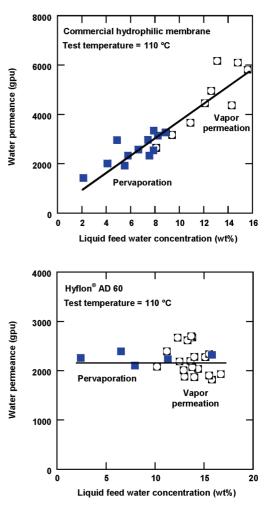
first to the last test was observed. We concluded that the Aquarius membrane and the PFP membrane have no short-term stability issues.

3.3. Comparison of Pervaporation and Vapor Permeation Results. In principle, there should be no difference in permeability data obtained from pervaporation tests and vapor permeation tests. However, this concept has been challenged in the past. Because we were using the same membrane for pervaporation and vapor permeation experiments, we were able to make a valid comparison between the two operating modes. The results of pervaporation and vapor permeation stamp test conducted at the same test temperature (110 °C) are compared in Figure 11. The figure summarizes water permeances of a commercial hydrophilic cellulose ester membrane and a PFP membrane at different feed water concentrations. The water concentration in each of the pervaporation tests was the measured feed water composition. The liquid water concentration in the vapor permeation tests was calculated from the measured feed vapor composition and the known vapor−liquid equilibrium diagram at 110 °C. Figure 11 results show that the two sets of pervaporation and vapor permeation data for each membrane fall (with some scatter) on the same general line. We conclude that solution-diffusion [and the related eqs 1 and 2] can be relied upon as an accurate model of membrane transport in pervaporation and vapor permeation.

4. Conclusions

A number of companies are developing vapor permeation membranes for separation of aqueous ethanol mixtures as an alternative to conventional distillation-molecular sieve technology. The energy used to perform the separation by conventional technology is a significant fraction of the energy content of the bioethanol produced. Membrane technology described in an earlier paper[1] is expected to cut this energy use in half. The membranes needed for this separation must be able to operate at temperatures up to 130 °C, in the presence of ethanol/water vapor mixtures with high water concentrations. These conditions are outside the normal operating range of current pervaporation and vapor permeation membranes. In this paper, we described the development of hydrophobic perfluoro membranes, perfluoro-coated hydrophilic membranes and hydrophilic Aquarius membranes for aqueous ethanol separations. These membranes show good thermal and chemical stability as well as good separation performance for ethanol/water mixtures in laboratory tests. The membranes have now been packaged into spiral-wound membrane modules, and the first field trials are under way. The module laboratory and field test results will be described in a later paper.

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