Effects of Incorporation of Fluorocarbon and Hydrocarbon Surfactants into Perfluorosulfonic Acid (Nafion) Membranes

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Significant permeability improvements can be made to perfluorinated ionomer films by incorporating sulfonated surfactants of suitable size into the membrane microstructure. A variety of 20-μm composite Nafion/surfactant membranes were prepared from DMF casting solutions containing Nafion and the sodium salts of perfluoro-1-butanesulfonic acid (*perf*-$ButSO_3Na$), perfluoro-1-octanesulfonic acid (*perf*-$OctSO_3Na$) and 1-octanesulfonic acid ($OctSO_3Na$). The time required for 50% extraction of the surfactants from the membranes into water was 1 min for $OctSO_3Na$, 5 min for *perf*-$ButSO_3Na$, and approximately 3 days for *perf*-$OctSO_3Na$. Extraction of *perf*-$OctSO_3Na$ into isooctane contacting solutions was not observable over periods of days. For membranes containing surfactants and exchanged with silver(I) ion, 3-fold permeability improvements can be obtained for the separation of 1,5-hexadiene from 1-hexene and *n*-hexane without any decreases in separation factors. Observed flux improvements are larger than the increase in ion-exchange site density and are attributed to increased mobility of olefins between carrier sites due to the presence of specific surfactants. Results indicate that movement of olefins in Nafion occurs primarily through an interfacial region of the film structure. The ability of a surfactant to improve transport performance is dependent on its ability to partition into the interfacial region.

Introduction

Perfluorinated ionomer membranes such as Nafion[1] have numerous uses in both industrial chemical practice and in chemical research. Applications include the chlor–alkali process,[2,3] H_2/O_2 fuel cells,[3–5] biomedical sensing[6,7] and other types of chemical sensors based on modified electrodes.[8,9] Recent findings also demonstrate their effectiveness in chemically facilitated separations of molecules. Way and Noble have shown that contaminated natural gas can be purified using protonated ethylenediamine as a facilitated transport carrier,[10,11] and Koval et al. have shown that olefins can be effectively separated from similar compounds using a Nafion film in the Ag^+ form.[12–15] Favorable physical and chemical properties such as solvent resistance, permselectivity, and physical stability make Nafion a particularly useful membrane material. A significant barrier to more widespread use of perfluorinated ion-exchange membranes in separations processes is their relatively high resistance to mass transport. Molecules diffusing through the polymeric matrix of Nafion show much smaller diffusivities than through other membranes such as immobilized liquid films.[16] Previous workers have had some success in decreasing membrane resistance by swelling a Nafion film in various alcohols, but these strategies typically reduce the separating ability and favorable physical properties of the membrane.[13,17] Another group attempted to increase mass transport by restructuring the microenvironment of Nafion when supported in the pores of a polycarbonate membrane.[18]

Goals of the present work were to increase the facilitated transport performance of Nafion membranes while preserving the favorable physical characteristics of the native polymer film and to clarify the transport mechanisms operating within these membranes. The strategy was to incorporate surfactant molecules (dopants) into the membrane microstructure during the membrane casting procedure such that they would be retained within the film and available to improve facilitated transport. A previous report described gas transport properties through

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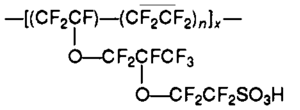
surfactant-doped Nafion membranes from which the dopants had been extracted.[19]

Extensive evidence suggests that Nafion is a phase separated material consisting of a hydrophilic network of reverse micellar ionic clusters within a hydrophobic semicrystalline fluorocarbon region.[20,21] The ionic regions can absorb large amounts of water, amounting to 10–40% of the dry mass of the membrane depending on treatment protocol and counterion.[3,13] The fluorocarbon and ionic regions are likely separated by an interfacial region with properties between those of the other two phases. Previous work in our group has shown that molar concentrations of species such as 1-hexene can partition into a Nafion membrane containing Ag^+ as a complexing agent.[12] Such large quantities of hydrophobic organic complexed to silver must, for solubility reasons, be localized in an interfacial region of the film. For the present study, a dopant was sought that would associate itself in this interfacial region. The preferred molecule would resemble the basic structure of Nafion to allow effective incorporation, have an ion-exchangeable site to carry Ag^+, and not be very water soluble. The dopants investigated here were the sodium salts of perfluoro-1-butanesulfonic acid (*perf*-ButSO$_3$Na), perfluoro-1-octanesulfonic acid (*perf*-OctSO$_3$Na), and 1-octanesulfonic acid (OctSO$_3$Na). The structure of Nafion(H^+) is



$$\begin{array}{l} -[(CF_2\underset{|}{C}F)-(CF_2CF_2)_n]_x- \\ \qquad O-CF_2\underset{|}{C}FCF_3 \\ \qquad\qquad\quad O-CF_2CF_2SO_3H \end{array}$$

Experimental Methods

Membrane Casting Procedures. Membranes were cast from a Nafion polymer solution prepared in the following way: A 5% solution of Nafion (1100 EW, H^+ form, Solution Technologies, Inc., Mendenhall, PA) was evaporated at room temperature to form a thick (~150 μm) film. The film was hydrated in H_2O followed by neutralization in excess 1 M NaOH. The resulting film was rinsed in H_2O, dried at room temperature, and added to sufficient dimethylformamide (DMF) to produce a mixture of 1% Nafion (by mass) in DMF. The mixture was sonicated for 1 h, producing a solution that was visually free of all solid material. The solution was then filtered through a 5-μm Millex LCR filter (Millipore Corp., Bedford, MA). This solution of 1% Nafion(Na^+) in DMF constituted the fundamental casting solution. Straight-chain 98% $CH_3(CH_2)_6CH_2SO_3Na$ was obtained from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. $CF_3(CF_2)_7SO_3Na$ was prepared by stirring 98% $CF_3(CF_2)_7SO_2F$ (Aldrich) in excess aqueous NaOH overnight at 45 °C and recrystallizing from water. $CF_3(CF_2)_3SO_3Na$ was made in the same fashion from 96% $CF_3(CF_2)_3SO_2F$. Each dopant was dissolved in sufficient DMF to make 1% solutions (by mass) and filtered through 5-μm Millex LCR filters.

Membranes were made by mixing the Nafion casting solution with varying amounts of one of the dopant solutions in a shallow glass dish and evaporating the solvent at 150 °C and reduced pressure (250 Torr) for 2–3 h. After cooling, immersion in water for 1 min detached the film from the glass surface. Film thicknesses were measured using an Ames model 135 GF Bench Comparator (Waltham, MA) and are accurate to ±1 μm.

Scanning Electron Microscopy. Electron micrographs of cross sections of an undoped membrane and a membrane doped with *perf*-OctSO$_3$Na at the 20% level (see membrane casting results) were obtained using a Cambridge Instruments Model 250MK3. Membrane samples cast as described above were dried overnight in a vacuum desiccator, mounted on SEM stubs using double-sided tape, sputter-coated with gold, and placed in the SEM instrument. The magnification factor was 3000.

Extraction of Dopant from Membranes. The rate of dopant extraction from cast membranes was determined using high-performance liquid chromatography (HPLC). Each membrane sample (0.1 g) was stirred in 20 mL of either water or water-saturated 2,2,4-trimethylpentane (isooctane), with aliquots taken at various time intervals for analysis by HPLC. The chromatographic system consisted of a Hewlett-Packard 1050. Aqueous samples were injected directly into the HPLC, while isooctane samples were extracted into H_2O and the aqueous phase injected. Those membrane samples stirred in isooctane were subsequently stirred in 20 mL of water for 1 week, after which the extracting solutions were examined for dopant by HPLC. The separation of alkylsulfonates by HPLC has been previously reported.[22]

Ion Exchange Rate. The ion-exchange rate of Na^+ for Ag^+ in cast Nafion films was studied by atomic emission (AE) spectroscopy. The AE instrument was a Perkin-Elmer 360 detecting the sodium emission line at 589 nm. Each membrane sample (0.015 g) initially in the Na^+ form was dried in a vacuum desiccator overnight, weighed, contacted with 10 mL of 0.3 M $AgNO_3$ for a specific length of time, and then removed. Excess 1 M HCl was added to each solution to isolate the Ag^+ as AgCl, and the precipitate was separated out by centrifugation. The solutions were then introduced into the AE instrument for Na^+ analysis. Control experiments verified that the precipitation of AgCl did not interfere with Na^+ quantitation at the levels involved in this analysis.

Flux Measurements. Olefin-transport experiments using Ag^+ as a facilitated transport carrier in cast Nafion films were performed using an experimental protocol similar to that previously described with the following modifications.[13] The transport cell was designed such that a vertically mounted membrane separated the feed and sweep solution reservoirs. Samples were ion exchanged in excess 1.0 M silver nitrate for 3 min with stirring, rinsed in water for 1 min, and then contacted with the organic feed and sweep solutions. The feed consisted of isooctane containing 0.5 M each of 1,5-hexadiene, 1-hexene, and *n*-hexane (Aldrich). The sweep phase consisted of pure isooctane. The stirred solutions were saturated with H_2O to reduce water loss from the membrane. Aliquots were taken from the sweep phase and analyzed for permeates by gas chromatography.

Olefin Concentrations in Membranes. Concentrations of 1,5-hexadiene and 1-hexene in hydrated membranes (Ag^+ form) were measured by a previously described method with the following modifications.[13] Each membrane sample (0.1 g, Na^+ form) was dried in a vacuum desiccator overnight, weighed, contacted with water for 1 min, immersed in 10 mL of 1.0 M $AgNO_3$ for 3 min, quickly rinsed (5 s) in H_2O, and then shaken in 15 mL of a water-saturated solution containing 0.5 M each of 1,5-hexadiene and 1-hexene in isooctane for 24 h. Each sample was then quickly rinsed (2 s) in fresh isooctane and then shaken in 20 mL of fresh water-saturated isooctane for 48 h. Olefin concentrations in extracting solutions were determined using gas chromatography by the method used for flux measurements. The prior work cited for this procedure indicates that 48 h is sufficient time to quantitatively extract similar olefins from Nafion films into the volume of isooctane specified.

Results and Discussion

Membrane Casting. Dimethylformamide was selected as the casting solvent in part because previous work has shown that Nafion films cast at elevated temperatures from high-boiling polar solvents have superior mechanical strength.[23] DMF is also a good solvent for the dopants studied and does not leave significant solvent residue in the finished film. Membranes were 20 ± 1 μm thick and

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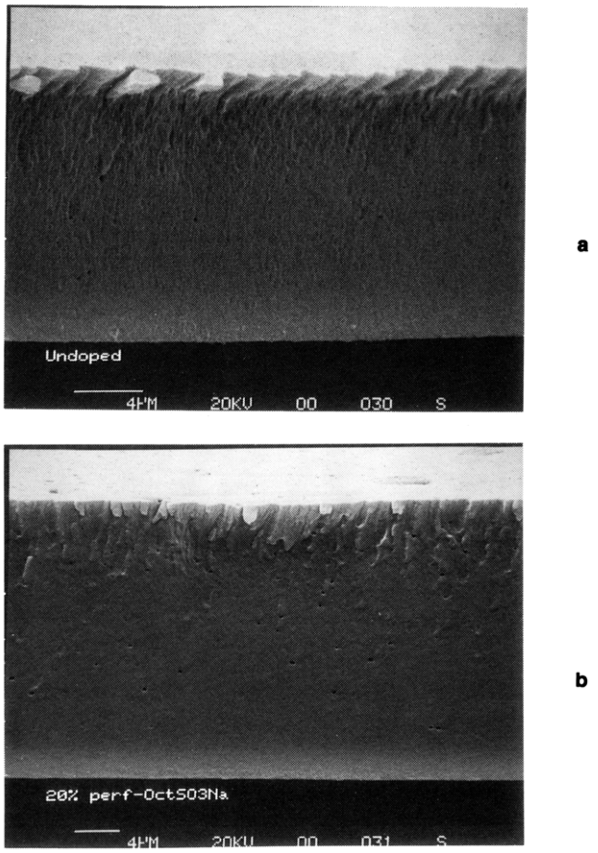

Figure 1. Scanning electron microscope images of membrane samples which are (a) undoped and (b) doped 20% with *perf*-$OctSO_3Na$.

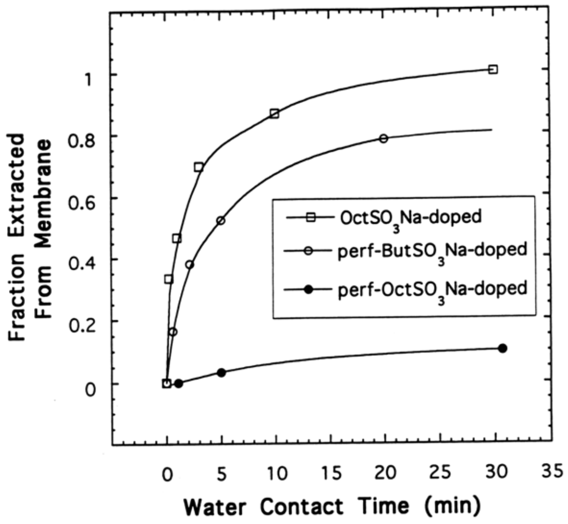

Figure 2. Leaching behavior of doped membranes.

Table 1. Diffusion Coefficients for Dopants and Ions of Similar Size in Nafion

diffusing species	D_{app} (cm^2/s)
$[HO_2C(Pyr)Ru^{II}(Hedta)]^-$	2×10^{-7} (ref 25)
$OctSO_3Na$	3×10^{-9}
$(methylviologen)^+$	4×10^{-10} (ref 26)
perf-$ButSO_3Na$	7×10^{-10}
perf-$OctSO_3Na$	1×10^{-12}

contained dopant mole fractions of 0%, 10%, 20%, and 30%. Mole fractions represent the fraction of sulfonate sites contributed by the dopant in the final cast films prior to contact with any solvents. To provide a sense of the dopant concentration in these films, the concentration of dopant in a 20%-doped membrane would be approximately 1 M if the dopant was homogeneously distributed throughout the film volume. Local dopant concentrations are probably much higher due to localization within the cluster regions. The cast films were free of significant defects (see flux measurements) and were sufficiently sturdy to be easily handled.

Scanning Electron Microscopy. Electron micrographs of an undoped membrane sample and a sample doped with *perf*-$OctSO_3Na$ are shown in Figure 1. The two are very similar, showing the polymer structures to be dense and essentially featureless at this magnification. The presence of this dopant at the 20% level causes no obvious change in the morphology of the membrane. The only discernible features are small voids (0.3–0.4 μm in diameter) observable in both the doped and undoped samples, probably the result of the high-temperature casting procedure.

Extraction of Dopant from Membrane. Figure 2 describes the leaching behavior of 20%-doped membranes in contact with water. The maximum dopant concentrations in the H_2O extractant solutions assuming 100% extraction would be about 1 mM, which is below the solubility limit for these compounds in water. Expansion of Figure 2 indicates that the time required for 50% extraction of each of the dopants is 1 min for $OctSO_3Na$, 5 min for *perf*-$ButSO_3Na$, and approximately 3 days for *perf*-$OctSO_3Na$. While leaching experiments were performed only on membranes doped at the 20% level, one can assume roughly similar behavior for membranes doped at the 10% and 30% levels.

The final result from the leaching experiments is that a film doped with *perf*-$OctSO_3Na$ does not leach any measurable quantity of dopant into water-saturated isooctane, in which it is virtually insoluble, even after several days of contact. Following isooctane contact, these films were extracted into water which was then found to contain 95% of the dopant initially cast into the membrane. This eliminated any concern regarding the efficiency of extracting *perf*-$OctSO_3Na$ from isooctane into water. The lack of any leaching of dopant from the membrane into isooctane demonstrated that the dopant concentration in the membrane was constant during an olefin transport experiment.

The polyanionic nature of Nafion creates an internal membrane environment very inhospitable to additional free anions, and the slow ejection of *perf*-$OctSO_3Na$ is surprising at first glance. Since the process of dopant leaching out of a membrane is analogous to that of reactant consumption in a thin-layer electrochemical cell, one can estimate the effective diffusion coefficient (D_{eff}) of a dopant in a membrane by applying the relationship $M_t = M_0[1 - (8/\pi^2)\exp(-\pi^2 D_{eff} t/l^2)]$, where M_0 = initial mass of dopant cast into membrane, M_t = mass of dopant leached out at time t, and l is the membrane thickness.[24] At the time required for leaching of 50% of the initial mass of dopant ($t_{1/2}$), the expression reduces to $D_{eff} = 0.05l^2/t_{1/2}$. Table 1 provides a comparison of the estimated diffusion coefficients in hydrated Nafion of the dopants studied here to values for ions of similar size that have been studied

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Table 2. Fluxes and Separation Factors for Olefin Permeation through Cast Nafion Films

dopant	dopant amount[a]	flux × 10^9 mol/cm^2 s		separation factor
		1,5-hexadiene	1-hexene	
none	0	11.9	0.428	27.8
$OctSO_3Na$	10%	12.0	0.450	26.7
$OctSO_3Na$	20%	12.4	0.381	32.5
$OctSO_3Na$	30%	11.4	0.420	27.1
perf-$ButSO_3Na$	10%	11.9	0.433	27.5
perf-$ButSO_3Na$	20%	14.4	0.561	25.7
perf-$ButSO_3Na$	30%	15.5	0.588	26.4
perf-$OctSO_3Na$	10%	17.1	0.667	25.6
perf-$OctSO_3Na$	20%	26.4	0.899	29.4
perf-$OctSO_3Na$	30%	31.4	1.14	27.5

[a] Refers to the percentage of sulfonate sites contributed by the dopant in a freshly cast membrane prior to any leaching.

previously.[25,26] The dopants are listed as the ion-paired species, but it is not entirely clear whether they are present in Nafion as free ions or as neutral pairs. The ruthenium complex is both anionic and quite water soluble, therefore its rapid expulsion from the membrane is unsurprising. The dopants $OctSO_3Na$ and *perf*-$ButSO_3Na$ have less water solubility and begin to resemble the Nafion side chains and show diffusive rates more similar to cations such as methylviologen. This slower diffusion out of the membrane indicates that these two dopants have some affinity for the interfacial region of the film structure. The dopant *perf*-$OctSO_3Na$ shows by far the slowest rate of ejection from the membrane of any of the species in Table 1. The extremely slow rate of leaching combined with low water solubility (2–4 mM) indicates that this dopant must partition into the interfacial region.

Ion-Exchange Rate. To determine if a 20-μm cast Nafion membrane could be ion exchanged to near completion quickly at room temperature, the Na^+/Ag^+ exchange reaction rate was studied. Sodium atomic emission measurements following the reaction of Ag^+ replacing Na^+ in a cast film confirmed that the exchange was at least 98% complete within 2 min. Membranes for the facilitated transport experiments described below were exchanged for 3 min to ensure complete reaction.

Facilitated Transport of Olefins. To determine the effect of a sulfonated dopant within the membrane on transport productivity, the separation of 1,5-hexadiene, 1-hexene, and *n*-hexane using Ag^+ as the facilitated transport carrier was selected as a screening tool. This type of separation has been studied previously by our group.[12] Table 2 gives the separation factors and fluxes for the two olefins permeating through each membrane type. Prior to performing the facilitated transport experiments, each membrane was in contact with H_2O for 5–7 min to release the film from the casting dish and perform Ag^+ ion exchange. On the basis of Figure 2, this length of time in contact with water will extract 80% of the dopant initially cast into an $OctSO_3Na$-doped membrane. As Table 2 indicates, the fluxes and separation factors are essentially the same for this type of membrane at all three dopant levels as the undoped film. For the membranes doped with *perf*-$ButSO_3Na$, approximately 50% will have leached out prior to the transport experiment, and a small flux enhancement is observed for both olefins as the dopant level increases. In contrast, the membranes doped with *perf*-$OctSO_3Na$ contain well over 90% of the initial mass of dopant during the transport experiments and exhibit much higher fluxes. The increase in flux with increasing content of this dopant is fairly linear for both olefins. Reproducibility of olefin fluxes through different membrane samples of the same type was ±10%. Given the reproducibility of olefin fluxes, the separation factor for 1,5-hexadiene and 1-hexene was essentially constant for all of the membranes examined. The unfacilitated fluxes of *n*-hexane are not given in Table 2 because they were so low as to be virtually at the detection limit of the GC and resulted in very poor data, reproducible to no better than ±100%. The *n*-hexane flux values for all of the membranes examined were between approximately 1×10^{-11} and 4×10^{-11} mol/cm^2 s. Additional transport experiments were performed on *perf*-$OctSO_3Na$-doped membranes that had been soaked in water to quantitatively extract the dopant. The fluxes and separation factors through films from which all dopant had been extracted was the same as that of initially undoped samples, indicating that the physical presence of the dopant is required for flux enhancement.

Although we have not specifically probed these membranes for changes in internal structure due to the presence of the dopant by techniques other than SEM, the constancy of the separation factor for 1,5-hexadiene/1-hexene combined with the roughly constant low flux of *n*-hexane and the requirement that the dopant be physically present indicate that the increased permeabilites are due to improvements to the facilitated transport mechanism rather than to morphological changes or defects in the polymer matrix. Any significant morphological changes in the membrane due to the presence of the dopant seem to be unimportant for this separation.

One possible explanation for the large effects in the *perf*-$OctSO_3Na$-doped membranes is that the addition of the dopant increases the ion exchange capacity of the membrane. This would increase the concentration of the silver ion carrier which should, according to the predictions of models, result in a flux enhancement for facilitated species that is directly proportional to the increase in carrier concentration.[27] The equivalent molecular weight of an undoped Nafion membrane in the Na^+ form is approximately 1120 g/(mol of sulfonate sites). When casting *perf*-$OctSO_3Na$ into a Nafion membrane such that 20% of the sulfonate sites in the film are due to the dopant, the average equivalent molecular weight of the resultant membrane is 1000 g/mol. Therefore, adding the dopant increases the ion exchange capacity by 11%, assuming all of the sulfonate sites in the membrane are accessible to Ag^+ exchange. However, Table 2 shows that the facilitated flux through such a film is more than double that of an undoped sample, far exceeding the predicted improvement based on carrier capacity.

Olefin Concentrations in Membranes. Another possible explanation for the flux enhancement is that the presence of the dopant may allow larger concentrations of olefins into the Ag^+ form membrane resulting in greater permeation. However, measurements revealed that the concentrations of the two olefins in membranes initially doped with *perf*-$OctSO_3Na$ at the 20% level exceeded the concentrations in undoped samples by less than 10%. Total olefin concentrations in all of the membranes tested were

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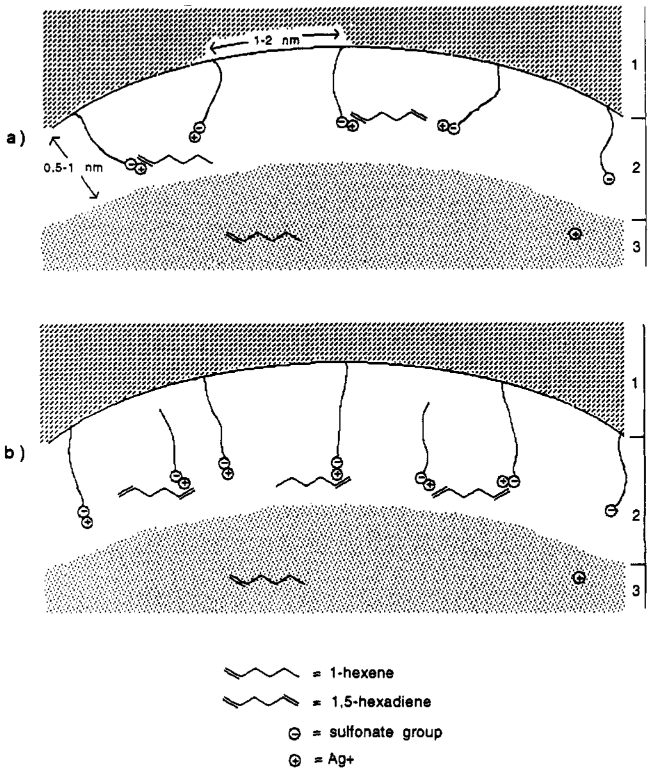

Figure 3. Proposed path of facilitated olefin transport through (a) undoped and (b) doped Nafion cast films.

on the order of several molar. For a detailed description of competitive olefin absorption into Nafion membranes, the reader is directed to prior work.[12]

Clearly, small increases in either the olefin concentrations or ion-exchange capacity within doped membranes cannot explain the observed flux enhancements. Figure 3 depicts a possible scenario for the movement of facilitated olefin species through the ionic clusters within two different types of Nafion membranes. These clusters are thought to be approximately spherical and 5 nm in diameter as previously determined by X-ray scattering.[20] In Figure 3a, region 1 represents the hydrophobic Teflon-like polymer backbone. Practically no water may reside here, and because dry Nafion films have extremely low permeability, very little transport occurs through this region. Area 2 represents an interfacial region which contains the polymer side chains and some water. These side chains are bound to the polymer backbone and terminate in an ion-exchange group, as depicted in the figure. High olefin concentrations located in this region will impart substantial hydrophobicity which favors ion pairing between silver ions and sulfonate sites. Region 3 represents an area containing mostly water, where hydrated silver ions may also be present. When olefins partition into the Ag^+ form of these membranes, they exist primarily as Ag^+–olefin complexes. The hydrophobic nature of the olefins should cause the Ag^+–olefin complexes to favor region 2 and may cause this region to contain less water than would be present in the absence of olefins. The lower concentration of water in region 2 will tend to favor ion pairing of the Ag^+–olefin complexes with the sulfonate groups of the polymer side chains. Very low concentrations of uncomplexed olefins are also present in regions 2 and 3 which give rise to the fluxes observed in Na^+ form membranes, which are 2–3 orders of magnitude smaller than in Ag^+ form membranes.[12]

Figure 3b is identical to 3a except that it represents a membrane which has been cast to contain *perf*-$OctSO_3$-Na. The dopant species is depicted in similar fashion to the polymer side chains, except that it is not bound to the polymer backbone. This dopant should be located in the interfacial region based on its slow rate of extraction from the membrane and the fact that the presence of the dopant improves facilitated transport flux. Membranes cast with either $OctSO_3Na$ or *perf*-$ButSO_3Na$ probably contain the dopant mostly within region 3 as indicated by the rapid rejection rates from the membrane and small contributions to flux observed for these dopants.

In either of the membrane environments depicted in Figure 3, olefin transport via an Ag^+–olefin complex freely diffusing through the membrane is unlikely to be the dominant mechanism for two reasons. Mobile Ag^+–olefin complexes would require a significant concentration of unpaired complex cations and anionic sulfonate groups. However, the hydrophobicity of the interfacial region due to extremely high olefin concentrations (~2 M) would favor ion pairs rather than free ions. Second, if the silver ions were freely mobile, the flux increase with dopant present would be no greater than the increase in carrier capacity.[27] A more likely scenario involves ion-paired silver sites passing olefins from one site to the next utilizing the wagging motion of the side chains, as depicted in region 2 of Figure 3a. With dopant present, as in region 2 of Figure 3b, the passing distance between complexation sites will be reduced and less movement of the side chains required. The dopant may also act as a highly mobile shuttle moving olefin between ion-paired silver sites.

Conclusion

The results presented here demonstrate that anionic perfluorinated sulfonates of suitable chain length can be incorporated into Nafion films and are not quickly rejected from the membrane. Furthermore, the presence of a perfluorinated dopant within the membrane microstructure induces significant permeability improvements for facilitated transport without loss of separation factor. These findings point to the idea that the facilitated transport of olefins in Nafion occurs at an interfacial region, and the addition of the dopant to the interfacial region may reduce the distance olefin molecules must move to pass from one carrier site to the next.

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