Incorporation of Fluorinated Surfactants into Polysulfone Films and Asymmetric Gas Separation Membranes

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Received 1 October 1997; accepted 18 January 1998

ABSTRACT: This study investigated the effect of incorporating strong surfactants into hollow fiber membranes and solution cast films made from polysulfone (PSF). During membrane formation, various (mostly fluorinated) surfactants were added to the spinning solution, quench medium, and bore fluid. Both the gas transport properties and the membrane structure were affected. Some membranes showed a modest increase in selectivity or in permeation rate. At low concentrations the addition of perfluoro ammonium octanoate (PAO) increased the O₂ permeation rate by 44% with only a small loss of selectivity. Surfactants were also incorporated into dense PSF films by solution casting. Only pure PSF films and those with low concentrations of short-tailed fluorinated surfactants were clear and transparent; higher concentrations and other surfactants yielded cloudy or defective films. The presence of surfactants decreased the glass transition temperature of PSF to varying extents. Increased total and polar surface free energy correlated with changes in the gas transport properties. It is proposed that the surfactants interact with the polymer both during membrane and film formation, and also affect chain packing after the solvent has been removed. SEM images confirmed that membranes with surfactants have larger voids in the porous matrix of the membrane. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 163-175, 1999

Keywords: fluorinated surfactants; polysulfone; gas separation membranes; films; gas permeation

INTRODUCTION

An asymmetric gas separation membrane typically comprises a thin (1000–5000 Å) separating layer or "skin," which is supported on a much thicker (>100 μ m) porous substructure. Such membranes may be in the form of flat sheets or hollow fibers, and are formed either as composite membranes or as integrally skinned membranes. In the latter case, the skin and support are formed from the same polymer solution during a single-phase separation process. Homogeneous dense polymer films are generally not suitable for commercial use, but can be used to study the gas transport properties of the membrane polymer.^{1–3}

The improvement of the transport properties of membranes has been the subject of many investigations. One strategy is to modify the surface of the separating layer of a membrane, for example, by surface fluorination^{4–7} or solvent treatment.⁸ A second strategy is to develop new polymers with better separation properties.^{2,3,9,10} and a third strategy would be to form the separation layer from a blend of polymers^{11–13} or to combine a polymer and monomeric additives.^{2,14} Maeda and

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Paul¹⁴ have shown that at low concentrations monomers can act as antiplasticizers to increase the selectivity of polysulfone for certain gas pairs. Kesting et al.² incorporated Lewis acids during membrane formation to modify the membrane structure.

Surfactants can also be used as additives. Hayes^{15,16} describes a method of treating polyaramide and polyimide gas separation membranes with various surfactants. A hollow-fiber membrane is treated with a dilute solution of a surfactant dissolved in a nonsolvent for the membrane polymer and then dried. The nonsolvent is preferably a swelling agent for the polymer. Only generic detail is given about the surfactants, which may be nonionic, anionic, or amphoteric surfactants. Although fluoro-aliphatic polymeric esters are preferred, a number of other fluorinated surfactants is listed. The patent claims considerably increased selectivity for helium over nitrogen. For example, summarizing a number of his results, He/N₂ selectivities (α) from 1.1 to 2.2 were increased to values ranging from 200-400, accompanied by a four- to sevenfold decrease in He permeance. Clearly, the initial membranes contain defects, and the swelling solvent-surfactant treatment serves to eliminate those defects. Unfortunately, the final selectivity and permeance are never compared to that of the untreated polymer in a thick defect-free polymer film.

The presence of surfactants in the skin of a membrane or in a polymer film could also affect such surface properties as adhesion, wetting, and resistance to aggressive environments during use. In a polymer solution, the surfactant can be expected to interact with the polymer and the solvent.¹⁷ These interactions may then affect the ultimate structure of an integrally skinned membrane that is formed by the phase separation of complex mixtures of polymers, solvents, and non-solvents.

An objective of this study was to modify the gas separation properties of hollow-fiber phase-inversion membranes by introducing a strong surfactant into the spinning solution during the membrane formation process. Surfactants were also added to the quench medium and bore fluid during membrane formation. To investigate the effect of polymer–surfactant interactions, homogeneous dense polysulfone films with different concentrations of various surfactants were prepared from solution and analyzed.

Fluorinated Surfactants

Surface-active materials or surfactants have a lyophilic (solvent-associating) head portion and lyophobic (solvent-repelling) tail portion. The head can be anionic, cationic, nonionic, or amphoteric in nature. The tail may be derived from a wide variety of chemical structures, including straight or branched, saturated, or unsaturated alkyl chains, fluorocarbons, polydimethyl siloxanes, and many others.¹⁷ The effect of substituting fluorine atoms for hydrogens on the hydrophobic tail of a surfactant often has a drastic effect on its surface active properties.^{18,19} For example, the surface tension of water can be lowered from 72,8 dynes/cm to about 28 dynes/cm by addition of 10,000 mg/L of $C_{12}H_{22}COO^-$ Na⁺, while the surface tension will be lowered to 18 dynes/cm by the addition of only 50 mg/L of C₈F₁₇COO⁻ Na⁺.¹⁸ Thus, fluorinated surfactants are among the strongest of their kind, and often exhibit properties different from unfluorinated surfactants.¹⁹

Three of the surfactants in this study had fluorocarbon tails and anionic heads. Their action was compared to one surfactant with a hydrocarbon tail and another with a nonionic head. Generally, a surfactant with a hydrocarbon tail will align at the interface between water and oil layers where the surface energy is minimized. However, fluorinated surfactants do not align at the interface but remain soluble in the water phase, because the fluorocarbon tail is not attracted to the oil phase.¹⁸ When a solvent system (e.g., a solution used during membrane formation) is a mixture of solvents and nonsolvents, the exact interaction of the surfactant with the various components of the solution is not straight forward. Moreover, when a polymer is present in the solution, the situation becomes even more complex, because the surfactant may associate either with the polymer or with the solvent. If solventsurfactant complexes are formed, the solvent power of the solvent is changed, and this could affect the phase separation step during membrane formation. Yet other effects can be expected if the surfactant forms micelles at higher concentrations.¹⁷ It can be appreciated that the effect of a surfactant added to a five-component spinning solution may be substantial and complex, and this study was limited to consideration of the effects of polymer-surfactant interactions after removal of all solvents, i.e., films and membranes in the solid polymer phase.

Surfactant	Acronym	Chemical Formula	HLB Value ^a		
Perfluoro ammonium octanoate	PAO	$C_7F_{15}CO_2^-NH_4^+$	~ 23		
Perfluoro potassium octanoate	PKO	$C_7 F_{15} C O_2^- K^+$	22.0		
Potassium octanoate	KO	$C_7 H_{15} CO_2^- K^+$	24.8		
Potassium trifluoroacetate	PFA	$CF_{3}CO_{2}^{-}K^{+}$	27.2		
Benzene Trifluoroacetate	BFA	$CF_3CO_2(C_6H_5)$	6.9		

Table I Surfactants Employed in this Study

^a HLB value = Hydrophilic Lipophilic Balance calculated according to Lin.²⁰

EXPERIMENTAL

Surfactants

A number of surfactants were used in different experiments to determine the effect of the surfactant's chemical nature on the properties of membranes and dense films. The surfactants, with their chemical structures and HLB values,²⁰ are listed in Table I.

These surfactants permit a comparison of different structural characteristics: (1) except for KO, all surfactants have perfluorinated lyophobic segments; (2) except for BFA, all are anionic surfactants; (3) PAO and PKO differ only in respect of their cationic counterion; (4) KO is the unfluorinated analogue of PKO; (5) PFA differs from PKO by its shorter fluorinated tail; and (6) PFA differs from BFA in that the latter has a benzene ring instead of an ionic head.

All surfactants were synthesized for this study and were used in the purified form. The surfactants were white crystalline powders, except BFA, which was a liquid; they were soluble in highly polar solvents, such as dimethyl acetamide, methanol, ethanol and water, but not in chloroform.

Membrane Formation

Integrally skinned asymmetric hollow-fiber membranes were made according to the dry–wet phase inversion process.^{21,22} The spinning solution,²² contained polysulfone (PSF), a volatile solvent tetrahydrofuran (THF), a less volatile solvent dimethyl acetamide (DMAc), and a nonsolvent ethanol (EtOH). The composition by mass was 30.0% PSF, 37.9%THF, 18.9% DMAc, and 13.2% EtOH. The spinning solution was first made up with half of the amount of ethanol, after which the surfactant was dissolved in the residual ethanol and added to the solution. Membranes were spun according to known procedures,^{21,22} which included extrusion, forced convection, quiescent evaporation, quenching, and rinsing in water. All membranes were dried at 100°C, and were then coated with a layer of poly(dimethylsiloxane) dissolved in hexane to caulk defects that may have formed in the skin. Usually two membrane production units were run simultaneously: one unit was used for the surfactant experiments, and the other served as a simultaneous control.

Gas Transport Properties

Experimental membrane modules containing seven fibers ($\sim 100 \text{ cm}^2$ membrane area) were tested after about 7–10 days. Prior to testing the membranes, they were coated with poly(dimethylsiloxane) to caulk skin defects that may have formed during fabrication. According to in-house procedures, the modules were tested for oxygen permeation rate (mL/min) and percentage oxygen recovery from air at 6-bar and 10-bar feed pressure. The procedures and units are those employed by the commercial membrane production plant and were used to allow comparison with unmodified membrane units. It can be assumed that the effective stage cut is close to zero. When the (mixed gas) feed is air (about 21% O₂) the separation factor (α) can be approximated by dividing the O_2/N_2 molar ratio of the permeate by the O_2/N_2 molar ratio of the feed.

Introduction of Surfactants during Membrane Formation

The surfactants listed in Table I were added to the spinning solution at a concentration of 0.1%by weight in separate runs on one of two production units. Each experimental run produced six batches of membranes that were tested separately. Three different surfactants (PAO, PKO, and KO) were added to the water-quench medium at concentrations of 0.1 and 0.2% by weight. These experiments were conducted in a single run (seven separate batches) to limit the influence of extraneous variables. The quench bath was first filled with pure water as a control, and fibers were spun for 15 min (first batch). The spinning process was interrupted to drain the quench bath and to add a prepared solution of water with 0.1% of surfactant (second batch). To increase the concentration to 0.2% (w/w) a small amount of water containing the required concentration of the same surfactant was added to the bath and thoroughly mixed, before recommencing the run for the next batch. For each new surfactant the quench bath was drained and washed.

In a separate experiment, different bore fluids were used. A comparison was made between bore fluids consisting of pure water, water containing a surfactant, pure methanol, ethanol, and isopropanol. Concentrations of 0.1 or 0.2% (w/w) of three surfactants (PAO, PKO, and KO) were employed.

SEM Analysis of Membrane Structure

Scanning electron micrographs (JEOL JSM 840) were taken of a number of the asymmetric membranes to illustrate the effects of various surfactants on the physical structure of the porous membrane matrix and the skin layer. Micrographs were obtained only for those membranes where the dope had been modified with a surfactant.

Solution Casting of Dense Polymer Films

Thick films of PSF were cast into glass Petri dishes from a chloroform solution; 18 g PSF was added to 882 g CHCl₃ to make a stock solution. The surfactants were not all soluble in the chloroform, and were premixed with a small amount (10 mL) of methanol, which was added to the stock solution before casting. The films were left for 24 h to allow the solvents to evaporate, and then dried for 24 h at 120°C, which is well above the boiling point of chloroform. Thermogravimetric analysis indicated that <1% of chloroform remained in the films after drying. The amount of solution was calculated to produce a film with a thickness of about 100 microns for a casting dish of a specific diameter.

Analysis of Dense Films

The films were cut into 5×10 mm rectangles for analysis with a Cahn dynamic contact angle analyser. Water and methylene iodide were selected as polar and nonpolar measuring liquids, and



Figure 1. Oxygen permeation rate through hollow fiber membranes after addition of different surfactants to the spinning solution. Rates were measured at 6 and 10 bar.

both advancing and receding contact angles were determined. The difference between these contact angles represents the contact-angle hysteresis. At least three, but usually more, runs were performed on each film. Total surface free energy, as well as its dispersion and polar components, was calculated from the advancing contact angles by a method adapted from Owens and Wendt.²³ The glass transition temperatures of the films were determined by differential scanning calorimetry on a Perkin-Elmer DSC7 at a scanning rate of 10°C/min. The permeability of the films to several pure permanent gases was measured in barrers on a Yanaco GTR20 Gas Permeability Analyzer connected to a gas chromatograph. One barrer is $10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm/cm}^2 \cdot \text{s} \cdot \text{cmHg}.$

Hollow Fiber Membranes

Surfactant in the Spinning Solution

The summarized results of surfactant addition on the gas transport properties of the hollow-fiber membranes are shown in Figures 1 and 2. Figures 3 and 4 show the effect of increasing the concentration of one surfactant (PAO) in the spinning solution. When evaluating membranes, it is important to consider the flux of the product gas (e.g., O_2) together with the efficiency of O_2 separation or selectivity. In practice, an increase in either will effectively reduce the membrane area for a given separation, but it is frequently found that there is a trade-off between selectivity and permeation rate or flux.²⁴ Figures 1 and 2 show that the major effect of adding a surfactant is that it changes the O_2 permeation rate, whereas the oxygen recovery (i.e., O2/N2 selectivity) does not vary significantly. Recovery at 10 bar is increased



Figure 2. Percentage O_2 recovery from air (selectivity) at 6 and 10 bar for the membranes of Figure 1.

by addition of PKO, KO, and PFA, but at the expense of permeation rate. The most notable improvement was an increase of 1.6% in O_2 recovery. By way of perspective, the standard deviation on $\%O_2$ recovery for the control (16 membranes) was 1.6 (3.2%) at 6 bar and 2.1 (4.3%) at 10 bar. For the membranes containing surfactants (Figs. 1-6) the standard deviation on $\%O_2$ recovery (four to six membranes) ranged from 0.6-2.3(1.2-4.5%) at 6 bar, and from 0.5-2.6 (0.9-4.8%) at 10 bar. Therefore, the abovementioned selectivity improvement of 1.6% is not considered significant. In general, the O_2 permeation rate is reduced when the oxygen recovery or selectivity is improved. The most promising results are found for PAO where the permeation rate is about 44% higher than that of the controls, with only a slightly reduced O_2 recovery.

With regard to Figures 3 and 4, an increase in the concentration of PAO from 0.1 to 0.5% reduces the permeation rate. At 0.5% PAO the O_2 recovery is significantly higher than the control, while the permeation rate is about 70–75% lower. At 0.1% PAO the converse is true, and at 0.2% PAO both

 O_2 recovery and permeation rates are higher than the control. It appears that the addition of PAO at low concentrations can be used to produce membranes with a higher flux and only a negligible change in O_2 recovery (selectivity).

These results were extended by measuring the permeation rate of some of the membranes to six permanent gases: He, H₂, CO₂, O₂, N_{,2}, and CH₄. The membranes were formed with each of two fluorinated surfactants: PAO (long fluorinated tail) and PFA (short fluorinated tail). As shown in Table II, the trade-off between selectivity and permeation rate was also observed for the separation of He, H₂, CO₂, and O₂ from the heavier gases N₂ and CH₄. Thus, improved selectivities of the four gas pairs with PFA were accompanied by a loss in permeation rate of the fast gas of each pair. Conversely, PAO increased permeation rate at the cost of selectivity.

These results suggest that two aspects of the membrane structure could have been modified by the addition of a surfactant to the spinning solution. The first aspect is that the surfactant incorporated into the polymer of the selective layer (skin) of the membrane could have changed the gas separation properties of the polysulfone skin. The second aspect is that the surfactant could have changed the physical structure of the porous membrane substrate or the transition region immediately below the skin. In this case, a more open porous structure could account for an increase in permeation rate by increasing the porosity of the transition region below the skin and there by reducing the resistance to gas flow. In some membranes there may have been damage to the skin, which would account for a concomitant decrease in selectivity (O_2 recovery). Because all of the membranes had been coated with a thin layer (about 1 μ m) of poly(dimethyl siloxane)



Figure 3. Oxygen permeation rate at different concentrations of PAO in the spinning solution. Rates were measured at 6 and 10 bar.



Figure 4. Percentage O_2 recovery from air (selectivity) at 6 and 10 bar for the membranes of Figure 3.

		G	Permeation Rate (mL/min)						Ideal Selectivity				
Bore Fluid		(wt %)	He	H_2	O_2	N_2	CH_4	CO_2	O_2/N_2	$\rm CO_2/CH_4$	$\rm H_2/CH_4$	$\rm He/CH_4$	
Water (Contro Water and	l)		255	265	28.3	4.5	4.7	133	6.3	28.3	56.4	54.3	
Surfactant	PFA PAO	$\begin{array}{c} 0.1 \\ 0.1 \end{array}$	$\begin{array}{c} 153 \\ 260 \end{array}$	$\begin{array}{c} 158 \\ 305 \end{array}$	$\begin{array}{c} 16.5 \\ 28.5 \end{array}$	$2.2 \\ 5.3$	$2.6 \\ 5.9$	$\frac{88}{155}$	$\begin{array}{c} 7.5 \\ 5.4 \end{array}$	$33.9 \\ 26.3$		$\begin{array}{c} 58.9\\ 44.1\end{array}$	

 Table II Effect of Surfactant in the Spinning Solution on Permeation and Selectivity

 of Permanent Gases

prior to testing, it is unlikely that skin damage is a significant issue. To further clarify the possibilities raised above, the macroscopic membrane structure was investigated by SEM analysis, and the effect of incorporating surfactants into the polymer was determined by casting dense homogeneous PSF films and subjecting them to various analyses.

Membrane Structure

The SEM micrographs for the different surfactants are shown in Figure 5. These indicate a clear difference between the porous substructure of the control membrane and that of the membranes impregnated with the surfactants PFA and PAO. The impregnated membranes appeared to have larger voids and a more open porous structure. Although the detailed structure of the transition region directly below the skin cannot be seen on the micrographs, it is also expected to have larger voids and, consequently, offer less resistance to gas permeation.

When a surfactant is added to the spinning solution, it will usually affect the surface energy (surface tension) of one or more of the components of the solution. It is not clear whether the primary effect would be to associate with the polymer or with one or more liquid components of the solution. Kesting² has suggested the presence of spheroidal nodular structures during the formation of a membrane from solution, and SEM studies by Panar et al.²⁵ have shown such structures in the vicinity of the membrane skin. Kesting proposes the formation of micellar aggregates immediately prior to phase separation, which later rupture to form the open porous structure of a phase inversion membrane. Such structures were also confirmed by Wienk et al.²⁶ for polyethersulfone membranes.

From another perspective, a three-component or ternary spinning solution passes into the binodal and subsequently the spinodal regions on a ternary phase diagram during membrane formation.²⁷ Binodal decomposition results in spheroid solvent-rich regions in a continuous polymerrich phase, while spinodal decomposition gives rise to an interpenetrating network of polymer and solvent-rich phases. It is generally assumed that the membrane substructure results from spinodally decomposed phases, but the effect of binodal decomposition cannot necessarily be ignored. In both cases, the resulting solvent- and polymer-rich phases have predominantly curved surfaces. Although the more complex spinning solutions of this study contain five and not three components, the essential mechanism is expected to be broadly similar to that of a ternary spinning solution.

How these nodular or spheroidal structures form, is not at issue. However, it is suggested that the presence of a surfactant reduces the surface tension of the spinning solution to create larger spheroidal phase-separated regions during membrane formation than in conventional solutions that do not contain a surfactant. After removal of the solvents and nonsolvents the solvent-rich phase constitutes the voids in the final membrane.

This proposition would only partially explain the results reported above, because the surfactant increased the gas permeation rate in certain cases only. For instance, higher concentrations of PAO caused an increase in selectivity and a reduction in productivity of the membranes. The increased selectivity could be due to a number of possible microstructural effects, all of which are related to surface activity during membrane formation; for example, by reduction of the number of minute skin defects or by antiplasticization of the polymer. Pinnau and Koros²⁷ have suggested that skin formation is caused by surface tension forces that draw together the spheroidal structures of





(c)

Figure 5. Scanning electromicrographs of cross-sections of hollow-fiber membranes; (a) no surfactant in the spinning solution, (b) 0.1% of a long-tailed fluorinated surfactant PAO and (c) 0.1% of a short-tailed fluorinated surfactant PFA.

the nascent membrane as the solvent evaporates. Because addition of a surfactant modifies the surface tension of the spinning solution, it appears possible that the closing of defects during skin formation may also be affected.

Although the surfactant appears to have modified the membrane structure, there was still the possibility that polymer–surfactant interaction in the skin could account for the observed increase in selectivity of the membranes. To investigate this issue, different surfactants were incorporated into a simple polymer (PSF) solution and cast as homogeneous dense thick films, so that the intrinsic properties of the polymer could be studied independently of the membrane. These results are considered after the following two subsections.

Surfactant in the Quench Medium

Initially, the formation of a hollow-fiber membrane involves two simultaneous phase separation processes: one in the bore of the membrane induced by the bore fluid, and another at the outer surface to form the skin. The outer surface is first exposed to a convective air current and is then quenched in water. In separate experiments, surfactant was added to either the bore fluid or to the quench bath medium. The transport properties of the membranes prepared in this way are shown in Figures 6 and 7 for O_2 recovery from air, and in Table III for a series of six permanent gases: He, H₂, CO₂, O₂, N₂, and CH₄.

Figure 6 shows that 0.2% of PAO and PKO increased the oxygen flux through the mem-



Figure 6. Oxygen permeation rate through hollowfiber membranes made by the addition of different surfactants (at 0.1 or 0.2%) to the aqueous quench medium. Rates were measured at 6 bar and 10 bar.

branes, with PKO having the greater effect at both 6- and 10-bar testing pressure. In both cases, the increase in flux was accompanied by a decrease in O₂ recovery, the effect for PKO being quite drastic. A similar tradeoff between O₂ recovery and permeate flux was apparent for the other concentrations and types of surfactants. Thus, 0.1% of KO in the quench bath improved the O_2 recovery, but the flux was considerably lower than that of the control. Table III indicates that the addition of 0.2% PAO yields a membrane that is particularly suitable for oxygen/nitrogen separation. The membrane with 0.2% KO in the quench medium had the highest selectivities for He/CH_4 and H_2/CH_4 , and also the highest fluxes for He and H_2 .

These results suggest that the surfactant in the quench medium either influences the integrity of the skin, i.e., the number of defects, or that some surfactant is transferred from the quench medium to the polymer of the skin where the



Figure 7. Percentage O_2 recovery from air (selectivity) from the hollow-fiber membranes of Figure 6.

permeability of the polymer is changed. All membranes were coated with silicone rubber prior to permeability tests, so that the effect of the surfactant on defect formation is not readily detectable. Rather, it is proposed that the surfactant has produced some form of physical modification of the polymer in the skin region, such as modified interchain spacing.

Modification of the Bore Fluid

The motivation for adding a surfactant to the bore fluid is to influence the formation of the membrane's porous matrix through phase separation. The effect of the bore fluid was investigated by dissolving surfactants in the bore water, or alternatively by substituting the water with an alcohol. Three surfactants (PAO, PKO, and KO) were added at concentrations of 0.1 or 0.2%. Results were compared to the use of methanol, ethanol, or iso-propanol, instead of pure water. The gas transport properties of the resultant membranes are shown in Table IV.

		~		Perme	ation]	Rate (r	nL/min))	Selectivity				
Bore Fluid		Conc (wt %)	He	${\rm H}_2$	O_2	N_2	CH_4	CO_2	0 ₂ /N ₂	$\rm CO_2/CH_4$	$\mathrm{H_2/CH_4}$	${\rm He/CH}_4$	
Water (Con Water and	ntrol) Surfactar	nt	270	268	28	4.1	4.2	132	7.0	32.2	45.7	41.7	
In Quench													
Bath	PAO	0.2	304	360	33	4.8	7.6	170	6.9	22.4	47.4	40.0	
	PKO	0.1	250	250	28	6.0	5.6	124	4.7	22.1	44.6	44.6	
		0.2	260	290	30	5.4	7.2	130	5.6	18.1	40.3	36.1	
	KO	0.1	210	240	23	4.2	4.8	80	5.5	16.7	50.0	43.8	
		0.2	310	310	34	6.4	6.4	170	5.3	26.6	48.4	48.4	

Table III Effect of Quench Medium on Gas Permeability and Selectivity for Permanent Gases

		a	Permeation Rate (mL/min)						Selectivity				
Bore Fluid		Conc (wt %)	He	${\rm H}_2$	0_2	N_2	CH_4	CO_2	O_2/N_2	$\mathrm{CO}_2\!/\mathrm{CH}_4$	$\rm H_2\!/\rm CH_4$	${ m He/CH}_4$	
Water (control Water and)		270	268	28	4.1	4.2	132	7.0	32.2	65.7	66.6	
Surfactant	PAO	0.1	266	256	26	3.2	4.8	126	8.1	26.3	53.3	55.4	
		0.2	250	262	25	4.4	6.0	128	5.8	21.3	43.7	41.7	
	PKO	0.1	310	310	32	5.2	5.6	150	6.2	26.8	55.4	55.4	
		0.2	264	270	28	4.6	5.8	130	6.1	22.4	46.6	45.5	
	KO	0.1	256	290	27	5.2	6.4	150	5.2	23.4	45.3	40.0	
		0.2	260	264	28	5.0	4.6	150	5.6	32.6	57.4	56.5	
Methanol			264	286	32	8.4	10.0	170	3.8	17.0	28.6	26.4	
Ethanol			280	320	30	5.4	5.2	150	5.6	28.8	61.5	53.8	
Isopropanol			20	21	а	а	а	9	а	а	а	а	

Table IV Effect of Bore Fluid Composition on Gas Permeability and Selectivity for Permanent Gases

^a Permeation rate too slow to measure.

Table IV indicates that the selectivities of the control membranes mostly exceeded that of the other membranes. The exception is the higher O_2/N_2 selectivity after the addition of 0.1% PAO, which is due to the low N₂ permeation rate. The small increases in productivity resulting from surfactants in the bore fluid were offset by a concomitant decrease in O_2 recovery. The substitution of methanol and I-propanol for water had a deleterious effect on the membrane properties, although ethanol yielded results comparable to pure water. It appears that no apparent advantage is gained by addition of surfactants to the bore fluid. Presumably, the bore fluid affects only the macroporous membrane matrix, which has no impact on gas transport properties, while the porous transition region immediately beneath the skin is not affected.

Surfactant-Modified Homogeneous Dense Films

Film Morphology

It proved impossible to cast homogeneous and clear films from chloroform solutions of all of the surfactant/polymer combinations. In particular, PAO yielded films with a lacy appearance and large holes that could not be used for permeation or contact angle measurements. Even the use of other solvents, such as *N*,*N*-dimethyl acetamide, could not produce viable films with PAO. Films produced with PKO and KO had a milky appearance that indicates an inhomogeneity of some kind. Milkiness and crack formation were observed at higher surfactant concentrations.

When a PSF solution dries, the solvent evaporates and the PSF concentration of the remaining solution increases steadily. During this process the surfactant may associate preferentially with either the polymer or the solvent. The two surfactants, BFA and PFA, with the shortest fluorinated tails produced the clearest films, particularly at lower surfactant concentrations. The counterion also appears to play an important role, because PAO with the NH_4^+ counterion would not produce homogeneous films at all. This is in contrast to PKO, which is identical but for its potassium counterion. When both have a coordination number of six, the potassium ion has an estimated radius of 1.38 Å, compared to the ammonium ionic radius of about 1.46 Å.²⁸ However, the latter is expected to have strong hydrogen bonding potential in addition to its ionic character.

One explanation for the observations is that the lyophobic tail of the surfactant associates primarily with the polymer chain in solution and so increases the ionic interchain interactions as the solution becomes more concentrated. Surfactants with longer tails (PAO, PKO, and KO) may limit the polymer chain's flexibility more than those with short tails (PFA and BFA) and cause aggregation of the polymer at lower surfactant concentrations. The $\rm NH_4^+$ counterion of PAO may then promote interchain attractions, resulting in aggregation as the polymer becomes concentrated, possibly through a combination of ionic and hydrogen bonding attractions.

Surfactant	None	BFA		PI	FA	PI	KO	KO		PAO	
Conc (wt %)	0	1.0	1.65	0.33	1.65	0.33	1.65	0.33	1.65	0.33	1.65
T_g [°C]	181	175	174	177	174	162	166	176	181	177	170

Table V T_g of PSF Films Impregnated with Surfactant

Glass Transition Temperature

Table V compares the glass transition temperatures (T_g) of PSF films containing various concentrations of the five surfactants, as determined by differential scanning calorimetry. It was possible to obtain a T_g for the PSF impregnated with PAO, because the DSC analysis does not depend on the integrity of the cast film. The concentration indicates the mass percentage of surfactant in the dry polymer film.

These data indicate that the addition of surfactant decreases the T_g . This suggests a disruptive effect or interference with interchain packing in the solid polymer. PKO has the most pronounced effect, and its unfluorinated analogue KO has the least effect. The effect of surfactant concentration does not show the same trend for all of the surfactants; the PKO and KO (both having a potassium counterion) cause an increase in T_g with increasing concentration, whereas the other surfactants have the opposite effect. The significance of this observation is not readily apparent.

Contact Angles and Surface Free Energy

Figure 8 shows the advancing contact angles of PSF films impregnated with the two short-chain surfactants, PFA and BFA. The advancing con-



Figure 8. Advancing contact angles for water and methylene iodide (MI) on PSF films impregnated with short-tailed anionic fluorinated surfactants: PFA and BFA.

tact angles for water and methylene iodide (MI) were measured at surfactant concentrations in the film ranging from 0 to 3.0 g surfactant per gram of PSF. It appears that the ionic surfactant (PFA) reduces the water contact angle relative to the control film, which contained no surfactant, while the presence of BFA had no measurable effect. The contact angles for methylene iodide, which is essentially a nonpolar liquid, are not markedly influenced by the addition of surfactant. Thus, the addition of the ionic surfactant tends to increase the polarity of the polymer surface, i.e., improve the water wettability. The water contact angle continues to decrease as progressively more PFA is added. The concentration of 1.5 g PFA/g PSF apparently constitutes a minimum contact angle.

The contact angles for water and MI were used to compute the total surface free energy of the impregnated PSF films, as well as the polar and dispersive free energy components. Figures 9 and 10 show these free energies for PFA and BFA, respectively. In both figures the total free energy is maximized at a surfactant concentration of 1.5 g surfactant/g PSF; this corresponds to the observed maximum of PFA on the water contact angle. A comparison of the two figures shows that the polar and dispersive components respond dif-



Figure 9. Surface free energies of solution cast PSF films impregnated with PFA, showing total (\blacktriangle) surface free energy, as well as its polar (\bigcirc) and dispersive (\blacksquare) components.



Figure 10. Surface free energies of solution cast PSF films impregnated with BFA. The symbols are the same as for Figure 6.

ferently to addition of the ionic (PFA) and nonionic (BFA) surfactants. In Figure 9, the polar component increases with increasing PFA concentration up to the maximum, while the dispersive component shows a continuous decrease. As expected for BFA in Figure 10, the total surface energy is due mainly to the dispersive component, with little change in the polar component as BFA concentration increases.

The only difference between PFA and BFA is that former has an ionic head, and the latter has an aromatic nonionic head. Table I shows that the HLB values (hydrophilic-lipophilic balance) of these surfactants differ markedly, emphasizing the large difference in polarity or solvent interaction between the head and tail portions of PFA. If the fluorinated tail portion of the PFA were to associate with the polymer chain, then the ionic head would extend outward and render the whole polymer more ionic in nature, resembling a polyelectrolyte. This would explain the marked increase in polarity of the polymer as increasing amounts of PFA are incorporated. An apparent maximum could be explained if a polymer chain becomes saturated with PFA molecules and some surfactant molecules form an inverse "double layer" on associated PFA molecules. Such headto-head associations could be mediated by counterions, which bridge the negatively charged heads of the surfactant, and this should lower the polarity of the polymer chain. It is also possible that micelles form, either attached to the polymer chain or in the free solution. The results for BFA do not indicate whether the fluorinated tail or aromatic head is preferentially associated with the polymer.

Gas Separation

Figure 11 shows the effect on the gas transport properties of dense polysulfone films when different concentrations of PFA and BFA are dispersed in the polymer. A feature of both graphs is that the selectivity for the gas pair O_2/N_2 is increased above that of the control by addition of both PFA and BFA. The concomitant reduction in permeability is almost negligible. A second feature is that these observations are valid up to a concentration of 1.5 g surfactant/g PSF. Higher concentrations lead to a drastic deterioration in transport properties. This could be due to several factors, i.e., to inhomogeneity or actual cracks in the films, or to the presence of surfactant double layers or micelles, as discussed.

The improved selectivity is significant, in that it corresponds to the change in transport proper-



Figure 11. Oxygen permeation rate and O_2/N_2 selectivity of solution cast dense polysulfone films impregnated with PFA (upper graph) and BFA (lower graph). The left ordinate (\bullet) shows O_2 permeability, and the right ordinate (\blacktriangle) the selectivity.

ties observed for membranes containing surfactants, as demonstrated in previous sections. The surface energy and glass transition temperature measurements suggested that the surfactants associate with the polymer chain, and this can be expected to influence chain packing and interchain spacing, both of which may influence the diffusion properties of a gas in a polymer. Generally, an increase in interchain distances, such as occurs during plasticization of a polymer, would increase diffusion coefficients and reduce the separation factor or selectivity. However, certain additives may have the opposite effect at low concentrations in a phenomenon known as antiplasticization. Antiplasticization has been shown to increase the selectivity of a pure polymer, such as polysulfone.¹⁴ If the surfactants in this study do act as antiplasticizers, then their presence in the polymer skin may increase the selectivity at the expense of the permeability. Maeda and Paul¹⁴ showed that this effect is accompanied by a reduction in intramolecular free volume, which suggests more closely packed polymer chains. It should be noted that antiplasticization effects also depend on the concentration of the additive.

CONCLUSIONS

This study has demonstrated that surfactants introduced into the spinning solution have a definite and measurable effect on the gas transport properties of hollow-fiber polysulfone (PSF) membranes. In general, there is a modest increase in selectivity, expressed as the percentage recovery of O₂ from air. For all but two of the surfactants, the change in selectivity was accompanied by a decrease in permeation rate, i.e., the O_2 flux through the membrane. In particular, the addition of perfluoroammonium octanoate (PAO) produced membranes with significantly improved properties. At 0.1% PAO the membrane flux was increased by 44%, with only a small loss of selectivity. At the same concentration, addition of PKO and KO had improved selectivities with only a modest decrease in permeation rate.

The concentration of surfactant appears to affect both the selectivity and the permeation rate of these membranes. Increasing the concentration of PAO from 0.1 to 0.5% (by weight) steadily decreased the permeation rate, but had varying effects on the selectivity. At 0.2% PAO, both the selectivity and permeability were increased, indicating that this was the optimum concentration for the particular polymer-surfactant combination.

In an attempt to better understand the origin of these effects, different surfactants at different concentrations were incorporated into thick PSF films by solution casting. Films made from pure PSF, and from PSF with PFA and BFA (both short-chain fluorinated surfactants), were clear and transparent at low surfactant concentrations and somewhat milky at higher concentrations. All films cast from the other surfactants (long-tailed, fluorinated and unfluorinated) showed considerable cloudiness or structural defects. The glass transition temperatures were reduced by all surfactants, PKO having the greatest effect. Increasing concentrations of PFA and BFA caused an increase in total surface free energy up to a maximum; this correlated with an increase in O_2/N_2 selectivity and a corresponding small decrease in O_2 permeation rate.

It is suggested that the lyophobic tails of the surfactants interact with the polymer chains, both during membrane formation and film formation. This may alter the packing of polymer chains after the solvent has been removed. SEM images show that membranes with surfactants have larger voids in the porous part of the membrane matrix, which could explain the higher permeation rate for oxygen. Permeation studies on thick films impregnated with surfactant also suggest that surfactants improve selectivity in the membrane skin, possibly by an effect similar to antiplasticization.

The authors wish to thank the Atomic Energy Corporation of South Africa, and particularly Dr. Venter, who supplied the surfactants; Dr. Wagener for assistance with the DCA; and Dr. Carstens, Ms. Pieterse, Ms. Willemse, and Mr. Strydom for technical support and assistance.

REFERENCES

- Paul, D. R.; Morel, G. in Kirk-Othmer: Encyclopedia of Chemical Technology; John Wiley & Sons, Inc.: New York, 1981.
- Kesting, R. E. Synthetic Polymeric Membranes; John Wiley & Sons: New York, 1985.
- Koros, W. J.; Fleming, G. K.; Jordan, S. M.; Kim, T. H.; Hoehn, H. H. Prog Polym Sci 1988, 13, 339.
- 4. Langsam, M. 1987, U.S. Pat. 4,657,564.
- Mohr, J. M.; Paul, D. R.; Mlsna, T.; Lagow, R. J. J Membr Sci 1991, 55, 131.
- Le Roux, J. D.; Paul, D. R.; Kampa, J.; Lagow, R. J. J Membr Sci 1994, 90, 21.

- Le Roux, J. D.; Paul, D. R.; Kampa, J.; Lagow, R. J. J Membr Sci 1994, 94, 121.
- Rezac, M. E.; Le Roux, J. D.; Chen, H.; Paul, D. R.; Koros, W. J. J Membr Sci 1993, 90, 213.
- 9. Stern, S. A. J Membr Sci 1994, 64, 1.
- Pixton, M. R.; Paul, D. R. in Polymeric Gas Separation Membranes, D. R. Paul and Y. P. Yampol'skii, Eds., CRC Press: Boca Raton, FL, 1994.
- Lerma, M. S.; Iwamoto, K.; Seno, M. J Appl Polym Sci 1987, 33, 625.
- Tam, C. M.; Matsuura, T.; Tweddle, T. A.; Hazlett, J. D. Sep Sci Technol 1993, 28, 2621.
- Bikson, B.; Nelson, J. K.; Muruganandam, N. J Membr Sci 1994, 94, 313.
- 14. Maeda, Y.; Paul, D. R. J Polym Sci Polym Phys Ed 1987, 25, 957.
- 15. Hayes, R. A. 1991, U.S. Pat. 5,034,024.
- 16. R. A. Hayes, 1991, U.S. Pat. 5,032,149.
- 17. Myers, D. Surfactant Science and Technology; VCH Publishers, Inc.: Weinheim, 1988.

- Allison, M. C. in Industrial Applications of Surfactants, D. R. Karsa, Ed., The Royal Society of Chemistry: London, 1986.
- Esumi, K. K. and Ogiri, S. Colloids Surfaces A: Physicochem Eng Aspects 1995, 94, 107.
- 20. Lin, I. J. J Phys Chem 1972, 76, 2019.
- 21. Pinnau, I.; Koros, W. J. 1990, U.S. Pat. 4,902,422.
- 22. Pesek, S. C.; Koros, W. J. J Membr Sci 1994, 88, 1.
- Owens, D. K.; Wendt, R. C. J Appl Polym Sci 1969, 13, 1741.
- 24. Robeson, L. M. J Membr Sci 1991, 62, 165.
- 25. Panar, M.; Hoehn, H.; Herbert, R. Macromolecules, 1973, 6, 777.
- Wienk, I. M.; Van den Boomgaard, T.; Smolders, C. A. J Appl Polym Sci 1994, 53, 1011.
- 27. Pinnau, I.; Koros, W. J. J Polym Sci Polym Phys Ed 1993, 31, 419.
- Shriver, D. F.; Atkins, P. W.; Langford, C. H. Inorganic Chemistry; Oxford University Press: Oxford, 1990.