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Polyaniline Membranes for Pervaporation of Carboxylic Acids and Water

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ABSTRACT: Free-standing polyaniline films are studied as pervaporation membranes for separating carboxylic acid/water mixtures. Changing polyaniline membranes from an undoped to a fully doped state has a dramatic effect on their selectivity. For example, with a 52 wt % acetic acid/48 wt % water feed, the undoped, base form of polyaniline leads to only a relatively modest separation of water (68 wt % water in permeate; $\alpha_{H_2O} = 2.4$), while the doped, acid form of polyaniline shows a remarkably enhanced separation ability (>99 wt % water in permeate; $\alpha_{H_2O} > 1300$). The improved selectivity of doped polyaniline is due in part to the hydrophilicity induced in the polymer by the acid dopants. Fully doped polyaniline appears to restrict the permeation of carboxylic acids mainly based on their effective sizes. Whereas formic acid (solvated diameter = 3.5 Å) can permeate through a doped polyaniline membrane, the larger acetic acid (4.5 Å) has an exceedingly low rate of permeation, and the even larger propionic acid (5.5 Å) is virtually excluded. Pervaporation of a mixture of all three carboxylic acids and water confirms that acetic and propionic acid are effectively blocked by doped polyaniline. The compositions of all feed and permeate mixtures were determined by ^{1}H NMR, which was found to be a very accurate method for quantitative analysis. Although the permeation rates of acetic acid/water feeds through dense, as-cast polyaniline membranes (~80 μm thick) are relatively low (2−13 g/(m^2 h)), a 2-fold or more increase in the permeation rate can be obtained by using asymmetric membranes of approximately the same overall thickness. Increasing the temperature of the pervaporation experiment can also lead to large increases in permeation rate. For example, the permeation rates of 50 wt % acetic acid/50 wt % water feeds through doped polyaniline membranes double on going from room temperature to 85 °C.

Introduction

Membrane separation processes can be divided into several categories according to the pore sizes of the membranes, i.e., conventional filtration (10−100 μm), microfiltration (0.1−10 μm), ultrafiltration (50−1000 Å), and the processes of reverse osmosis, gas separation, and pervaporation (<50 Å).[1−3] In pervaporation, a liquid mixture is placed on the upstream side of a membrane, while the downstream side is either evacuated or swept by a gas flow to produce a driving force. This force causes the liquid(s) from the upstream side to permeate through the membrane to the downstream side, where the liquid desorbs from the membrane in the form of a vapor. The vapor is then condensed in a cold trap, or swept away by a flowing gas, to maintain a low vapor pressure on the downstream side.

Separation systems utilizing membranes are of great value for developing more energy-efficient technologies. Traditional liquid separations by distillation can be energy-consuming when dealing with close-boiling-point mixtures or impossible when dealing with azeotropes. Pervaporation, on the other hand, can be used for separating azeotropes and close-boiling-point mixtures. Due to the potential energy savings, the Department of Energy (DOE) has ranked pervaporation as a top research priority.[1]

Different liquids permeate through membranes at different rates, which can lead to the separation of a liquid component from a mixture. The separation characteristics strongly depend on the chemical properties of the membrane. For example, both hydrophilic and hydrophobic membranes have been investigated for separation of acetic acid/water mixtures. Hydrophilic membranes, including poly(vinyl alcohol),[4] silica,[5] and graft poly(acrylic acid)/nylon 6[6] are water permselective. On the other hand, many hydrophobic membranes, such as poly(dimethylsiloxane)[7] and polybutadiene[8] are acetic acid selective, although some hydrophobic membranes, such as poly(1-butyl methacrylate) and poly(2-ethylhexyl acrylate)[9] are water selective. Among those membranes tested at approximately room temperature, poly(sodium acrylate)/poly(divinylbenzene) has the highest permeation rate (1.3 kg/(m^2 h) for 50% acetic acid/50% water, at 30 °C),[10] while graft poly(acrylic acid)/nylon 6 has the highest separation factor ($\alpha_{H_2O} = 300$ for 50.1% acetic acid/49.9% water, at 15 °C)[6] reported for acetic acid/water feed mixtures (see Table 1).[4−18]

There is a strong demand for separating acetic acid from aqueous solutions, since acetic acid is one of the top 50 chemicals (number 33 in 1995)[19] produced in the U.S. Acetic acid is an important chemical intermediate in the syntheses of vinyl acetate, terephthalic acid, cellulose ester, and other esters. In the past decade, there have been many reports on utilizing membrane pervaporation systems to separate acetic acid/water mixtures (Table 1).[4−18]

Conjugated polymers form a new class of membrane materials whose properties, such as permselectivity, can be tailored *after* membrane formation through the doping/undoping process.[20] Investigations utilizing conjugated polymers as membranes to separate various liquid or ion mixtures have been reported.[21−24] Poly(3-methylthiophene) and poly(*N*-methylpyrrole) membranes were used for the separation of acetone/water, 2-butanol/water, and 2-butanol/heptane mixtures.[21] Doping poly(3-methylthiophene) with perchlorate ions led to a greater than 2-fold increase in the permeation rate of acetone (from ~70 to ~180 mL/min). However, the

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Table 1. Pervaporation of Acetic Acid/Water Mixtures through Selected Membranes

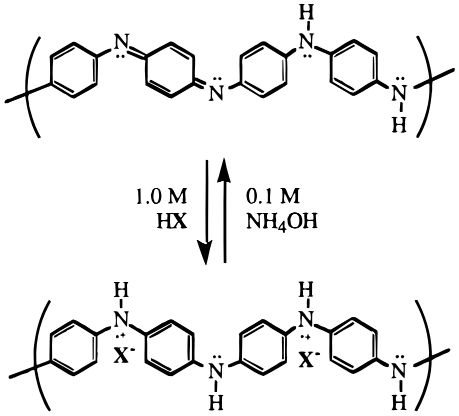
type of membrane	feed (wt % H_2O)	temp (°C)	thickness (μm)	selectivity (α)	perm rate (g/(m^2 h))	analysis of permeate[g]	ref
polyaniline (salt)	47.62	RT[c]	100	1370	4.1	NMR	this paper
polyaniline (base)	47.62	RT[c]	100	2.4	13	NMR	this paper
silica	4.16	90	1	450	950	GC	5
	50	90	1	125	5400	GC	5
polyimide (BDTA/ODA)[a]	20	65	22	417	48	DR	12
grafted polyacrylic acid−nylon 6	49.9	15	NR[d]	300	38	DR	6
polyacrylic acid/nylon 6 blend	50	25	NR	32	170	DR	13
poly(4-vinylpyridine-*co*-acrylonitrile)	40	21	13	100	45	GC	14
poly(vinyl chloride)	50	40	25	45	6.0	IC	15
poly(sodium acrylate)/poly(divinylbenzene)	50	30	300	11	1320	GC	10
modified poly(vinyl alcohol)	50	25	NR	6.7	1200	GC	11
cross-linked/poly(vinyl alcohol)	50	30	1400−1800	20	350	DM	4
poly(vinyl alcohol)−CC[b]	10	40	30	14[e]	550	GC	16
poly(vinyl alcohol)/poly(hydroxycarboxylic acid)	10	25	30	33[e]	140	GC	17
poly(1-butyl methacrylate)	50	25	35	5.3	10	GC	9
poly(2-ethylhexyl acrylate)	50	25	20	2.1	2.5	GC	9
polystyrene	50	25	35−40	1	105	GC	9
poly(dimethylsiloxane)	47	23	25	3.4[f]	780	DR/RI	7
cross-linked polybutadiene	50	25	150	3.0[f]	8.0	GC	8
poly(dimethylsiloxane)-coated poly(ether imide)	50	RT[c]	25	3.9[f]	31	GC	18

[a] BDTA = 3,3′,4,4′-benzophenonetetracarboxylic dianhydride; ODA = 4,4′-oxydianiline. [b] Poly(vinyl alcohol)−CC = poly(vinyl alcohol) containing covalently bonded carboxylic group. [c] RT is room temperature (~22 °C). [d] NR means that the value was not reported. [e] The separation factor (α) was converted from the enrichment factor (β) by the equation: $\alpha = [(1 - c)/(1 - c')]\,\beta$, where c and c' are the weight fractions of the preferred component in the feed and permeate, respectively. [f] Acetic acid is the favored component in the permeate instead of water. [g] NMR = proton nuclear magnetic resonance, GC = gas chromatography, DR = differential refractometry, IC = ion chromatography, DM = density meter, and DR/RI = differential refractometry/refractive index.

opposite behavior was seen with poly(*N*-methylpyrrole), where the permeation rate was higher in the undoped form. The rates of transport of methanol and methyl *tert*-butyl ether using thin films of the conjugated polymers polypyrrole, poly(*N*-methylpyrrole) and polyaniline have also been reported.[22] While polypyrrole films had no separating capability, both poly(*N*-methylpyrrole) (α = 3.9) and polyaniline (α = 4.9) showed some modest separating abilities, based on the permeation rates of the individual solvents through the membranes. Electrochemically synthesized polyaniline and polypyrrole films have been used as pervaporation membranes for the transport of methanol[23] and water.[24] The permeation rates of methanol and water were larger for oxidized polyaniline than for reduced polyaniline. Conversely, methanol has a higher permeation rate in the reduced (undoped) form of polypyrrole than that in the oxidized form.

Here we report the use of the conjugated polymer, polyaniline, in both its doped and undoped form, for the pervaporation of carboxylic acid/water mixtures. The chemical structures of the emeraldine base (undoped) form, and the emeraldine acid (HCl-doped) form, of polyaniline are shown in Scheme 1. Polyaniline can be cast as free-standing, dense films with pore sizes (<20 Å diameter) falling in the useful range for reverse osmosis, pervaporation and gas separation membranes.[25−27] Previous research by our group and others have demonstrated that these films can be used as gas separation membranes, and show high selectivities for important gas pairs, such as the selective permeation of oxygen over nitrogen.[25−27] Polyaniline can be controllably and reversibly doped and undoped by simply reacting it with common aqueous acids and bases. The doping/undoping process leads to morphological and chemical changes that affect both permeability and selectivity of polyaniline.[28] Hence, the separation properties of polyaniline membranes can be tailored by the doping process after their formation.

Scheme 1



Polyaniline membranes, in their base form, are quite hydrophobic; i.e., water does not wet their surfaces.[29−32] As polyaniline is doped, the positive charges induced in the polymer and the negative charges on the counterions increase polyaniline's hydrophilicity. Additionally, doping causes morphological changes in the membrane on the nanoscale which affects the diffusion of permeating species.[28] This study focuses on the effects of doping and undoping on the permselective properties of polyaniline membranes with different sized acid permeates.

Experimental Section

Materials. Aniline, ammonium peroxydisulfate ($(NH_4)_2S_2O_8$), tetrahydrofuran, *N*-methylpyrrolidinone (NMP), hydrochloric acid (HCl), and ammonium hydroxide (NH_4OH) (all from Fisher Scientific) were used as received.

Synthesis of Polyaniline. Polyaniline was synthesized by chemical oxidation in an acidic medium by an established method.[33] Aniline (80 mL, 880 mmol) was dissolved in 1.2 L of a 1.0 M HCl solution. A mass of 46.4 g (200 mmol) of ammonium peroxydisulfate was dissolved in 0.8 L of 1.0 M HCl to serve as the oxidizing solution. When both solutions were cooled to approximately 0 °C in a NaCl/ice/dry ice bath, the ammonium peroxydisulfate solution was added dropwise to the monomer solution over a period of approximately 45 min. After the addition of the oxidant, the reaction mixture was allowed to stir for at least $1^1/_2$ h. The dark blue powder formed in the reaction was collected by filtering through a Büchner funnel and washed repeatedly with 1.0 M HCl and 0.1 M NH_4OH until the filtrate was clear in color. After the washing process was completed, the dried powder was swelled in tetrahydrofuran.

Polyaniline Film Formation. The resulting emeraldine base powder was then dispersed in NMP (~7% wt/wt) with grinding, poured into a Petri dish (9 cm diameter), and heated in an oven at 110 °C for approximately 1 h until the film was dry. Each cured polyaniline film was removed from the Petri dish by soaking in water for several minutes. This procedure produced dense, pinhole-free, free-standing polyaniline membranes. Individual membranes (2.5 cm diameter membranes cut from the 9.0 cm diameter films) varied slightly in thickness (on average about 10%) so the thickness of each individual membrane was measured in several different locations, and these values were averaged. This average membrane thickness was used in the calculations of the permeation rates. The thicknesses of the various resulting membranes ranged from 50 to 120 μm.

Doping and Undoping. Polyaniline in the emeraldine base oxidation state is comprised of half imine and half amine nitrogens (Scheme 1). Upon full doping, all the imine nitrogens of polyaniline become protonated. Solutions of 1.0 M HCl and 0.1 M NH_4OH were used for the doping and undoping of the polyaniline membranes, respectively. To ensure a fully doped or undoped state, the membranes were placed in the acid or base solution for approximately 1 day. The doping and undoping process also removes any residual NMP left from the membrane-formation process; therefore, as-cast and undoped membranes have somewhat different properties. As polyaniline films can always be returned to the undoped state but not to the as-cast state; this study focuses on doped/undoped membranes called "undoped" and doped membranes called "doped". Undoped films appear bronze in color, while doped films are deep blue.

Calorimetry. The heat of doping (ΔH_{doping}) of polyaniline can be determined from the heat of mixing (ΔH_{mixing}) and the heat of dilution ($\Delta H_{\text{dilution}}$), as shown in eq 1. The $\Delta H_{\text{dilution}}$ of

$$\Delta H_{\text{mixing}} = \Delta H_{\text{doping}} + \Delta H_{\text{dilution}} \tag{1}$$

both HCl and acetic acid in water were measured using the following procedure. A capped Dewar was filled with 100 mL of deionized water, and stirred, and the temperature of the solution was monitored until the temperature remained constant. A 100 mL solution of 6.0 M acid was prepared separately and was heated or cooled until its temperature was equal to that of the water solution in the Dewar. At this point, the 6.0 M acid solution was immediately added to the water stirring in the Dewar. The temperature of the mixture was monitored until the temperature of the solution in the Dewar reached a stable maximum (~10 min). Before the heat of dilution can be calculated, the heat capacity (C_p) of the final 3.0 M acid solution must be determined from eq 2, where Φ_C

$$C_p = \frac{(\Phi_C m) - (1000C°)}{(1000 + mM_2)} \tag{2}$$

is the apparent molal heat capacity ($\Phi_C = -20.65$ cal/(mol °C) for HCl; $\Phi_C = 36.7$ cal/(mol °C) for acetic acid),[34] m is the molality, $C°$ is the specific heat (per unit mass) of water and M_2 is the molecular weight of the acid. The $\Delta H_{\text{dilution}}$ can then determined from eq 3, where V is the total volume of the

$$\Delta H = V\rho C_p \Delta T \tag{3}$$

solution (200 mL), ρ is the density of the solution (1.05 g/mL for 3.0 M HCl;[35] 1.02 g/mL for 3.0 M acetic acid[36]), ΔT is the change in temperature of the solution upon mixing, and C_p is the heat capacity ($C_p = 0.8455$ cal/(g °C) for HCl; $C_p = 0.9408$ cal/(g °C) for acetic acid) as calculated from eq 2. To obtain the total heat of mixing (ΔH_{mixing}), 0.2 mol (1.81 g) of polyaniline was added to 100 mL of deionized water in the Dewar. The temperature of this solution was allowed to equilibrate before addition of the 6.0 M acid. The total ΔH_{mixing} was obtained using eq 3. When ΔH_{mixing} and $\Delta H_{\text{dilution}}$ are obtained, the heat of doping, ΔH_{doping}, can be calculated from eq 1.

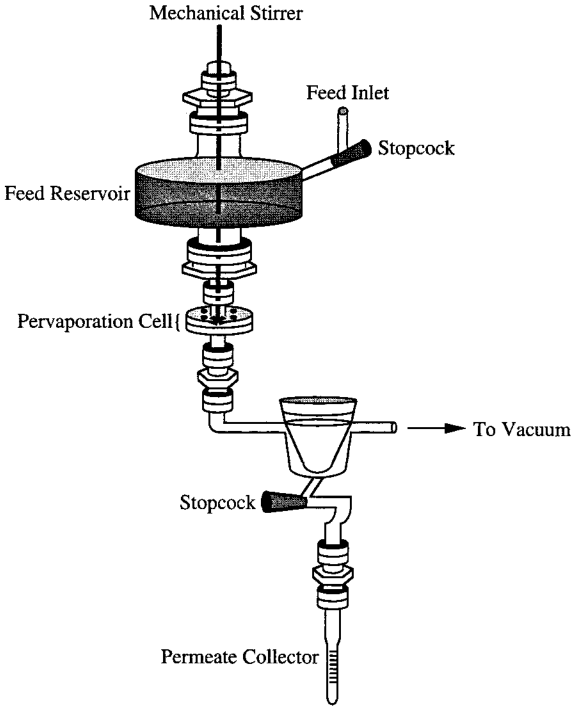


Figure 1. Pervaporation setup shown schematically. The polymer membrane rests on a porous metal support within a stainless steel pervaporation cell. The feed reservoir can hold up to 500 mL. The graduated permeate collector is immersed in a 2-propanol bath at −65 °C during pervaporation.

Synthesis of Asymmetric Polyaniline Membranes. Polyaniline powder (0.5 g), in the emeraldine base form, was dispersed in 8 mL of NMP with grinding. This polyaniline/NMP dispersion was poured into a Petri dish and heated at 80 °C for ~25 min. It was then removed from the oven. After the dispersion had cooled to room temperature, about 5 mL of either methanol or toluene was added to the Petri dish to extract the residual NMP. The methanol or toluene was left in the Petri dish for 3 min, after which the liquid was decanted. The Petri dish was placed back in the oven and heated at 110 °C for an hour. The resulting asymmetric membrane was removed from the glass dish by soaking with water. After film formation, a sample of the asymmetric polyaniline membrane was freeze-fractured and was analyzed by scanning electron microscopy (SEM, Cambridge Stereoscan 250). The bulk thickness of the asymmetric membrane was measured in several locations and averaged. An as-cast dense polyaniline film was used in a pervaporation experiment to compare to the pervaporation results for the as-cast asymmetric membrane.

Pervaporation. The pervaporator is shown in Figure 1. A polyaniline membrane (2.5 cm diameter) was placed on top of a stainless steel porous support, mounted in a stainless steel flange test cell, and sealed with O-rings. The actual permeating area of the membrane utilized in pervaporation was ~3.14 cm^2 (2.0 cm diameter). The pervaporation system was evacuated for at least 15 h prior to the start of each experiment to remove air and moisture from the downstream side of the pervaporator. A 200 mL feed solution, at room temperature, was added to the reservoir on the upstream side of the pervaporator. During the pervaporation experiment, a static vacuum was maintained on the downstream side of the membrane. The permeate collector was immersed in a 2-propanol bath maintained at −65 °C with a coldfinger (NESLAB Instruments, Model CC-65II) to condense the permeate, so that the downstream side of the pervaporator is maintained at a low vapor pressure of permeate. The pervaporation experiment was performed for 24 h, and the volume of the liquid permeate collected in a graduated tube during each experiment was recorded. All the permeation rates through polyaniline membranes reported here have been normalized to a membrane thickness of 100 μm, so that comparisons between pervaporation runs can be made.

Several test experiments were carried out to ensure the validity of the pervaporator and the stability of the polyaniline membranes. First, a blank test with no feed was conducted to ensure that the system does not collect moisture from the atmosphere. No observable amount of liquid was collected after 1 day. A second experiment was carried out in order to check the permeability of the porous stainless steel support. This was accomplished by adding feed solution without the presence of a membrane. The added liquid flowed right through the support into the downstream side of the pervaporator, indicating that the interference of the porous support to permeation is negligible.

The permeation rate (also known as the permeation flux), J, of a liquid can be determined using the following equation:

$$J = \frac{F}{tA} \tag{4}$$

where F is the collected permeate (in grams), t is the duration of the experiment (in hours), and A is the permeating area of the membrane (in m^2). The permselectivity (α_P) of the membrane is defined by

$$\alpha_P = \frac{X_2/Y_2}{X_1/Y_1} \tag{5}$$

where X and Y are the mass percentages of the permeating species; 1 denotes the feed composition and 2 denotes the permeate composition.

Temperature-Dependent Pervaporation. The apparatus used in the temperature-dependent pervaporation studies[37] was similar to the one used in room-temperature experiments, with the following modifications: (1) a larger cell holding a 5.0 cm diameter film was used, with an actual permeating area of 12.6 cm^2 (4.0 cm diameter); (2) the feed solution was warmed before the experiment; (3) the feed reservoir was wrapped with heating tape, and the temperature of the feed solution was monitored throughout the course of the experiment; (4) a larger permeate collector was used. All the feed solutions consisted of approximately 50 wt % acetic acid and 50 wt % water. Several temperatures between room temperature and ~100 °C were studied, and each experiment lasted for 24 h. All the fluxes were also normalized to a membrane thickness of 100 μm.

Determination of the Compositions of the Feed and Permeate Mixtures. A feed or permeate mixture was dissolved in acetone-d_6 for ^{1}H NMR acquisition. The positions of the peaks (relative to a standard, such as tetramethylsilane) represent protons in different environments. The molar ratio of each component in a mixture is calculated from the ratio of the integrated areas of each corresponding peak. The molar ratios can then be converted to mass or volume percentages. The results obtained from ^{1}H NMR were compared to those calculated from measured volumes to check the validity of ^{1}H NMR in the determination of the concentrations of the mixtures (Figure 2).

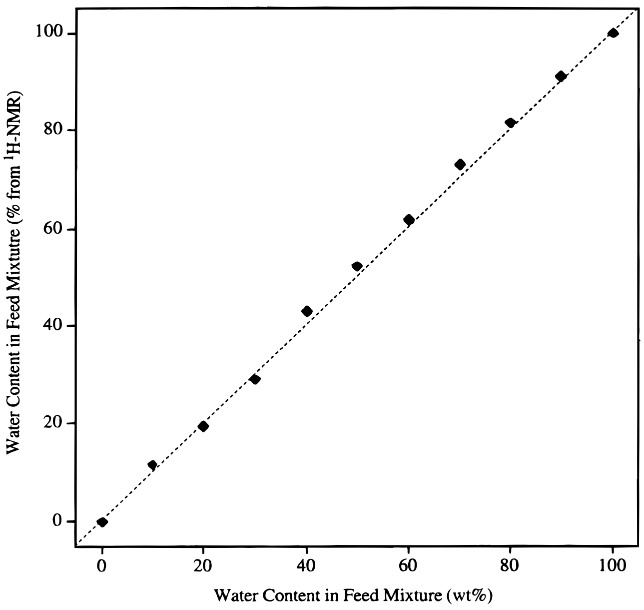


Figure 2. Acetic acid/water ratios determined from ^{1}H NMR and by mass. The dotted line represents a one to one match between water content measured by mass vs the water content determined from ^{1}H NMR.

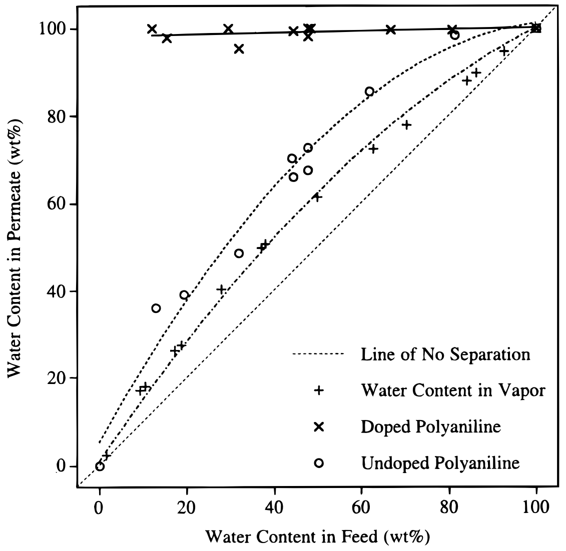


Figure 3. Pervaporation of acetic acid/water mixtures of various concentrations through doped and undoped polyaniline membranes at room temperature. The water content of the vapor from these mixtures are included for comparison.[38]

Table 2. Permeation Rates and Selectivities of Water/Acetic Acid Feeds of Various Concentrations through Doped Polyaniline (Selected Data from Figures 3 and 4)

feed content (wt % water)	water perm (g/(m^2 h))	acetic acid perm (g/(m^2 h))	total perm (g/(m^2 h))	selectivity (α_{H_2O})
0	0.000	0.000	0.000	
12	1.014	0.002	1.016	4000
29.36	3.353	0.006	3.359	1600
47.62	4.061	0.003	4.064	1400
66.84	8.014	0.024	8.038	230
80.84	6.570	0.018	6.588	240
100	10.637	0.000	10.637	

Results

Effect of Membrane Doping State on Acetic Acid/Water Permeation and Selectivity. Figure 3 shows the compositions of the permeates through both doped (Table 2) and undoped (Table 3) polyaniline membranes, as compared to the compositions of the feeds of acetic acid (CH$_3$COOH) and water. The water content in the vapor of acetic acid/water mixtures is

Table 3. Permeation Rates and Selectivities of Water/Acetic Acid Feeds of Various Concentrations through Undoped Polyaniline (Selected Data from Figures 3 and 4)

feed content (wt % water)	water perm (g/(m^2 h))	acetic acid perm (g/(m^2 h))	total perm (g/(m^2 h))	selectivity (α_{H_2O})
0	0.000	3.560	3.560	
12.90	3.772	6.731	10.503	3.8
19.40	3.099	4.837	7.936	2.7
31.87	5.676	6.012	11.688	2.0
44.24	6.010	2.553	8.563	3.0
47.62	8.920	4.203	13.123	2.4
61.80	5.981	1.021	7.002	3.8
81.25	2.311	0.040	2.351	23
100	1.706	0.000	1.706	

included for comparison,[38] as is the “line of no separation.” All the data points shown in Figure 3 represent the average of several separate runs. In two early runs, poor quality polyaniline films containing pinholes led to high concentrations of acetic acid in the permeate; these two runs have been omitted from the data. In all cases, the permeate is enriched with water as compared to either the feed solution or the vapor. This demonstrates that polyaniline can be used as a water-selective pervaporation membrane for acetic acid/water mixtures.

Although the permeate through undoped polyaniline becomes slightly enriched with water, the selectivity of undoped polyaniline toward water is low. At lower feed concentrations of water, the permselectivity, α_{H_2O}, is equal to or greater than 2.0, but never exceeds 4.0. At higher water concentrations, the selectivity of undoped polyaniline rises to greater than 20 (feed = 19 wt % acetic acid/81 wt % water). In comparison, the selectivities of doped polyaniline membranes are far superior to those of undoped. At essentially all feed concentrations, the composition of the permeate is >99 wt % water. This corresponds to very high selectivities ($\alpha_{H_2O} > 100$), with one exception. The exception is the point corresponding to a feed of 32 wt % water; in this case, it appears that one of the membranes used in that run contained small pinholes that let a higher amount of acetic acid through the membrane. In all other cases (even in the case when the feed is only 29 wt % water), the permeate is almost exclusively water, yielding selectivities with $\alpha_{H_2O} > 100$.

With dense membranes of doped polyaniline, the permeation rate ranges from essentially 0 for concentrated acetic acid to >10 g/(m^2 h) for pure water (Figure 4). The permeation rate of an approximately 50 wt % acetic acid/50 wt % water feed is on average 5.0 g/(m^2 h), independent of whether 2 cm diameter membranes or 4 cm diameter membranes were used. The permeation rates of these same feeds through undoped polyaniline display a different behavior than with doped polyaniline. While in the case of doped polyaniline the permeation rates of acetic acid/water mixtures rise with increasing water content, the permeation rates through undoped polyaniline reach a maximum (13 g/(m^2 h)) at ~45 wt % water and then decline. The average permeation rate of concentrated acetic acid (3.6 g/(m^2 h)) through undoped polyaniline is higher than the average rate of pure water (1.7 g/(m^2 h)).

Pervaporation of Different Carboxylic Acid/Water Feeds. Pervaporation experiments with doped polyaniline membranes using mixtures of water, and formic acid (HCOOH) or propionic acid (CH_3CH_2COOH), were performed. The results of these experiments are shown in Figure 5. They indicate that doped polyaniline membranes separate water from propionic acid/water feeds as well as, or even better than, they separate water from acetic acid/water feeds. At nearly all concentrations, water is virtually the only component in the permeate (>99 wt % in permeate, $\alpha_{H_2O} \gg 100$). However, doped polyaniline shows little capacity for separating formic acid/water mixtures. The selectivity of doped polyaniline for these feeds is low (α_{H_2O} varies from ~1 to 20), even at high concentrations of water.

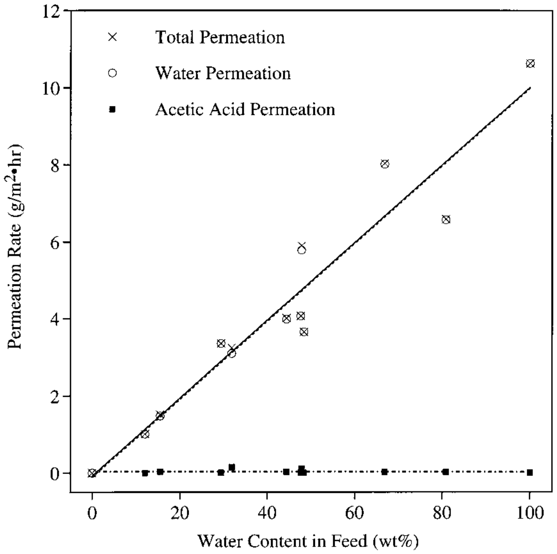


Figure 4. Permeation rates of acetic acid/water mixtures through doped polyaniline at room temperature. At all concentrations, water is virtually the only component transporting through doped polyaniline.

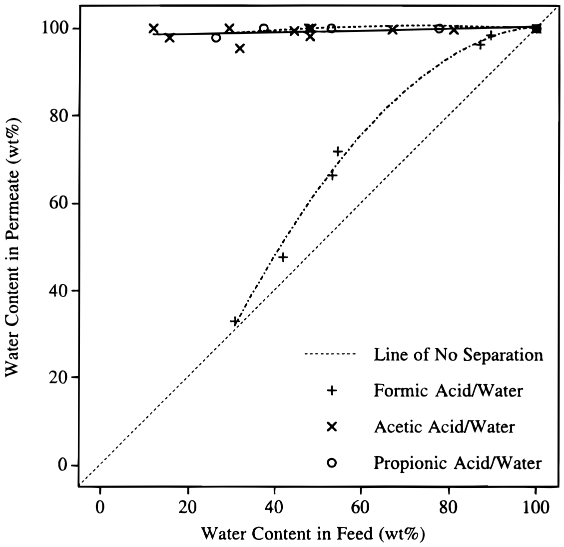
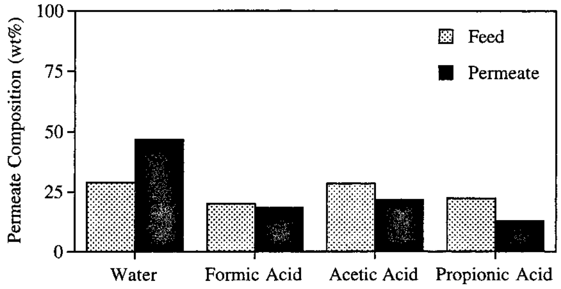


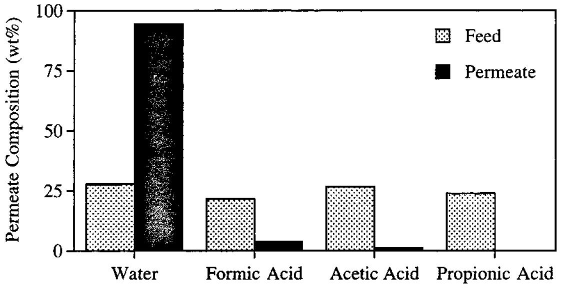
Figure 5. Compositions of carboxylic acid/water feed mixtures after permeation through doped polyaniline membranes.

The permeation rate of formic acid/water mixtures is significantly higher than those for acetic acid or propionic acid and water mixtures. At all concentrations, the permeation rate of formic acid/water feeds is above 10 g/(m^2 h), while the permeation rate of the acetic acid and propionic acid mixtures is <10 g/(m^2 h) at nearly all concentrations. Only when the percentage of water in the feed is very high does the permeation rate of the mixtures with the larger acids begin to rise toward 10 g/(m^2 h).

Pervaporation of Multicomponent Feeds. To test the separation capability of polyaniline membranes



Undoped Polyaniline



Doped Polyaniline

Figure 6. Pervaporation of a feed mixture, composed of three carboxylic acids and water, through an undoped polyaniline membrane (top) and a doped polyaniline membrane (bottom). The feed for the undoped polyaniline experiment consisted of 29 wt % water, 20 wt % formic acid, 29 wt % acetic acid, and 23 wt % propionic acid; the composition of the feed for the doped polyaniline experiment was 28 wt % water, 22 wt % formic acid, 27 wt % acetic acid, and 24 wt % propionic acid.

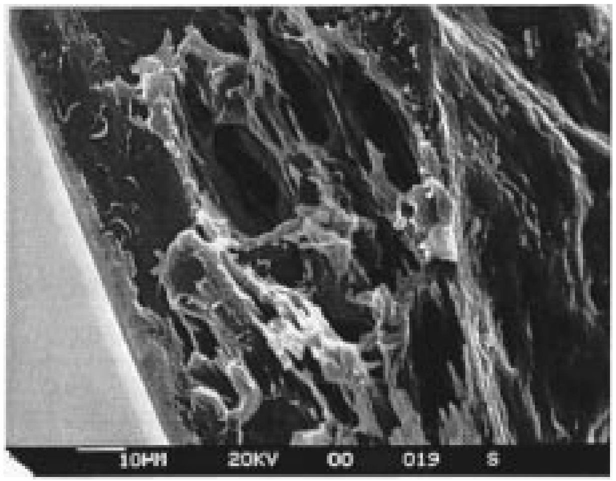


Figure 7. Scanning electron micrograph of the freeze-fractured cross section of an as-cast asymmetric polyaniline membrane. The dense skin layer of the membrane is on the left; the porous bulk support is clearly visible in the center.

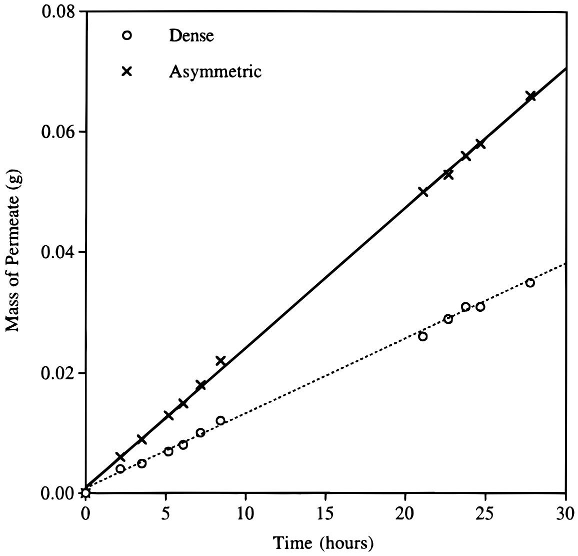


Figure 8. Comparison of the accumulation of the permeates of a 29 wt % acetic acid/71 wt % water feed through a dense polyaniline membrane (thickness = 79 μm) and an as-cast asymmetric polyaniline membrane (bulk thickness = 73 μm) vs time.

toward a multicomponent mixture, water and all three carboxylic acids were mixed together as a feed solution. The feed consisted of 20–30 wt % of each component as listed in Figure 6. For undoped polyaniline membranes, the water content in the permeate solution increased moderately, e.g. from 29 wt % in the feed to 47 wt % in the permeate. The concentration of the three acids in the permeate was correspondingly lower than in the feed: formic acid (19 wt % in permeate vs 20 wt % in feed), acetic acid (22 wt % in the permeate vs 28 wt % in the feed), and propionic acid (13 wt % vs 23 wt %), respectively. When a doped polyaniline film was used, the water content increased dramatically from 28 wt % water in the feed to 94.5 wt % in the permeate. The content of formic acid decreased appreciably from 22 to 4.3 wt %, while the content of acetic and propionic acids decreased dramatically, from 27 to 1.1 wt % and from 24 to 0.2 wt %, respectively.

Pervaporation of Asymmetric Membranes. To examine how the effective thickness of the membrane affects the permeation rate, both fully dense (79 μm thick) and asymmetric (73 μm thick) free-standing as-cast polyaniline films were used in pervaporation experiments. As seen from the SEM micrograph in Figure 7, the skin layer (left side of Figure 7) is dense, while the bulk of the film (center of Figure 7) is filled with microvoids and is porous. To compare the permeation properties of dense and asymmetric membranes, an acetic acid/water feed of the same concentration (29 wt % water) was permeated through each membrane (Figure 8). For each membrane, the permeation rate remained approximately constant throughout the 1 day experiment. The slope of the line for the dense polyaniline membrane in Figure 8 is 0.0012 g/h, which yields a permeation rate of 3.9 g/(m^2 h). In the case of the asymmetric membrane, the slope is 0.0023 g/h, which yields a permeation rate of 7.4 g/(m^2 h). The composition of the permeate using the asymmetric polyaniline membrane was 49 wt % water ($\alpha_{H_2O} = 2.4$), while the permeate was 59 wt % water ($\alpha_{H_2O} = 3.7$) in the case of the dense membrane.

Temperature-Dependent Permeability. The temperature-dependent permeation of 50% acetic acid/50% water feeds through polyaniline membranes is shown in Figure 9. The permeation rate of these feeds through doped polyaniline shows a 2-fold increase between 20 and 85 °C, increasing from 5.9 g/(m^2 h) at room temperature to 12 g/(m^2 h) at 85 °C. The selectivity of these doped membranes ($\alpha_{H_2O} \sim 1000$) appears to remain constant over this temperature range. However, the permeation rate of the same feed through undoped polyaniline increases 12-fold over nearly the same temperature range, going from ~10 g/(m^2 h) at room temperature to 120 g/(m^2 h) at 85 °C. The selectivity (α) of undoped polyaniline falls from 2.4 to 1.8 over this temperature range.

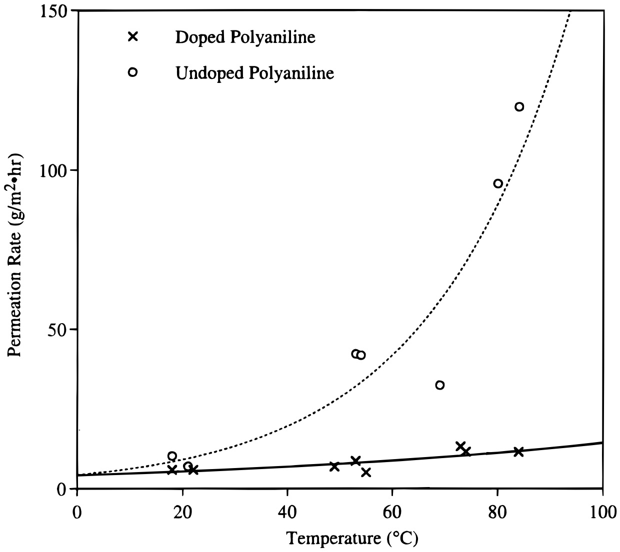


Figure 9. Pervaporation of 50% acetic acid/50% water feeds through doped and undoped polyaniline membranes at various temperatures.

Discussion

Analysis of Permeating Mixtures by ^{1}H NMR. In this work, ^{1}H NMR was used as a characterization technique for determining the feed and permeate compositions. Traditionally, GC-mass spectroscopy, refractometry, or density meters have been used.[4−18] However, each of these analytical techniques has drawbacks. For example, due to the presence of water in these mixtures, a special column is needed in order to use GC−mass spectroscopy as a characterization technique. Different compositions can also have the same index of refraction, which complicates the determination of the concentrations of mixtures by refractometry. Use of a density meter requires that larger amounts of liquid be collected to obtain sufficient accuracy. Here, we introduce NMR as an alternative method for determining the concentrations of permeating mixtures. Proton NMR is found to be an excellent technique for quantitative analysis of solutions because of its ease of use and high accuracy. As a test, the concentrations of several samples of aqueous acetic acid solutions were determined from the peak ratios of their NMR spectra and compared with those obtained from mass ratios (Figure 2). When the concentrations calculated from the ^{1}H NMR peak areas and from the masses are plotted against each other, they agree very well, as shown in Figure 2. This demonstrates that NMR is another useful technique for determining the concentrations of mixtures, provided that the proton peaks of the components do not overlap.

All feed mixtures reported in this paper were measured out by volume (and converted to weight percent) and the compositions checked by ^{1}H NMR. For example, the six feed mixtures measured out to be “50% acetic acid/50% water” by volume were actually found to be 49.8, 48.4, 47.8, 47.6, 44.4, and 44.2 wt % water by ^{1}H NMR. All weight percent values of solutions reported in this paper were determined by ^{1}H NMR.

Effect of Membrane Doping State on Selectivity and Permeation. The generally accepted mechanism for molecules transporting through a membrane during pervaporation is “adsorption−diffusion−desorption”.[2] When polyaniline changes from the undoped to the doped form, ionic charges are created in the polymer.[29] These charges increase the hydrophilicity of the polyaniline membrane and lead to stronger interactions with water. The increased hydrophilicity in turn causes better sorption of water molecules into the polymer. A doped polyaniline membrane clearly has better separating capabilities in the pervaporation of acetic acid/water feeds than does an undoped membrane, as can be seen in Figure 3. For example, when the water content in the feed mixture is approximately 50 wt %, the permeate consists of approximately 70 wt % ($\alpha_{H_2O} \sim 2.4$) water when an undoped polyaniline membrane is used. However, when a doped film is employed, the permeate is >99 wt % ($\alpha_{H_2O} > 100$). Even when ~88 wt % of the feed solution is acetic acid, fully doped polyaniline membranes selectively transport water to the point where the permeate is well over 99% water ($\alpha_{H_2O} \sim 4000$). However, water transports only slightly better than acetic acid through undoped polyaniline at any feed concentration, as shown in Figure 3.

When polyaniline is in its doped form, it becomes relatively hydrophilic due to the presence of separated charges. Clearly, the ionic character of the membrane facilitates the transport of water. On the other hand, undoped polyaniline has only a small affinity for transporting water. This result is due to a combination of competing factors:

(1) Water (1.4 Å radius) is smaller than acetic acid (4.5 Å radius in aqueous solution).[39]

(2) Undoped polyaniline is hydrophobic.

(3) Acetic acid can interact with the base form of polyaniline by doping the imine nitrogens.

Thus, with undoped polyaniline, water is preferred in terms of diffusion, while acetic acid is favored in terms of sorption. In the case of the pure solvents, the acid−base interaction between acetic acid and undoped polyaniline accounts for the higher permeation rate of concentrated acetic acid (3.6 g/(m^2 h)) as compared to pure water (1.7 g/(m^2 h)). In the case of doped polyaniline, both diffusion (size effect) and sorption (chemical interaction effect) appear to favor water. Water is therefore selectively transported through doped polyaniline films to a much greater degree. This is supported by the fact that the permeation rate of pure water through doped polyaniline is approximately 10 g/(m^2 h), whereas the rate of water through undoped polyaniline is only 1.7 g/(m^2 h).

Since water is readily adsorbed into doped polyaniline, some of the HCl dopants might be expected to leach out of the membrane and into the feed solution. Indeed, dopant leaching does take place to a small extent. Dopant leaching, its effect on the pervaporation of several different solvents, and methods for avoiding dopant leaching, such as the use of polymeric dopants, will be discussed in a forthcoming publication.[40] However, this effect does not appear to affect the permselectivities of doped polyaniline membranes toward acetic acid/water solutions. Calorimetry experiments indicate that HCl binds strongly to polyaniline ($\Delta H_{\text{doping}} \sim 5.3$ kcal/mol), while acetic acid binds less strongly ($\Delta H_{\text{doping}} \sim 1.9$ kcal/mol). Hence, polyaniline displays a definite preference for associating with HCl over acetic acid.

Effects of Feed Concentration on Selectivity. The effects of acetic acid/water concentration on pervaporation through both doped and undoped polyaniline membranes have been investigated, as shown in Figure 3. The vapor−liquid equilibrium line for acetic acid/water mixtures is shown for comparison (Figure 3).[38]

The permeation of water through both undoped and doped polyaniline membranes is above the vapor−liquid equilibrium line, demonstrating that both types of membranes selectively permeate water at all feed concentrations. However, at most feed concentrations, the selectivity of water through undoped polyaniline is only 2−4, as shown in Table 3. Only at high concentrations of water does the selectivity of undoped polyaniline begin to climb above 5. This selectivity is far too low for use as an effective separation membrane. The low selectivity of undoped polyaniline is due to the competition of factors outlined in the previous section, specifically, diffusion favoring water permeation, while sorption favors the acid. As the concentration of water rises, there is less acid available to swell the membrane, so the favorability of acid permeation declines. When the concentration of water is high enough, the favorable diffusion of water becomes the dominating factor in permeation through the membrane, and the selectivity rises.

Interestingly, doped polyaniline shows a vastly different permeation behavior than undoped. At low concentrations of water, the selectivity of doped polyaniline is generally greater than 1000. As the concentration of water in the feed rises above 50%, the selectivity of doped polyaniline declines into the hundreds or below, due to a small amount of acetic acid transporting through the polymer membrane at all concentrations. Thus, at virtually all feed concentrations, the composition of the permeate is always approximately 99.5% water.

Chemical Properties of the Permeates and Their Effect on the Permeation Rate. To understand how chemical/physical properties of permeates affect the permeation rate, pervaporation of formic acid/water and propionic acid/water mixtures were also conducted. Doped polyaniline membranes were used for these experiments since they are far superior to undoped polyaniline membranes at separating acetic acid/water mixtures. The separation efficiency of water from carboxylic acid/water feeds was found to follow the order

$$\text{propionic acid} \geq \text{acetic acid} \gg \text{formic acid}$$

as can be seen in Figure 5. This order is due to the size of the permeating acids, along with chemical factors such as the polarity of these acids. As the size of the carboxylic acid decreases, propionic (~5.5 Å radius in aqueous solution) > acetic (~4.5 Å) > formic (~3.5 Å),[39] diffusion through the membranes becomes easier. Additionally, as the acids become less polar (dielectric constant: formic, 58; acetic, 6.2; propionic, 3.3),[41] their interactions with the doped polyaniline membrane are reduced, resulting in weaker adsorption in the films. Thus, the rejection of the larger acids from doped polyaniline can be attributed to the larger sizes and the smaller polarities of acetic and propionic acid, which causes these larger acids to be blocked most effectively by doped polyaniline membranes.

The effects of both the size of the acid and the dopant state of the polyaniline membrane are clearly demonstrated by studying pervaporation of multicomponent mixtures (Figure 6). The decrease in the acid concentration from the feed to the permeate is related to both the doping state of the polymer and the chemical and physical properties of the acids. Thus, the larger the size and the smaller the polarity of an acid, the better it is separated from water by polyaniline membranes.

Dense and Asymmetric Membrane Permeabilities. Generally, membrane separation processes using flat sheet membranes suffer from low permeation rates. One approach to increasing the permeation rate is to reduce the membrane thickness. A common method for achieving thinner flat-sheet membranes, while maintaining mechanical robustness, is the synthesis of asymmetric membranes.[42] An asymmetric membrane usually consists of a dense outer skin, which does the bulk of the separation, and a porous inner layer, which provides the structural support for the dense skin (Figure 7).

The rates of permeation through both a dense and an asymmetric membrane display a linear increase after a short time lag (Figure 8). This linear behavior indicates that both types of polyaniline films are well-behaved membranes. As expected, the rate of permeation through the asymmetric membrane (7.4 g/(m^2 h)) was higher than that through the dense membrane (3.9 g/(m^2 h)). The permeation rate through the asymmetric membrane was approximately twice as high, even though the overall thicknesses were nearly the same (73 μm for the asymmetric membrane; 79 μm for the dense membrane). However, the asymmetric membrane displayed a somewhat lower separation ability than the dense membrane ($\alpha_{H_2O} = 2.4$ vs 3.7 for the dense membrane). The ratio of the asymmetric membrane's selectivity (α_{asym}) to the intrinsic selectivity (α_{int}), as measured from the dense film, is $\alpha_{asym}/\alpha_{int} = 0.65$, which seems to indicate that the membrane resistance of the porous polyaniline support plays a significant part in the overall selectivity of the asymmetric membrane, a phenomenon that has been described by Huang and Feng.[43] Overall, these results indicate the possibility of improving the rate of permeation through polyaniline by using asymmetric membranes. Other methods for synthesizing asymmetric membranes with improved properties are presently being developed.

Temperature-Dependent Permeability. Another method for increasing the permeation rates through a membrane is by increasing the temperature of the permeating solution. The temperature-dependent permeability of 50 wt % acetic acid/50 wt % water through polyaniline membranes is shown in Figure 9. A 2-fold increase in the permeation rate through doped polyaniline is observed, without any appreciable loss in selectivity. This is consistent with the exceedingly low permeability of acetic acid through doped polyaniline membranes. Even at the higher temperatures, the permeability of the acetic acid component of these feeds is negligible. Thus, the increase in the flux over this temperature range is likely due to the increased diffusion of water through doped polyaniline.

In contrast, the permeability of 50 wt % acetic acid/50 wt % water feeds through undoped polyaniline is much higher, especially at high temperatures. Even at room temperature, the permeation rate of these feeds through undoped polyaniline is relatively high, ~10 g/(m^2 h). As the temperature goes up, so does the permeability, increasing 12-fold at 85 °C. Thus an increase of only ~65 °C leads to a permeation rate of 50 wt % acetic acid/50 wt % water through undoped polyaniline on the order of 120 g/(m^2 h). Such a large increase is likely due to both increased diffusion and increased sorption of both acetic acid and water in the undoped polyaniline membrane. However, since this increase in temperature leads to greater increases in acetic acid solubility and diffusion, the favorable permselectivity of water declines over this temperature range (from $\alpha = 2.4$ to $\alpha = 1.8$).

Conclusions

Polyaniline membranes can be used for the separation of carboxylic acid/water mixtures. Whereas undoped polyaniline displays relatively poor selectivities, fully HCl-doped polyaniline selectively permeates water over acetic acid. Separation factors, α, of >1300 for 50 wt % acetic acid/50 wt % water through doped polyaniline put it among the most selective membranes reported for acetic acid/water. Water transport through doped polyaniline is most likely favored because of a combination of favorable diffusion, due to water's small size, and favorable solubility, due to the hydrophilicity of polyaniline induced by doping. Doped polyaniline effectively blocks the larger carboxylic acid, propionic, but the smaller acid, formic, permeates to some extent. Pervaporation of a mixture of all three carboxylic acids and water confirms that doped polyaniline is effective at blocking acetic and propionic acids. Proton NMR has been demonstrated to be another sensitive quantitative technique for the analysis of these aqueous acid feeds and permeates. The relatively low permeation rates obtained with dense polyaniline membranes can be readily improved by forming asymmetric films. Even with crude asymmetric films, the flux has been increased by a factor of 2. Additionally, increasing the feed temperature by 65 °C leads to a 2-fold increase in the permeation rate of 50 wt % acetic acid/50 wt % water through doped polyaniline, without any detectable corresponding loss of selectivity.

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