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Morphological Changes and Facilitated Transport Characteristics for Nafion Membranes of Various Equivalent Weights

D. S. Manley, D. L. Williamson,† R. D. Noble,‡ and C. A. Koval*

Department of Chemistry and Biochemistry, Campus Box 215,
University of Colorado, Boulder, Colorado 80309

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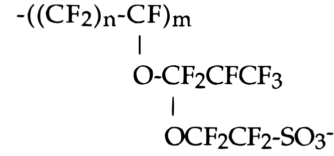
Perfluorosulfonic acid materials such as Nafion[1] that have been exchanged with Ag(I) ion have been shown to exhibit high selectivities with respect to membrane separations of mixtures of unsaturated organic compounds. This unusual behavior cannot be explained solely by the interaction of the unsaturate with Ag(I) ion. The membrane morphology appears to also contribute to the observed selectivities. To better understand the connection between morphology and membrane selectivity, Nafion materials with equivalent weights (EW) ranging from 1100 to 1500 g/equiv were characterized through their uptake of water and through small-angle X-ray scattering (SAXS) studies for materials in the dry, Ag^+ forms and hydrated, Na^+-forms. The water contents decreased with increasing EW from 34% to 10%. The SAXS data indicated that the ionic cluster sizes were similar (1.6 ± 0.1 nm) for the different materials in their dry, Ag^+ forms but decreased slightly with increasing EW in the hydrated forms from 4.4 to 3.6 nm. Fluxes of 1,5-hexadiene and 1-hexene through the hydrated Ag^+ forms of these materials decreased with increasing EW, but both the ideal and observed separation factors**,** while different, maintain approximately the same values for each membrane evaluated. The amount of alkenes absorbed into these materials from single-component or mixed feed solutions per mol of Ag^+ sites was virtually the same for all materials. This result appears to be the basis for the observed high selectivities. Calculations based on the water contents and SAXS data show that for the series of Nafion materials the distances between ionic clusters vary by only 6% for the dry membranes and by only 3% for the hydrated membranes.

Introduction

The separation of dienes from monoolefins of the same carbon number is difficult by conventional techniques, i.e., distillation. One approach which has shown promise is to use a complexing agent in a membrane which can reversibly react with the solute of interest. Silver(I) ion is used as a complexing agent for dienes and monoolefins due to its reversible interaction with the double bonds. One method used to stabilize the Ag^+ in the membrane is to use an ion-exchange membrane and maintain the Ag^+ in the membrane by electrostatic interaction. Nafion,[1] a perfluorocarbon polymer with sulfonate ion-exchange sites, has been used in previous studies by our group and shown unusual selectivities which appear to be due to the membrane morphology as well as the reversible reaction.[2−13]



$$-((CF_2)_n\text{-}CF)_m \text{ with } O\text{-}CF_2CFCF_3 \text{ with } OCF_2CF_2\text{-}SO_3^-H^+$$

Figure 1. Chemical structure of du Pont's Nafion.

Specifically, we have used Nafion 117 and other 1100 equivalent weight (equivalent weight, EW = grams of dry Nafion per mole of exchange sites) Nafion membranes. Recently, a variety of Nafion-like materials were obtained from E.I. du Pont de Nemours & Co. These Nafion materials are all similar in structure but differ in their equivalent weight; see Figure 1. The change in equivalent weight is a result of a change in distance between side chains along the Teflon backbone. As depicted in Figure 1, the change in equivalent weight was achieved by changing the value of *n* with no changes made to the ether-linked sulfonated side chain.

The goal of this research was to compare the transport properties of these Nafion-like membranes to Nafion 117 and to study any morphology changes in their physical structure. We are interested in determining any mor-

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† Department of Physics, Colorado School of Mines, Golden, CO 80401.

‡ Department of Chemical Engineering, University of Colorado, Boulder, CO 80309.

* Address correspondence to this author.

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Table 1. Dry and Wet Ion Site Densities for the Nafion Materials

	dry membrane	wet membrane			
EW	mole of sites/kg of dry memb	% weight gain	mole of sites/kg of wet membr	mole of sites/kg of H_2O	mole of H_2O/mole of sites
1100	0.91	34	0.68	2.7	21
1200	0.83	22	0.68	3.8	15
1300	0.77	17	0.66	4.5	12
1400	0.71	13	0.63	5.6	9.9
1500	0.67	10	0.61	6.7	8.3

phology-based characteristics of the materials to the high selectivities observed in membrane separations of olefins and dienes. The systems used to investigate transport were the separation of 1,5-hexadiene from 1-hexene and 1,9-decadiene from 1-decene. The morphology of the Nafion materials was studied by measured water content and by small-angle X-ray scattering (SAXS). Measurements of the amount of olefins absorbed into the membranes were also performed.

Experimental Section

Materials. Nafion 117 (1100 EW, 7 mil), Nafion 127 (1200 EW, 7 mil), Nafion 002 (1300 EW, 5 mil), Nafion 025 (1400 EW, 5 mil), and Nafion 004 (1500 EW, 5 mil) membranes were obtained from E.I. Du Pont de Nemours & Co. These membranes were received in the proton form. The membranes were cleaned by two sequential soakings in refluxing concentrated HNO_3 for 1 h. The membranes were thoroughly rinsed in DI water and refluxed in DI water for 1 h. Each membrane was ion-exchanged into the Na^+ form by soaking in 1 M NaOH for 10 min, followed by three consecutive rinses in DI water. For membranes that were ion-exchanged into the Ag^+ form, that exchange was performed by soaking the Na^+-form membranes in 1 M $AgNO_3$ for 10 min, followed by three consecutive rinses in DI water.

Isooctane, 1-hexene, 1,5-hexadiene, 1-decene, and 1,9-decadiene were all reagent grade and used as received. To avoid dehydration of the membrane, the isooctane was preequilibrated with DI water. High-purity water was obtained from distilled water filtered through a milli-Q water purification system.

Transport Experiments. For membrane-transport experiments, the feed side solutions consisted of the solutes of interest in water-saturated isooctane, while the sweep side solutions consisted only of water-saturated isooctane. The concentration of the solutes in the sweep side were measured over time using gas chromatography. Flux values were obtained from plots of solute concentration in the sweep solutions vs time which remained linear for hours.

Absorption Experiments. The concentrations of solutes in the membranes were determined by equilibrating pieces of the various equivalent weights of Nafion with the feed solution for 24 h, rinsing them briefly in pure solvent to remove solute from the surface, and thoroughly extracting the solutes from the membranes using pure solvent.[12] The extract was then analyzed using gas chromatography. Solute concentrations in Nafion were calculated in a variety of ways as described below.

Water Content Measurements. The extent of water uptake into the Nafion membranes was measured gravimetrically. Hydrated Na^+-form membranes of each equivalent weight were quickly patted dry of surface water and weighed on a balance. After weighing, the membranes were dried in a heated vacuum oven for 6 h at 100 °C and 130 Torr to remove water under nondestructive conditions. After drying, the membranes were cooled for 12 h in a desiccator. The dry weight of the membranes was measured. The percent weight gain due to water was calculated as the increased weight due to water, divided by the dry weight × 100.

SAXS Instrumentation. Small-angle X-ray scattering (SAXS) experiments were performed at the Colorado School of Mines using a Kratky compact small-angle system manufactured by Anton Paar K.G., Austria, and attached to a Rigaku rotating anode (Cu) X-ray generator with the Cu Kα radiation selected with a crystal monochromator ($\lambda = 1.542$ Å). The raw data consisted of the measured X-ray count rate versus the magnitude of the scattering vector, $h = (4\pi/\lambda)\sin\theta$, for a scan of the scattering angle 2θ from 0.15° to 8.4°. A reference scan was made without the sample to correct for parasitic scattering. Intensities were converted into absolute units (scattering cross section per unit volume, cm^{-1}).

Results

Membrane Water Content. Table 1 lists the values found and calculated for several properties of the Nafion membranes, both dry and wet. As shown in Table 1, the ion site density of the dry membranes (expressed as mole sites per kilogram of dry membrane) drops from 0.91 to 0.67 with the increase in equivalent weight. When the membranes are hydrated, the amount of water absorbed in the membrane decreases from a high of 34% for the 1100 EW membrane to a low of 10% for the 1500 EW membrane. As the equivalent weight increases, the number of sulfonation sites decreases, and, as expected, less water is needed to solvate the charges on the sites. However, while the 1100 EW material has only 36% more ions based on dry mass than does the 1500 EW material, the 1100 EW membranes absorb over 3 times the amount of water as do the 1500 EW membranes. The result is that the concentration of ionic sites per mass of wet membrane is similar for all the materials. Since previous studies have indicated that most of the absorbed water in Nafion is predominately located in the ionic clusters,[14] another logical way to express the ion site density is as mole of sites per kilogram of H_2O. Using this method of ion site density, the concentration of sites actually increases with increasing equivalent weight, but as shown in the last column, the exchange sites are less hydrated as the equivalent weight is increased.

Other groups have reported the extent of water absorption for Nafion and other perfluorinated membranes.[15-19] For 1100 EW Nafion membranes, these earlier reports determined that the water absorption is approximately 20 wt %. For the experiments presented here, a larger water absorption (≈34%) was measured. This difference in water uptake is due to differences in the membrane preparation techniques. Nafion membranes are known to vary greatly in many of their properties with changes in preparation procedures. The main differences in the procedure presented here is that these membranes were boiled in water for 1 h in the H^+ form followed by a rapid Na^+ exchange. This procedure results in larger water absorption values than would be obtained from membranes where the procedure included exchanging into the Na^+ form prior to a water boil.[8] It is important to remember that each of the membranes in these experiments were treated

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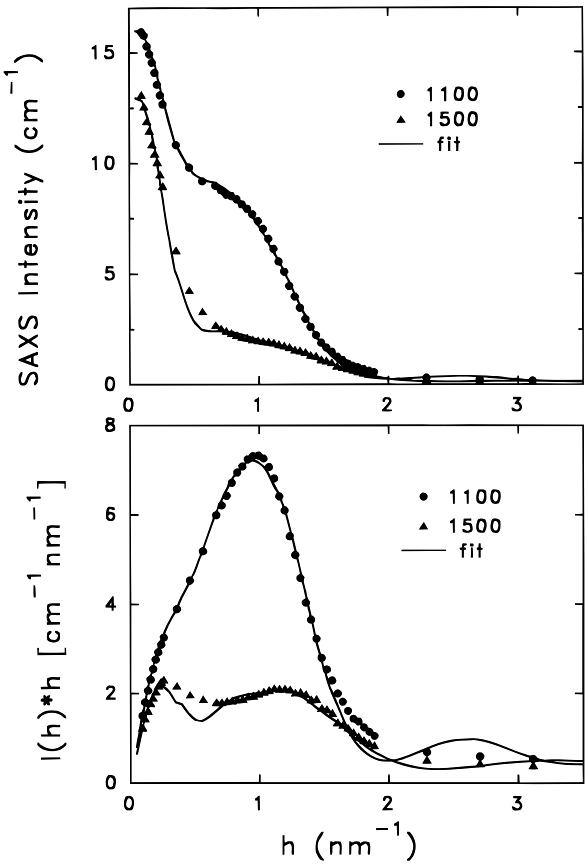

Figure 2. SAXS data and fits for hydrated, Na^+-form Nafion membranes. Top: line-focus SAXS intensity data, $I(h)$, vs h; circles: experimental data for EW 1100; triangles: experimental data for EW 1500; solid lines: fits using eq 1 (including smearing due to line-focus geometry). Bottom: $hI(h)$ vs h; circles: experimental data for EW 1100; triangles: experimental data for EW 1500; solid lines: fits using eq 1 (including smearing).

identically and that the differences in water uptake are due to difference in the membranes and not in preparation procedures.

Small-Angle X-ray Scattering. SAXS experiments were used to provide information about the morphological properties of the Nafion membranes. More specifically, SAXS was used to detect and measure the sizes of ionic clusters in the Nafion membranes. Hydrated Nafion membranes have a well-defined SAXS profile.[15,17,20,21] Point-focus SAXS intensity data, $I(h)$, are often plotted as $h^2I(h)$ versus h and this procedure typically yields two characteristic features for hydrated Nafion: (1) a maximum near $h = 1.0-1.5$ nm^{-1} which is associated with the ionic clusters, and (2) a weak maximum or shoulder near $h = 0.3-0.5$ nm^{-1} which has been attributed to Nafion crystallites. The relative position of these features indicates about a factor of 3 difference in relative size of the objects producing the SAXS.

Figure 2(top) shows the SAXS intensity versus h obtained for two of the equivalent weights of Nafion in the hydrated Na^+ forms. Since the SAXS system used here has a line-focus geometry, Figure 2 (bottom) shows $hI(h)$ versus h, which should be equivalent in appearance to point-focus $h^2I(h)$ plots, provided the system satisfies the so-called "infinite-slit" condition.[22] The two features described above are clearly seen in the data of Figure 2. The position of the maximum in Figure 2b shifts to larger h and decreases in intensity with the increase in equivalent weight. The shoulder at low h for the 1100 EW sample becomes more resolved for the 1500 EW sample due to the loss of intensity of the main peak.

Table 2. Fitting Results for Hydrated Na^+ Forms of Nafion

sample (EW)	R_S (nm)	R_L (nm)	D^a (nm)	f (%)	A (cm^{-1})	B (cm^{-1})	I (cm^{-1})
1100	2.2 ± 0.1	7.9 ± 1.0	4.4	16 ± 2	5.6 ± 1	0.12	0.10
1200	2.0	9.5	4.0	14	5.5	0.30	0.13
1300	1.9	9.5	3.8	12	3.5	0.20	0.11
1400	1.85	9.0	3.7	12	3.7	0.30	0.13
1500	1.8	7.5	3.6	13	1.9	0.22	0.10

[a] Fixed to be twice the value of R_S.

To extract quantitative data on the sizes of the scattering objects, the data were fitted with a model that assumes spherical objects and an interparticle interference based on hard spheres:

$$I(h) = AP(hR_S)S(hD) + BP(hR_L) + I_d \qquad (1)$$

where $P(hR_S)$ or $P(hR_L)$ is the scattering function for spheres of radius R_S or R_L appropriately weighted by their volume.[22] $S(hD)$ is a hard-sphere structure factor that accounts for interference between spheres of diameter D, and B, A, and I_d are constants. The Percus–Yevick hard-sphere model was used for $S(hD)$.[23,24] The constant I_d accounts for the diffuse background signal approached at high h and is due to atomic-scale structural and compositional disorder. The intensity from eq 1 was then smeared[22] by the line-focus weighting function determined by the slit conditions of the SAXS system. The fitting parameters used to generate the solid lines in Figure 2 included I_d, A, B, and R_L to represent the larger objects, R_S, to represent the smaller objects, D, and f, the volume fraction of hard-spheres of diameter D. The results of fitting the data from the five equivalent weight samples are listed in Table 2.

Following earlier interpretations,[15,17,20,21,25] $2R_L$ is associated with the average diameter of the crystallites and $2R_S$ with the average size of the ionic clusters. The use of spheres to represent the crystallites is a crude approximation but allows the extraction of the signal from the ionic clusters and determination of their approximate radius R_S. Deviations of the fits from the experimental data are attributed to this spherical approximation for the crystallites and to the likely polydispersity in both the ionic clusters and the crystallites. There is a small but systematic decrease in ionic cluster size with increasing EW similar to that obtained by Kumar and Pineri[25] in a similar analysis of Na^+-form membranes. Note that $D = 2R_S$ (also

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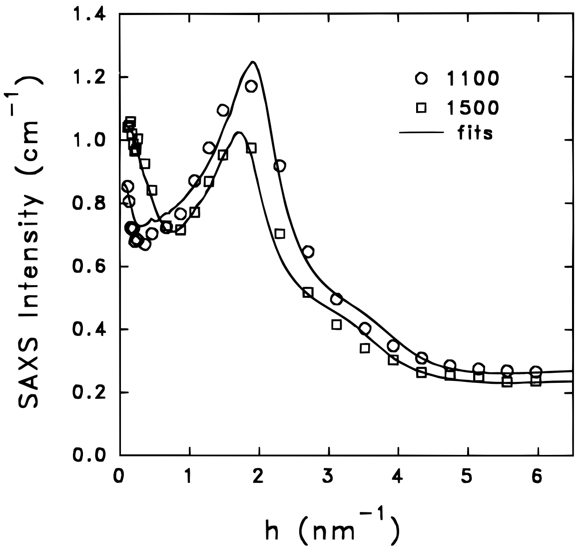

Figure 3. SAXS data and fits for dry, Ag^+-form Nafion membranes. Line-focus SAXS intensity data, $I(h)$, vs h; circles: experimental data for EW 1100; triangles: experimental data for EW 1500; solid lines: fits using eq 1 (including smearing).

assumed in ref 25) gave good fits consistent with a hard-sphere interaction associated with a simple diameter of the ionic clusters. The reduction in intensity from the ionic clusters with increasing EW (Figure 2) is caused by the decreased uptake in water with increasing EW such that a reduced electron density contrast between the clusters and the surrounding matrix results in weaker scattering from the clusters.

SAXS scans were also obtained from dry Nafion membranes. The electron density contrast was increased by exchanging Ag^+ ions with the Na^+ ions prior to drying. Figure 3 compares the data from the 1100 and 1500 EW samples. Note that a well-defined peak occurs in $I(h)$, dramatic evidence of interparticle interference. Results from fitting eq 1 to the data are shown as solid lines in Figure 3 and by the parameters in Table 3.

Comparison of the data in Tables 2 and 3 shows that the ionic cluster sizes are more than a factor of two smaller in the dry Ag^+ form compared to the wet Na^+ form. Also, since $D > 2R_S$ for the dry Ag^+ form ($D = 2R_S$ gave obviously poor fits), this suggests that the ionic clusters are not behaving as random hard spheres, i.e., they are correlated in position such that their "effective" diameter is D rather than their actual ionic diameter $2R_S$.[24] The crystallite sizes (R_L) seem to be smaller in the dry form.

The volume fractions (f) based on the $S(hD)$ term is about doubled for the dry Ag^+ forms of the Nafion and is relatively constant for the different EWs of the material. This lack of variation in f is difficult to understand, especially since the ionic diameters are also constant in size. Possibly the procedure used to dry the Ag^+ membranes did not remove the water from the different EWs equally well, or the drying produced an unanticipated heterogeneity in the dry membranes. Evidence of this can be seen from the nonsystematic variation of the A parameter (Table 3) with EW and, therefore, with the Ag^+ content. It is noteworthy that the diffuse background signal (I_d in Tables 2 and 3) is significantly larger for the Ag^+ membranes. This suggests that some of the Ag^+ (and Na^+) is randomly dispersed rather than clustered.

Transport Experiments. The flux values for the transport of 1-hexene and 1,5-hexadiene in single-component experiments are shown in Table 4. As can be seen in the table, the flux values for both alkenes decreases with increasing EW. Additionally, the ideal separation (i.e., the separation factor assuming that the presence of each solute in the membrane will not influence the solubility of the other components in the feed mixture and vice versa) factors based on the single-component experiments does not vary greatly as the EW of the membrane is changed.

The flux values for the transport of 1-hexene and 1,5-hexadiene in mixed feed component experiments are also listed in Table 4. The flux of 1-hexene in the mixed feed experiments diminishes to about 1/10 of its single-component flux for each membrane. Meanwhile, the flux of 1,5-hexadiene does not change significantly between the single-component and mixed feed experiments. This unexpected behavior has been discussed for Nafion 1100 in an earlier publication.[12] Even though the fluxes vary substantially for the membranes with different EWs, the observed separation factors stay relatively constant.

To test for a possible dependence of molecular size on the transport properties, fluxes for mixtures of 1-decene/1,9-decadiene were also determined for the 1100 EW and 1500 EW membranes. Table 5 shows the results obtained from these experiments. The flux values for both monoenes dropped by a factor of approximately 4.5 for both the 1100 EW and 1500 EW membranes. Similarly, the flux values for both dienes dropped for both membranes (by approximately a factor of 6.5).

Absorption Experiments. Previous research has shown that transport rates for unsaturated organics through Ag^+–Nafion membranes is highly correlated to the amounts absorbed from the feed solutions.[12] Figure 4 shows the concentrations of 1,5-hexadiene absorbed into each of the Nafion membranes from a feed solution that was 0.5 M in 1,5-hexadiene and 1-hexene. The concentration has been calculated in two ways, mol of 1,5-hexadiene/kg of hydrated membrane and mol of 1,5-hexadiene/kg of absorbed water. The results show that the water content is a more significant factor in determining the concentration of alkenes than is the total membrane weight.

An alternative way to view the effect of the EW on the concentration of alkenes absorbed into the membrane is to compare the mole ratios of alkenes to ion-exchange sites. Table 6 shows the amount of 1-hexene and 1,5-hexene in membranes as the ratio of moles of

Table 3. Fitting Results for Dry Ag^+ Forms of Nafion

sample (EW)	R_S (nm)	R_L (nm)	D (nm)	f (%)	A (cm^{-1})	B (cm^{-1})	I_d (cm^{-1})
1100	0.80 ± 0.1	15 ± 3	3.2 ± 0.2	35 ± 3	3.1	0.001	0.26
1200	0.85	8 ± 2	3.4	36	2.1	0.001	0.24
1300	0.80	7	3.5	36	2.4	0.005	0.24
1400	0.80	7	3.5	36	2.6	0.01	0.24
1500	0.80	5	3.5	33	2.4	0.02	0.23

Table 4. Fluxes and Separation Factors for Single Component and Mixed Feed Transport Experiments for 1-Hexene and 1,5-Hexadiene through Nafion Membranes of Various EW[a]

	[feed side] (M)		Flux × 109 (mol/cm^2 s) (normalized to 1 mil)		
membrane EW	1-hexene	1,5-hexadiene	1-hexene	1,5-hexadiene	sep factor
1100	0.50	0.00	5.6		5.0
	0.00	0.50		28	
	0.50	0.50	0.54	28	52
1200	0.50	0.00	3.9		5.1
	0.00	0.50		20	
	0.50	0.50	0.41	16	39
1300	0.50	0.00	3.5		2.9
	0.00	0.50		10	
	0.50	0.50	0.32	13	41
1400	0.50	0.00	1.6		3.8
	0.00	0.50		6.0	
	0.50	0.50	0.17	6.5	38
1500	0.50	0.00	1.6		3.6
	0.00	0.50		5.8	
	0.50	0.50	0.12	4.1	34

[a] Ideal separation factors were determined for the single-component mixtures for each membrane. All membranes were hydrated and Ag$^+$-exchanged.

Table 5. Fluxes and Separation Factors for Mixed Feed Transport Experiments of 1-Decene/1,9-Decadiene and 1-Hexene/1,5-Hexadiene through 1100 EW and 1500 EW Nafion Membranes[a]

	[feed side] (M)		flux × 109 (mol/cm^2 s) (normalized to 1 mil)		
membrane EW	1-decene	1,9-decadiene	1-decene	1,9-decadiene	sep factor
1100	0.50	0.50	0.012	1.0	83
1500	0.50	0.50	0.0025	0.16	64
EW	1-hexene	1,5-hexadiene	1-hexene	1,5-hexadiene	
1100	0.50	0.50	0.54	28	52
1500	0.50	0.50	0.12	4.1	34

[a] All membranes were hydrated and Ag$^+$-exchanged.

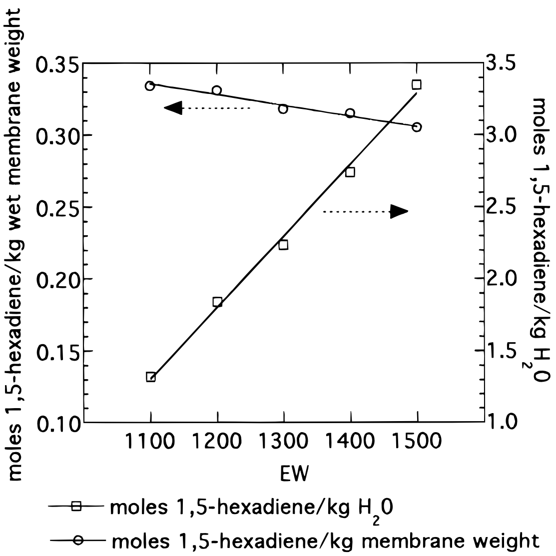

Figure 4. Amounts of 1,5-hexadiene absorbed into Ag$^+$–Nafion membranes with varying equivalent weights.

alkene per mole exchange sites for both single-component contacting solutions and mixed-feed contacting solutions. For single-component contacting solutions, the table shows that this mole ratio for either 1,5-hexadiene or 1-hexene is constant and of similar magnitude for each of the Nafion samples. These results indicate that the fraction of alkene complexed to Ag$^+$ ions in the membrane is not dependent on the EW. For the mixed-feed contacting solutions, the table shows that the mole ratio of 1-hexene drops to about 1/10 of its single-component mole ratio while the mole ratio of 1,5-hexadiene remains unchanged. By this comparison, each EW of the Nafion membrane shows the same absorption of both 1-hexene and 1,5-hexadiene. The competition between the alkenes is also the same for the Nafion materials with different EWs. This result appears to provide the basis for the high selectivities observed in transport experiments.

Discussion and Conclusions

The transport experiments demonstrated three interesting results with respect to the role of membrane morphology: (1) Nafion materials with different equivalent weights have significantly different organic fluxes; (2) the flux of monoolefins in mixtures are nearly 10 times lower than with single-component feed; and (3) the hexene flux is approximately 45 times higher than the decene flux for a given membrane. Combining the information from the water uptake, transport, absorption, and SAXS experiments, certain features of the morphology and the mechanism of transport for Ag$^+$–Nafion membranes can be deduced.

The absorption experiments show that the membrane has a finite capacity for unsaturates. This value is the same for both single component and binary feed mixtures. For mixtures, the diene is preferentially absorbed which effectively excludes the monoolefin and leads to the high selectivities observed. The SAXS experiments for the dry Ag$^+$-form membranes showed cluster sizes to be similar (1.6 ± 0.1 nm). However, as the EW is increased there are fewer exchange sites. Assuming that similar cluster sizes result from similar number of exchange sites per cluster, similar cluster sizes can result only if there are fewer clusters with increasing EW. If there are fewer clusters of similar size for the larger EW membranes, the separation between clusters must be greater. From the SAXS data on the hydrated

Table 6. Mole Ratio of 1-Hexene and 1,5-Hexadiene to Exchange Sites in Ag$^+$-Exchanged Nafion Membranes of Various EW

membrane EW	[exchange solution] (M)		olefin in membrane (mol of olefin/mol of sites)	
	1-hexene	1,5-hexadiene	1-hexene	1,5-hexadiene
1100	0.50	0.00	0.49	
	0.00	0.50		0.49
	0.50	0.50	0.039	0.48
1200	0.50	0.00	0.49	
	0.00	0.50		0.49
	0.50	0.50	0.044	0.46
1300	0.50	0.00	0.50	
	0.00	0.50		0.48
	0.50	0.50	0.047	0.47
1400	0.50	0.00	0.50	
	0.00	0.50		0.50
	0.50	0.50	0.047	0.47
1500	0.50	0.00	0.52	
	0.00	0.50		0.50
	0.50	0.50	0.047	0.48

Na$^+$-form membranes, it can be seen that the size of the ionic cluster decreases with increasing EW. The water absorption experiments also showed that less water is absorbed with increasing EW. These two pieces of information indicate that the change in ionic cluster size is due to the extent of water absorption.

As the carbon number of the unsaturate increases, the flux decreases for a given membrane. The diffusion coefficient decreases as the molecular size increases. Also, the sorption capacity should decrease as molecular size increases, although this hypothesis has not been verified. The combination of reduction in both sorption and diffusive mobility would contribute to the observed reduction in flux with increasing carbon number.

Combining the information from the transport experiments involving 1-hexene/1,5-hexadiene mixtures and the alkene absorption experiments, it is evident that the flux is sensitive to the water content in the membrane. The absorption experiments showed that the solubility of alkenes due to Ag$^+$ complexation is similar for all membranes, independent of water content. However, the flux values dropped for the higher EW membranes, which contained less water. From the absorption experiments reported here, it was found that the amount of each alkene entering the membrane per mole of ion-exchange sites is equal for each Nafion EW. This shows that differences in EW do not cause differences in the separation factor based upon alkene solubility.

The transport experiments for the separation of 1-decene/1,9-decadiene and 1-hexene/1,5-hexadiene shows that the length of the solute chain does not affect the mechanism of separation (as opposed to flux, which does change). This experiment showed that equivalent drops in the flux are obtained with increasing EW for different sized solute molecules.

As mentioned previously, one interpretation of the SAXS data is that the clusters are further apart in the larger EW membranes. On the basis of this assumption, calculations can be made to determine how the average distance between clusters varies. This distance is commonly associated with the length of “channels” between the ionic clusters. For 1100 EW Nafion, the number of cluster per volume can be calculated as follows:

$$\frac{0.91\ \text{mol sites}}{\text{kg dry membranes}} \times \frac{1\ \text{cluster}}{N\ \text{mol sites}} \times \frac{0.0020\ \text{kg}}{\text{cm}^3} = 0.0018/N\ \frac{\text{clusters}}{\text{cm}^3}$$

where N is the number of moles of sites that make up an ionic cluster. Similarly, the number of cluster per volume for 1500 EW Nafion can be calculated to be $0.0015/N$ clusters/cm^3. For any three-dimensional space, the number of objects per volume must be inversely proportional to the cube of their distance apart. Thus for Nafion, the number of sites per volume $\propto 1/d^3$, where d is the distance between clusters. By ratioing the number of sites per volume for two Nafion membranes of different EWs and assuming that N is the same for the two materials, the difference in channel length can be calculated. Thus for the dry membranes, the ratio $d(1500\ \text{EW})/d(1100\ \text{EW})$ is equal to 1.06, meaning that the channels are 6% longer for the 1500 EW Nafion membranes than for the 1100 EW Nafion membranes.

Calculations can also be made for the wet membranes to determine the different distances between clusters. For these calculations, the amount of physical swelling must be known. The following equation can be used to calculate the differences in channel length for the wet membranes:

$$\frac{d^3_{\text{wet}}(1500\ \text{EW})}{d^3_{\text{wet}}(1100\ \text{EW})} = \frac{d^3_{\text{dry}}(1500\ \text{EW})}{d^3_{\text{dry}}(1100\ \text{EW})} \times \frac{V_{\text{wet}}(1500\ \text{EW})/V_{\text{dry}}(1500\ \text{EW})}{V_{\text{wet}}(1100\ \text{EW})/V_{\text{dry}}(1100\ \text{EW})}$$

where $V_{\text{wet}}(1500\ \text{EW})/V_{\text{dry}}(1500\ \text{EW}) = 1.04$ and $V_{\text{wet}}(1100\ \text{EW})/V_{\text{dry}}(1100\ \text{EW}) = 1.14$, which both were calculated from the changes in thickness of the membranes upon hydration. It must be noted that using the relative change in thickness as a substitute for the relative change in volume is only an approximation. From this equation, the channel lengths can be calculated to be only 3% longer for the 1500 EW Nafion over the 1100 EW Nafion. From these results, it is obvious that the large change in flux values seen over the range of EWs is not due to the small changes in channel length over that same range of EWs.

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