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Solvent transport in hydrocarbon and perfluorocarbon ionomers

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Abstract

Transport behavior of a sulfonated triblock ionomer with a copolymer midblock of styrene and hydrogenated butadiene, Dais analytic (DA) is compared with Nafion™ (DuPont) using water, methanol, dimethyl methylphosphonate (DMMP), and dichlorohexane (DCH). Water solubility in Nafion is lower than that of DA, but the diffusion constant is an order of magnitude higher, indicating essentially unimpeded ionic pathways in Nafion. Differences in the properties or environment of the sulfonic acid groups are evident in the solubility of water and methanol, which are both much lower in the Cs than Ca form of Nafion, but comparable in the salt forms of DA. Water isotherms for DA and several uncrosslinked, sulfonated triblocks can be superimposed on the isotherm for Nafion by vertical scaling factors that represent the saturation concentration for the unrelaxed structure of each triblock ionomer. Water diffusion in both DA and Nafion is limited to ionic pathways and follows a free-volume relation, but the magnitude of the diffusion constant is determined by ionomer structure. High and nearly equal DMMP solubility in acid and salt forms is attributed mainly to solvation of the fluoroether interfacial region of Nafion, whereas, in DA the high solubility is due primarily to acid–base interactions with the sulfonate anion. Cation-modification has little effect on DMMP solubility but results in a dramatic reduction in DMMP diffusion constants. DMMP diffusion in DA and Nafion follow different diffusion pathways: fluoroether interfacial regions in Nafion, but ionic regions in DA.

Keywords: Nafion; Sulfonated triblock polymers; Solvent transport properties

1. Introduction

A variety of ion containing polymers for electrochemical applications, have been described in the literature, following the development of Nafion, which continues to be one of the most important commercial ionomers. Nafion precursor, a random copolymer of tetrafluoroethylene and a fluoroether sulfonyl fluoride comonomer, is largely amorphous with 10% or more crystallinity [1] and inert to most solvents. Upon hydrolysis to the sulfonic acid, the precursor undergoes phase separation to fluorocarbon and fluoroether regions with ionic domains formed by terminal sulfonic acid on fluoroether side chains. The fluoroether–sulfonic acid component comprises 33 wt% and the polymer has a density of 1.95 g/cm^3 with crystallinity similar in amount to the precursor [2,3]. Nafion has high-proton conductivity, anion rejection and stability at high temperatures in a caustic environment, which are properties required for its application as a membrane separator in the chloralkali process. The structure of Nafion has been the subject of extensive research, which has been summarized in an earlier [3] and more recent critical review [4]. The structural models are based largely on the results of scattering methods with the extensive involvement of molecular modeling to compensate for the limited directly accessible information. Any model for Nafion must also take into account information from studies of the transport behavior. Diffusion of water in Nafion is very high, largely Fickian, and follows a free volume concentration dependence [5]. Although resistant to non-polar solvents, Nafion is highly swollen by many aprotic dipolar solvents near ambient temperature [6–8]. Sorption kinetics with dimethylmethylphosphonate (DMMP) vapor are relaxation controlled, sometimes involving several discrete steps [9]. Both vapor and liquid exposure result in irreversible changes in transport properties. The common occurrence of a spectrum of small scale structural adjustments with DMMP vapor suggests that Nafion consists of small dispersed regions rather than large scale domain structure. Also, Nafion is heterogeneous with 25% or more extractable under mild conditions in aqueous propanol [10]. The extract is a waxy material and the remaining film is less flexible than the original Nafion, but of similar equivalent weight as determined by titration [10].

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The high cost of Nafion and high-methanol crossover rates, which limit applicability in direct methanol fuel cells, have driven the search for alternative ionomers. These include sulfonated versions of various thermoplastic polymers [11,12] and triblock hydrocarbon polymers containing partially sulfonated polystyrene end-blocks [13,14]. The latter class of polymers offers an interesting comparison with Nafion, in that a distinct and regular phase separated morphology, determined by styrene–olefin ratio exists prior to sulfonation [15]. Sulfonation of styrene units is expected to distort the original discrete morphology, due to incompatibility with unsulfonated polystyrene [16,17], promoting association of ionic groups within the polystyrene phase or as an additional phase. Moderately high-sulfonation levels result in high-proton conductivity and water transport approaching that of Nafion. However, in fuel cell applications sulfonated triblock polymers, require the addition of antioxidants to afford protection against degredation by peroxides.

Many variations of the triblock structure have been described. Elabd and Napadensky [14] sulfonated a polystyrene-*block*-polyisobutylene-*block*-polystyrene triblock copolymer (SIBS) containing 31 wt% styrene to various levels and determined some properties of the resulting ionomers. Saturation water uptake increased rapidly from 20 to 370 wt% with increasing sulfonation levels of 29–82% to give a range in ion exchange capacity (IEC) of 0.36–2.04. Serpico et al. [18] compared a sulfonated polystyrene-*block*-hydrogenated polybutadiene-*block*-polystyrene (sSEBS) containing 29% styrene and 55% sulfonation with a sulfonated pseudo-random styrene–ethylene copolymer. Won [19] carried out plasma treatment of the same polymer to produce surface succinic acid groups in an attempt to suppress methanol crossover. Small angle scattering studies were interpreted as a cylindrical morphology for the sulfonated polymer that was maintained in swelling with water but lost in swelling with methanol. Surface modification produced only minor improvement in proton conductivity relative to methanol permeability. In an alternative approach to reduce methanol crossover by fixing proton transport channels, cast films of a SEBS polymer, containing 30 wt% styrene, were first crosslinked with a photoinitiator to preserve the original morphology and then sulfonated [16]. Cylindrical morphology of the original triblock was maintained with crosslinking and with sulfonation up to IEC of 1.5 in the dry, but not in the hydrated state. The ratio of proton conductivity to methanol permeability was superior to that of sulfonated, crosslinked SBR, sSEBS and Nafion, in the first case due to higher proton conductivity, and for the latter two, due to much lower methanol permeability.

We have been interested primarily in the transport properties of sulfonated triblock polymers as permselective membranes for protective clothing applications, with high-water permeability and low permeability to hazardous organic chemicals. Sulfonated triblock polymers offer the potential for a variety of permselective barrier materials differing in morphology, sulfonation level and cation. We have chosen to work primarily with a lightly crosslinked, sulfonated triblock copolymer coated on a thin microporous support (DA). This membrane has polystyrene end blocks, a midblock consisting of equal weights of styrene and hydrogenated butadiene and is partially sulphonated. The effects of the microporous membrane and crosslinking on transport properties were determined by separate investigation of components of this membrane. Immersion sorption and liquid permeability of water and three organic solvents were made with the DA membrane and with Nafion in acid, Ca and Cs modifications to provide a comparison of the effect of the differences in chemical composition and phase morphology on transport properties.

2. Experimental

2.1. Materials

Dimethylmethylphosphonate (DMMP) and 1-6-dichlorohexane (DCH), reagent grade or equivalent (Aldrich) are nonhazardous simulants for chemical warfare agents Soman and sulfur mustard, respectively. Methyl alcohol (Baker) was chosen because of the interest in ionomers as the membrane separator for direct methanol fuel cells and the associated problem of methanol crossover.

A summary of the properties of the ionomer samples used in this study is provided in Table 1. Most of the measurements were made on ionomer membranes supplied by Dais analytic. The triblock precursor, Kraton 64 (K64, Kraton Polymers) is a poly(styrene-*block*-(hydrogenated butadiene-*co*-styrene)-*block*-styrene), which is unusual in that styrene is incorporated in the midblock, along with hydrogenated butadiene at 50–50 wt%. The triblock with 38% sulfonation, sK64, is the basis of the commercial version of this ionomer, DA, that is modified by crosslinking with trimethoxysilane through residual

Table 1
Triblock ionomer properties

Polymer	Mol wt polymer	Mol wt end block	Styrene (wt%)	End block % styrene	Sulfonation %	IEC[a]
sK64	125,000	18,100	64	45.3	38	2.01
DA	125,000	18,100	64	45.3	38	1.83
sK69	109,000	20,600	69	54.8	38	2.14
sSEBS[20]	89,000	22,250	29	100	50	1.25
sSIBS[18]	71,900	7518	31	100	69	1.76

[a] Ion exchange capacity.

midblock unsaturation and coated on a microporous polyethylene support. An additional polymer from Dais analytic, sK69 is based on a Kraton precursor, K69, similar to K64 in that it also includes styrene in the midblock, but with the differences in composition noted in Table 1. DSC scans on K69 at 10 °C/min (TA Instruments, Q100) revealed a strong T_g at −23.2 °C, associated with the midblock, and a T_g at 84 °C, associated with the endblock, indicating the existence of phase segregation despite the presence of styrene in the copolymer midblock. Films of K64 and K69 were cast from toluene. Variations of the DA membrane are listed in Table 4 in connection with water vapor sorption results and described in the associated text. Limited measurements were made on a few other hydrocarbon triblock ionomers. These include two sulfonated polystyrene-*block*-polyisobutylene-*block*-polystyrene (sSIBS) membranes from the series prepared by Elabd and Napadensky [14] at 69 and 77% sulfonation. Also, a film of sulfonated polystyrene-*block*-poly(ethylene-ran-butylene)-*block*-polystyrene (sSEBS), was cast from solution in propanol/dichloroethane as received from Aldrich.

Nafion 117 (C.G. Processing) was used as received. Cesium and calcium salts of the Nafion and DA membranes were prepared by immersion in 0.2 M aqueous solutions of the corresponding chlorides followed by extensive washing with conductivity water. The extent of proton exchange with cations, as determined by weight gain in the various ionomer membranes is given in Table 2. Previous studies with Nafion showed excellent agreement between cation content determined gravimetrically and by prompt gamma neutron activation analysis [20,21], and with the stochiometry based on equivalent weight by titration [10]. Cs uptake, in particular, provides a reliable method for determining ion exchange capacity (IEC). For the two DA ionomers the gravimetric Cs content is 7% smaller than the IEC value calculated on the basis of composition. However, the Ca content is one-third greater than stoichiometric, even following repeat washing, indicating that the excess is bound Ca. This suggests that steric limitations prevent all Ca ions from neutralizing two sulfonic acids. Extent of sSEBS sulfonation is reported as between 45 and 55% (Aldrich). The Cs content is in good agreement with 45% sulfonation, but Ca content is well above stochiometric. For sSIBS77 the Cs content indicates an IEC that is almost 30% lower than the value determined by elemental analysis [14], raising an uncertainty in comparisons based on IEC values.

2.2. Liquid measurements

Immersion measurements were made on 105 °C oven-dried films in 5–10 ml of liquid contained in 20-ml screw capped vials, immersed in a 35 ± 0.1°C water bath. A layer of Molecular Sieve 4A (MS4A) was included in the vials containing organic solvents to maintain anhydrous conditions. Exclusion of water is necessary because, it has been shown with Nafion, that aqueous mixtures with polar compounds e.g. alcohols, DMMP, exhibit positive deviations from additivity with marked increases in solvation [22]. Films were removed from the liquid, rapidly blot dried and weighed to 0.1 mg, then returned to the liquid, and the process repeated until constant weight was achieved. Liquid permeation measurements were made with a flooded surface, using a cylindrical cell with a central 1.9 cm diameter well and with sweep gas inlet and outlet ports in the lower section. Disc shaped samples were sealed in the upper section, under pressure supplied by a threaded metal cylinder that screws into the top of the cell and with the use of a Teflon disc with raised edge to localize the sealing force applied to the sample. The cell has been fully described and illustrated in a prior publication [23]. Liquid was supplied through a central opening, which was then sealed by a loose fitting plug to limit evaporation. The cell was located in an air thermostat maintained at 35 ± 0.2 °C. The bottom of the membrane was swept by a dry nitrogen stream, at 33 cm^3/min for water and methanol, 50 cm^3/min for DMMP and DCH, that carried permeant vapor to a detector. Water and methanol vapor concentrations were obtained with an auto-sampling thermal conductivity detector (MTI Analytical). An FID detector (SRI) was used to determine the concentration of the low volatility organic vapors.

2.3. Vapor measurements

Vapor sorption measurements were made with a Cahn D200 microbalance over a limited range of vapor activities, supplied by mixing vapor from a double chamber bubbler with a diluent nitrogen stream at set flow rate ratios and 200 cm^3/min total flow rate using electronic mass flow controllers (MKS). Bubbler and microbalance were housed in an air thermostat controlled at 35 ± 0.2 °C. Data recorded in chart mode at each activity, using a custom designed interface (Hiden) were exported as Excel compatible files for analysis. Extended vapor sorption measurements were conducted with an automated

Table 2
Cation uptake

Membrane	Ca (mg at/g)	Cs (mg at/g)	IEC[a] (mequiv/g)	Ca excess (wt%)	Ratio (Cs/IEC)
Nafion	0.45	0.91	0.909	−1.1	1.00
sK64	1.25	1.87	2.013	33.7	0.93
DA	1.14	1.71	1.830	33.3	0.93
sSEBS	0.84	1.1	1.140	52.7	0.96
sSIBS	Nd[b]	Nd	1.756		
sSIBS1	1	.5	1.929	33.3	0.78

[a] Ion exchange capacity.

[b] Not determined.

vacuum sorption system (HidenIsochema). This instrument incorporates an active vapor supply, using an absolute pressure sensor and computer controlled valve to admit vapor from a small liquid source maintained at least 10 °C above the sample chamber temperature. Runs were conducted automatically in sorption and desorption mode over a range of preset activities. The end point at each activity is determined by a curve-fitting algorithm that predicts the final weight when the data conforms to a preset condition in the approach to steady state, or failing that, by a preset final time. Data consisting of weight, temperature and pressure as a function of time were exported to Excel compatible files for analysis. One advantage of operating in vacuum is that the kinetics is not dependent on transfer in the boundary region, allowing determination of diffusion coefficients directly from sorption kinetics for liquids with low heats of condensation. An additional advantage of direct vapor pressure control is the ability to extend measurements to higher activities than with the flow system, where concentration errors can be introduced by small temperature differences between sample and bubbler vapor source and by vapor condensation in connecting lines at activities approaching saturation. When working with organic vapors that can damage the Cahn balance, a low-concurrent nitrogen flow is needed to purge the balance chamber, placing a further limit on the maximum vapor activity.

Permeation measurements were made with a cell that exposed a rectangular area 0.75 in by 1.25 in ($6.05\ \mathrm{cm}^2$), to vapor challenge and dry nitrogen sweep flows at $200\ \mathrm{cm}^3/\mathrm{min}$ in countercurrent mode on opposite surfaces of the film. The cell was housed in an air thermostatted cabinet maintained at 35 ± 0.2 °C and vapor concentrations at set activities were generated by use of a double chamber bubbler, as described above. High-nitrogen flow rates were required to minimize boundary layer resistance and to keep vapor concentrations within the linear range of the detectors. Effluent water vapor concentrations were measured directly with the MTI thermal conductivity detector. Permeation measurements with DMMP were made with stream splitting to reduce flow rate to $60\ \mathrm{cm}^3/\mathrm{min}$ to maintain flame stability of the flame ionization detector. Boundary layer resistances for water and DMMP were determined at a single vapor activity, using a very low-resistance microporous Teflon membrane. The flux, J ($\mathrm{kg/m^2\ s}$), determined for 1–3 layers of the membrane, was extrapolated to zero thickness and this value was converted to resistance, R (s/m):

$$R = \frac{\Delta C}{J} \tag{1}$$

where ΔC, concentration difference across the membrane, $\mathrm{kg/m^3}$, determined from challenge vapor activity and sweep concentration. The measured value of the boundary layer resistance is 94 s/m for water and 268 s/m for DMMP at a flow rate of $200\ \mathrm{cm}^3/\mathrm{min}$ used for sweep and challenge streams.

3. Results

3.1. Liquid sorption and permeation

Permeation measurements with DA and Nafion membranes were carried out in the liquid permeation cell at 35 °C with: water, methanol, DCH and DMMP. Steady state permeabilities, P ($\mathrm{g\ cm/cm^2\ s}$), uncorrected for boundary layer resistance, appear in Table 3 and, together with the corresponding solubilities, S ($\mathrm{g/cm^3}$) determined under immersion conditions. Permeability is most readily interpreted as the product of the solubility, a thermodynamic quantity that reflects the solvent–membrane interaction, and the diffusion constant, a kinetic quantity that depends on permeant size and membrane structure. Diffusion constants were estimated as the ratio of P/S and also from the half-time, $t_{1/2}$, to reach steady state flux,

Table 3
Liquid results

Solvent	DAIS membranes				Nafion membranes			
	S ($\mathrm{g/cm^3}$)	$D_{1/2}$ ($\mathrm{cm^2/s} \times 10^7$)	D_{calc} ($\mathrm{cm^2/s} \times 10^7$)	P ($\mathrm{g\ cm/s\ cm^2} \times 10^9$)	S ($\mathrm{g/cm^3}$)	$D_{1/2}$ ($\mathrm{cm^2/s} \times 10^7$)	D_{calc} ($\mathrm{cm^2/s} \times 10^7$)	P ($\mathrm{g\ cm/s\ cm^2} \times 10^9$)
Water								
H	0.97	2.24	2.95	286	0.37	14.0	28.61	1060
Ca	0.33	0.820	2.80	92.5	0.25	2.52	9.66	245
Cs	0.37	1.29	3.55	131	0.072		1.41	10.2
MeOH								
H	0.25	1.60	14.8	371	0.96	13.3	15.3	1460
Ca	0.17	0.050	0.20	3.3	0.55	1.29	2.97	162
Cs	0.12	0.160	0.75	9.0	0.082	0.130	0.937	7.67
DMMP								
H	1.72	0.155	0.060	10.3	2.59	0.015	0.014	3.67
Ca	1.57	0.003	0.008	1.3	1.68	0.007	0.013	2.17
Cs	0.45	Nd[a]	0.001	0.0	1.83	0.033	0.019	3.40
DCH								
H	1.33	0.084	0.051	6.8	0.78	0.018	0.010	0.750
Ca	0.43	0.097	0.034	1.5	0.003	Nd	Nd	$<1.0 \times 10^{-5}$
Cs	0.37	0.002	0.450	16.7	0.005	0.062	Nd	$<1.0 \times 10^{-5}$

[a] Not determined.

from Eq. (2), where l is the membrane thickness in centimeter [24]:

$$D_\infty = \frac{P}{S} \quad D_{1/2} = \frac{l^2}{7.2t_{1/2}} \tag{2}$$

Values determined later as a function of concentration upon exposure to vapor are referred to as diffusion coefficients to distinguish them from single-point values obtained with liquids. The steady state diffusion constants, D_∞, listed in Table 3, represent average values over the range of concentrations in the membrane. D_∞ is expected to be larger than the half-time diffusion constant, $D_{1/2}$, since the concentration at steady state is higher than that at the half-time and the solvent diffusion coefficient increases with concentration. For comparison purposes preference will be given to D_∞.

Water and methanol are small protonic solvents that are expected to interact strongly with the sulfonic acid group in the DA and Nafion membranes and to solvate the calcium and cesium cations to varying degrees [25]. Water solubility is lower in Nafion than DA, but permeability is much higher as a consequence of the nearly 10-fold higher diffusion constant of water in Nafion. Water solubility of the calcium and cesium form of these two ionomers present an interesting contrast. Whereas, solubility is much lower in Nafion–Cs than Nafion–Ca, solubilities are nearly equal in DA–Ca and DA–Cs. Despite the somewhat higher water solubility in DA–Ca, permeability is significantly higher in Nafion–Ca, due to the nearly fourfold higher diffusion constant, while permeability is much lower in Nafion–Cs than DA–Cs due to the far lower solubility.

A complication was encountered in determining methanol solubilities in the acid forms of the DA and Nafion membranes, but not in their salts. The solubility of methanol in DA reaches a maximum near 150 wt% in <10 min then decreases to a steady state value of 25 wt% in 8 h. When the immersion is carried out in the absence of MS4A drying agent methanol uptake smoothly increases to a steady state solubility of 150 wt%. This behavior is less pronounced in the case of Nafion, where weight gain in anhydrous methanol increases to a maximum of 81 wt% in 1 h then slowly decreases to a steady state solubility of 59 wt% in 24 h. The decrease in weight appears to be due to the lower solubility of methanol in the methyl ester of the sulfonic acid, which is produced in the presence of the molecular sieve. Permeation experiments employed neat methanol and reached steady state in a few hours. Therefore, the solubility values listed in Table 3 for the acid membranes are the early time solubility maxima.

In contrast to water, methanol solubility is significantly higher for Nafion than DA, but the diffusion constant is almost the same, with the overall result of significantly higher permeability in Nafion. Methanol solubilities are also lower in the DA salts than in the Nafion salts. There is a correspondence between methanol and water solubilities, in that methanol concentrations are comparable in DA–Ca and DA–Cs but, as with water, methanol solubility is much lower in Nafion–Cs than Nafion–Ca. Both ionomers exhibit a marked reduction in methanol diffusion constant between acid and calcium forms, but the reduction is much greater in DA–Ca than in Nafion–Ca. As a result of the lower diffusion constant, together with the lower solubility, methanol permeability in DA–Ca is nearly a factor of fifty lower than Nafion–Ca. The ratio of water–methanol permeability can be used as an index of selectivity, with higher values indicating a higher rejection of methanol transport compared to water. Selectivity is highest for DA–Ca, with a ratio of 28 compared to 1.5 for Nafion–Ca and 0.7 for either of the acid forms of the ionomers. The high-DA–Ca methanol selectivity is due to low-methanol permeability coupled with moderately high-water permeability. These results suggest that DA–Ca would be the preferred choice for a methanol fuel cell application requiring low-methanol permeability, provided that the proton conductivity is sufficiently high and also, if protection could be provided against degradation by peroxides.

DMMP solubilities recorded in Table 3 for Nafion salts are pseudo-equilibrium values obtained by immersion for periods <12 h, comparable to the time scale of the permeation experiments. True steady state solubility values for DMMP are about 30% greater, requiring more than 350 h for Nafion–Ca and Nafion–Cs, due to slow relaxation processes [9] and the final solubilities are close to those of Nafion. Relaxation also produces irreversible changes in Nafion structure, demonstrated by the change in kinetics on reimmersion in DMMP of samples dried following displacement of DMMP by water. Immersion kinetics of DA samples in DMMP proceeds without relaxation effects and usually reaches equilibrium in several hours. Resulting DMMP solubility is high for DA and even higher in Nafion. DMMP solubility remains at high levels in both calcium and cesium forms of Nafion. Although solubility is also high in DA–Ca, a significant decrease occurs in the Cs salt. Diffusion constants and permeabilities are lower in DA than Nafion, especially for the cesium salt. Selectivity for water versus DMMP is 10-fold greater for Nafion compared to DA, due primarily to the higher water diffusion coefficient of Nafion. Selectivity decreases for Nafion–Ca, due to the large decrease in water permeability, and the value is only slightly higher than that for DA–Ca.

DCH is a moderately polar liquid, in which the unsulfonated, uncrosslinked DA precursor and polystyrene are completely soluble. Solubility is high in DA, but limited by sulfonation and crosslinking. DCH is insoluble in the sulfonyl fluoride precursor of Nafion and is not expected to interact strongly with the perfluorinated composition of Nafion. Nonetheless, there is substantial DCH solubility in Nafion, suggesting interaction occurs with sulfonic acid. This conclusion is supported by near elimination of DCH solubility in salt forms of Nafion. The considerable concentration of DCH in salt forms of DA is a measure of the solubility contribution of the unsulfonated component of the polymer. The increased solubility in the acid compared to the salt forms of DA arises from interaction with the sulfonic acid, equivalent to 3.6 molecules of DCH per sulfonic acid compared to 2.8 in Nafion. Both the lower solubility and lower diffusion constant of DCH in Nafion contribute to permeability that is almost an order of magnitude lower than DA. The effect of salt modification on the diffusion constant in Nafion is pronounced and permeabilities in the salt modifications are immeasurably low. Nafion is a far better barrier than DA for DCH and also a much better barrier for DCH than for DMMP.

3.2. Water vapor sorption

Isotherms were obtained on the Hiden vacuum sorption system for DA membranes, 66–71 μm thick as acid, Ca and Cs modifications. The DA–Ca sample was run at 25 °C, followed by DA–Cs and DA films at 30 °C. There was modest hysteresis with DA, with desorption values higher by about 12–15% at activities 0.4–0.8. The DA–Ca and DA–Cs films exhibited greater hysteresis, a 40% displacement on desorption at activity 0.4, but less at much lower and higher activities where sorption and desorption isotherms converge. The hysteresis in these samples is primarily an indication of relaxation of the structure, which occurs on the highest activity exposure and which gradually recovers with progress to lower activities on the desorption cycle. The sorption isotherms for the three DA samples and for Nafion and Nafion–Ca are compared in Fig. 1. Note that the isotherms for DA–Ca and DA–Cs samples almost overlap, with DA–Ca results only slightly lower. DA–Ca and DA–Cs isotherms extrapolate smoothly, with moderately increasing slope to immersion values, Table 3, whereas DA exhibits a large change between the concentration at the highest vapor activity, 39 wt%, and the saturation water uptake, 107 wt%. Isotherms for Nafion, represented by the solid curve and Nafion–Ca are displaced to lower concentrations than those of DA, but appear to have the same overall form. Nafion–Cs is lower still, the reverse of the order for DA–Ca and DA–Cs, but in keeping with the lower immersion concentration.

An interesting comparison can be made of isotherms, when rescaled to 100 wt% at unit activity, by dividing by the saturation concentrations, as shown in Fig. 2. The rescaled Nafion isotherm is now much higher than that for DA. Rescaled isotherms for DA–Ca and DA–Cs are also lower than that of Nafion and have separated, with the isotherm for DA–Cs now close to Nafion. Despite differences in the isotherms in this representation, they are similar over the intermediate range of activities. In fact, isotherms for all samples can be superimposed on the Nafion isotherm by a suitable choice of values to replace the use of the saturation concentrations for rescaling. For DA the value is 48 wt% compared to 107 wt% at saturation, for DA–Ca the value is 32 wt%, compared to 36 wt% and for DA–Cs the value is 30 wt% compared to 41 wt%. The points representing rescaled DA isotherms now cluster around the solid line representation of the normalized Nafion concentrations in Fig. 2. That these rescaling values are not arbitrarily related to the saturation concentration will be made clear in what follows. However, data for Nafion–Ca do not follow this pattern. In this case, if concentrations from activity 0.4 and above are fitted to the normalized Nafion line with a saturation value of 15.5 wt%, concentrations at lower activities fall below that of Nafion.

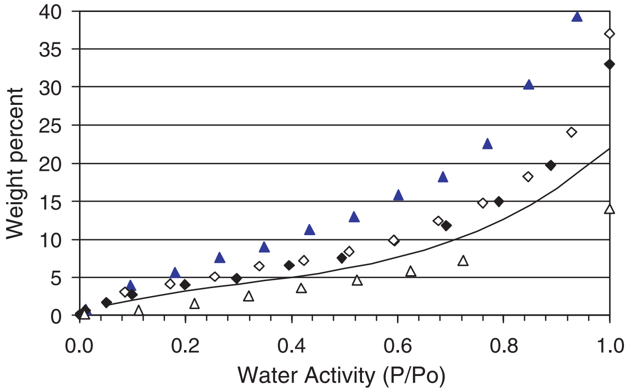

Fig. 1. Water isotherm: DA, filled triangle; DA–Ca, filled diamond; DA–Cs, open diamond; Nafion, solid line; Nafion–Ca, open triangle.

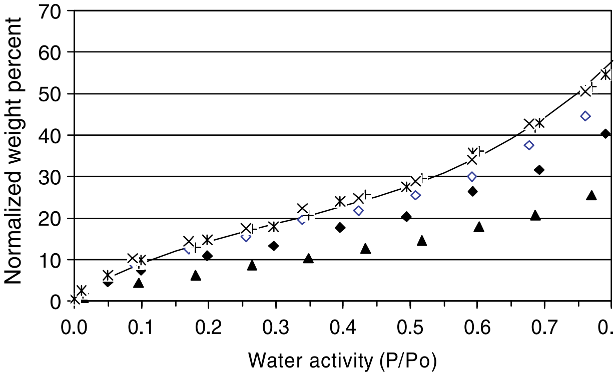

Fig. 2. Reduced water isotherm: Nafion, solid line; DA–Cs, open diamond; DA–Ca, filled diamond; DA, filled triangle. Rescaled values: DA, plus; DA–Ca, cross; DA–Cs, double cross.

As already noted, the DA membrane is a composite sample cast on a supporting microporous mesh and lightly crosslinked. When immersion water uptake was determined for sK64, an uncrosslinked membrane of similar composition without the microporous mesh, the result at 35 °C was 2.40 g/cm^3, almost 2.5 times the solubility for the DA membrane in Table 3. This is similar to the high-saturation water content for other uncrosslinked, sulfonated triblock polymers, as discussed below. When vapor sorption measurements were carried out on sK64 in the flow system at several activities, it was expected that concentrations would be proportional to the high-saturation value. However, as recorded in Table 4, concentrations are only slightly higher than those of the DA membrane. Apparently, isotherm concentrations for DA membranes at low to intermediate activity are not uniquely related to the saturation concentrations, a conclusion already suggested by superposition of DA and Nafion isotherms in Fig. 2, where isotherms for DA membranes are rescaled by amounts considerably smaller than immersion concentrations.

In order to determine how the modifications of the DA membrane affect solubility and permeation behavior and to make more meaningful comparisons with Nafion and other sulfonated ionomers, the vapor sorption measurements in the flow system were extended to DA-related samples of various compositions. The additional samples include: sK64-11 a polymer reacted with 11 wt% of trimethoxysilane crosslinking

Table 4
Water vapor solubility and permeability for several membranes

Membrane	Solubility[a]				Perm[b]
	0.5	0.7	0.8	0.9	
sK64	14.4	20.5	26.4	35.1	1.43
sK64-11	13.1	18.9	22.7	28.7	1.42
sK64-23m	11.1	15.7	19.1	24.0	9.88
sK69-11	13.1	18.9	23.4	Nd	1.28
DA	11.9	16.9	20.5	25.8	1.10
sSIBS	10.4	15.3	19.8	26.0	1.92
Ratios					
sK64/sK64-11	1.10	1.08	1.16	1.22	1.01
SK64-11/DA	1.10	1.12	1.11	1.11	1.29
sK64/DA	1.21	1.21	1.28	1.36	1.30
sK64-11/sK64-23m	1.18	1.20	1.19	1.20	1.44
sK64-11/sK69-11	1.00	1.00	0.97	Nd[c]	1.11

[a] Solubility (wt%) at activities 0.5–0.9.

[b] Permeability (g cm/cm^2 s$\times10^8$) at activity 0.5; membrane thickness 71.1–73.7 μm, except sK69-11, 81.3 μm and sSIBS, 255 μm.

[c] Not determined

agent, the same concentration as that for the commercial DA membrane, but without the microporous support; sK64-23 m with 23 wt% crosslinking agent and microporous support and sK69-11 another modification of the base polymer composition (Table 1) with 11 wt% crosslinking agent. The sorption results for all samples at several activities are recorded in Table 4 and the ratios in the lower section of the table indicate the effect of membrane variations on solubility. The effect of crosslinking is indicated by the ratio of sK64 and sK64-11. Concentrations are higher in sK64 and the ratio increases with activity. The effect of the microporous support is indicated by the ratio of concentrations for sK64-11, and DA membrane, which are uniformly higher in sK64-11 by about 10 wt% at all activities, an indication of the weight contribution of the membrane. The ratio of concentration in sK64 to DA indicates that the two effects of crosslinking and microporous support are completely additive. Comparison of sK64 with SK64-23 m indicates the effect of higher crosslinking, with concentrations that are higher in sK64 by 30% at activity 0.5, increasing to 46 wt% at activity 0.9. As noted in Table 1, sK69-11 is based on a polymer composition, which differs from sK64. Water concentrations are the same as sK64-11 at all activities, suggesting that the somewhat higher IEC in sK69-11 is offset by the higher ratio of endblock to midblock styrene.

Table 4 also contains data for sSIBS, which will be of interest in a later comparison. For now it should be noted that water concentrations in this uncrosslinked polymer are substantially lower than sK64 at vapor activities < 0.9, despite a saturation uptake of 350 wt% at 35 °C. Immersion solubility was also determined on sSEBS and on sSIBS1 with 77% sulfonation and IEC = 1.5 determined by Cs uptake. Water solubility for the acid form of sSEBS was 245 wt%, for the Cs modification 150 wt% and for the Ca modification 40 wt%. Water solubility determined for the acid form of sSIBS1 was 360 wt% and for the Cs modification 220 wt%, in very good agreement with published results [14]. Interestingly, IEC normalized solubilities for these two sulfonated triblocks are nearly the same, as are the ratio of acid to Cs solubilities, in both cases equal to 1.63. These results contrast with DA, where the ratio of acid to Cs water solubility is much larger, 2.6, and DA–Ca and DA–Cs solubilities are nearly equal. Since, styrene is limited to end blocks in sSIBS1 and sSEBS, the differences in solubility behavior of the DA salt modifications might be related to the styrene content in the midblock. Although IEC normalized water solubilities for sSIBS1 and sSEBS, with very different IEC values, are nearly equal this does not hold in the general case. In data for the series of sulfonated SIBS [14], the ratio of solubility to IEC increases rapidly with degree of sulfonation, from 70 to 160 and 196 at IEC values of 1.13, 1.41 and 1.78, respectively. This behavior suggests that changes in structural organization accompany the increasing degree of sulfonation in triblock polymers.

3.3. Water vapor permeability

While comparisons of the effect of membrane variations on water vapor solubility are straight forward, comparisons of permeability values are more complicated and subject to larger uncertainties. The final column of Table 4 lists estimated permeability at activity 0.5, corrected for boundary layer resistance by treating the total resistance as boundary and membrane resistances in series. Flux, is first converted to resistance using Eq. (1), then boundary layer resistance, equal to 94 s/m at 200 cm^3/min, is subtracted from the total resistance. The resulting membrane resistance is converted back to flux, Eq. (1), and normalized to 1-cm thickness, assuming that the flux scales as the inverse thickness. An indication of the effect of the membrane resistance is given by comparing the permeabilities of sK64-11 and DA, both with 11 wt% crosslinking agent. The ratio is 1.29, which represents the effect of the microporous membrane in the DA sample. The ratio for sK64, an uncrosslinked sample, and DA is also 1.29, indicating that the low degree of crosslinking in DA has little effect on permeability. This conclusion is also suggested by the equal permeabilities of sK64 and sK64-11, although the concentration in sK64-11 is also somewhat reduced by the crosslinking. Additional comparisons can be made with the data in Table 4, with broadly similar conclusions.

Water vapor permeability data for DA (74 μm), sK64 single layer (42 μm) and five layer (200 μm), sSIBS (267 μm) and Nafion (356 μm) are shown in Fig. 3, plotted as a function of activity. Values for all sulfonated triblock samples seem to follow the same general course, but the exceptionally high permeability of Nafion is clearly evident. Results for five-layer sK64 are displaced to higher values than single layer sK64 results which overlap DA values. It should be noted that the actual flux for single layer sK64 at activity 0.5 is nearly three times that of five-layer sK64. The boundary layer introduces a complication in normalizing flux for membranes of significantly different thickness, due to its influence on the effective concentration gradient. This is indicated by results in Table 5, where flux determined on single thickness sK64 is compared with flux for five layers of sK64. If it is assumed that steady state permeability scales as the inverse thickness, the ratio of measured to predicted flux varies from 1.7 to 2.5 (60% error) with activity 0.5–0.9. The apparent deviation from an inverse thickness dependence is due to the decrease in vapor concentration across the boundary layer resistance, with a change that is greater the higher the flux. In consequence, the concentration in the membrane depends on the flux. Since the diffusion coefficient is concentration dependent, the average diffusion coefficient in the membrane depends on both the boundary layer resistance and flux. Accordingly, it is preferable to compare the transport behavior of films in terms of diffusion coefficients as a function of concentration rather than the flux as a function of activity.

Diffusion coefficients were calculated by the method previously described for permeation measurements conducted with countercurrent challenge and sweep flows [9]. Changes in vapor concentrations across the boundary layer resistance, equal to 94 s/m, are calculated by application of Eq. (1) to obtain vapor concentrations at upper and lower membrane surfaces at inlet and outlet locations. Corrections are also made for the decrease in challenge concentration and accumulation of sweep concentration in flow along the sample length. Membrane concentrations are obtained from an analytical representation of the sorption isotherm, representing concentration, g/g, against vapor activity. An effective concentration gradient is obtained as the log normal average of inlet and outlet concentration gradients across the membrane, $(\Delta C1-\Delta C2)/\ln(\Delta C1/\Delta C2)$. Diffusion coefficients obtained as the ratio of flux to effective concentration gradient represent average values over the concentration gradient in the membrane and correspond to the average concentration in the upper membrane surface. Knowledge of the sorption isotherm and concentration dependence of the diffusion coefficient represents a complete description of the transport behavior and can be used to provide an accurate calculation of flux at different thicknesses in the presence of a defined boundary layer resistance.

Table 5
Effect of thickness on water flux ($\mathrm{g/cm^2\,s}\times 10^6$) for sK64

Quantity	Activity			
	0.5	0.7	0.8	0.9
Flux (42 μm)	2.13	4.55	5.68	6.78
Flux (200 μm)	0.763	1.97	2.65	3.53
Ratio	2.79	2.31	2.14	1.92
Flux (200 μm) predicted	0.448	0.956	1.19	1.42
Error %	41	51	55	60

Diffusion coefficients obtained from the analysis of flux and isotherm data for the various samples are compared in Fig. 4, plotted against concentration in g/cm^3. Diffusion coefficients for the 42 μm sK64 film (open triangles) and 200 μm sK64film (solid diamonds) are represented without any adjustments and largely overlap, indicating the importance of the extended boundary layer corrections. Diffusion coefficients for the triblock ionomers exhibit a similar concentration dependence in the order sSIBS > sK64 > DA. Nafion diffusion coefficients, represented by filled squares, are much higher than the values for any of the other samples, but the form of the concentration dependence appears to be similar to that represented for the sulfonated triblock polymers. In fact, diffusion coefficients for sK64, rescaled by a factor of 20, indicated by open diamonds, coincide with Nafion diffusion coefficients. By the choice of suitable factors the data for each of the samples can be shifted

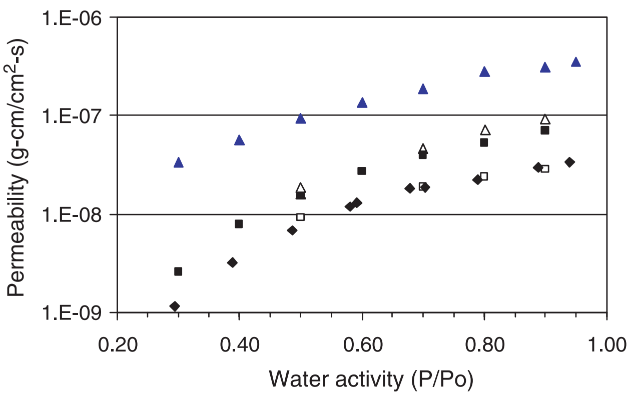

Fig. 3. Water permeability: Nafion, filled triangle; sSIBS, open triangle; sK64-200 μm, filled square; sK64-42 μm, open square; DA, filled diamond.

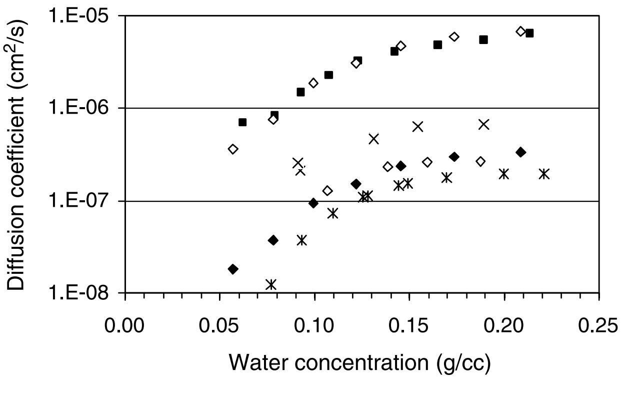

Fig. 4. Water diffusion coefficient: Nafion, filled square; sK64-42 μm rescaled times 20, open triangle; sSIBS, cross; SK64-42 μm, open diamond; sK64-200 μm, filled diamond; DA, double cross.

to overlap. sSIBS values when divided by 2.5 and DA values multiplied by 1.8 overlap the set of diffusion coefficients for sK64. The implication is that diffusion of water in all these ionomers occurs by the same mechanism, following sulfonated pathways, but the diffusion coefficients are displaced in magnitude by individual structural factors.

3.4. DMMP vapor sorption and permeation

Sorption measurements were conducted on a sample of the DA membrane at activities ≤0.9 in the flow system at 30 °C. Resulting DA concentrations were not corrected for the effects of crosslinking. The sorption isotherm in units of wt% against activity for DA is compared in Fig. 5 with the isotherm for Nafion determined previously. In both cases, the continuous curves represent calculated isotherms fitted to experimental vapor sorption and liquid immersion data with Table Curve V5 software. DA, as well as, Nafion membranes exhibit a rapid initial increase in uptake that, given the differences in composition, is probably due to specific interactions with sulfonic acid. A significant contrast between the isotherms, is the much lower slope over the extended range of intermediate activities for the DA membrane. The isotherms cross above 0.95 activity to accommodate the immersion solubilities, 189 wt% for DA and 133 wt% for Nafion. However, the marked discrepancy between the maximum vapor concentration for DA, 57 wt% at activity 0.9, and the nearly threefold higher immersion solubility reflects a change in structural organization, induced by the exceedingly high-DMMP concentration at saturation, similar to that occurring at saturation for water in triblock ionomers. The constrained interfacial volume between insoluble fluorocarbon domains tends to limit maximum swelling in Nafion, whereas, the dispersed sulfonated polystyrene regions and light crosslinking impart less resistance to swelling at high activity in DA.

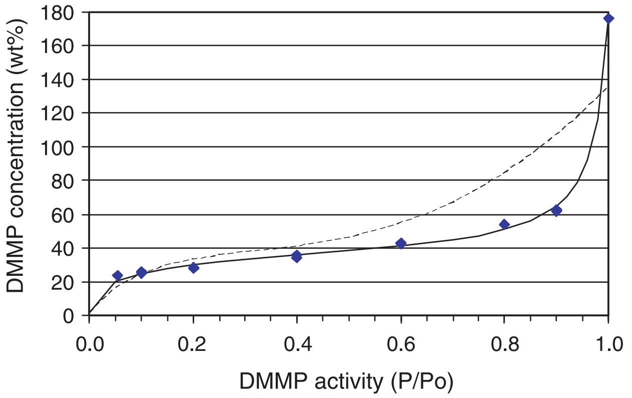

Fig. 5. DMMP isotherm: Nafion calculated, broken line; DA experimental, filled diamond; DA calculated, solid line.

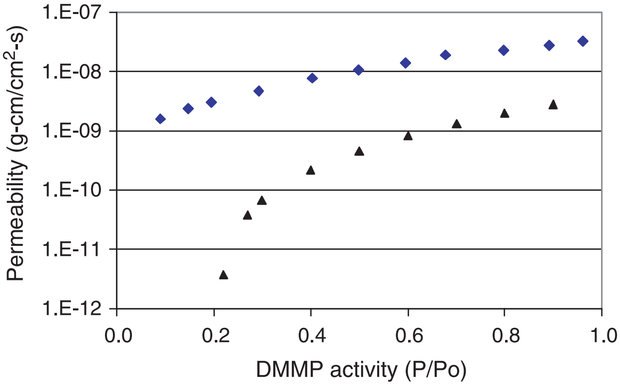

Fig. 6. DMMP permeability versus activity: Nafion, filled diamond; DA, filled triangle.

Thickness normalized values of permeability for DA and Nafion as a function of activity are compared in Fig. 6. The permeability in DA is much lower than that of Nafion and follows a different course, increasing rapidly at low activities, whereas the low activity increase for Nafion is modest. At the highest activity, DMMP permeability in DA is still an order of magnitude lower than in Nafion. The difference reflects both the higher DMMP vapor solubility in Nafion and, to a lesser extent, boundary layer effects discussed earlier for water, since DA thickness is 58 μm compared to 343 μm for Nafion. The effect of the non-linearity of DA and Nafion isotherms is evident in Fig. 7, where permeability is plotted as a function of concentration, g/cm^3, rather than activity. Concentration units of g/cm^3 are required to treat steady state permeability as the product of a diffusion coefficient and solubility. The initial low values and steep rise in DA permeabilities is magnified by the low isotherm slope, which compresses the data as a function of concentration. Also, the change to concentration units of g/cm^3 shifts Nafion values to twofold higher concentrations, because Nafion has a density of 1.95 g/cm^3.

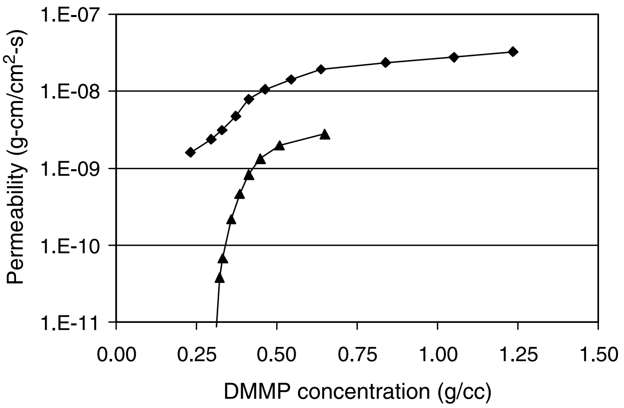

Fig. 7. DMMP permeability versus concentration: Nafion filled diamond; DA, filled triangle.

Diffusion coefficients are calculated by the procedure described earlier with water, in which corrections are applied for transfer across the boundary layer resistance, equal to 268 s/m. Tte results are shown in Fig. 8 as filled triangle for DA and open triangles for Nafion. Generally, results for DA are shifted to higher values, but are similar in appearance to permeability results as a function of concentration. Diffusion coefficients for Nafion exhibit a distinct transition with an order of magnitude increase in the intermediate range of concentrations. The exponential rise in DA diffusion coefficients at low-concentrations flattens out, merging with Nafion values at

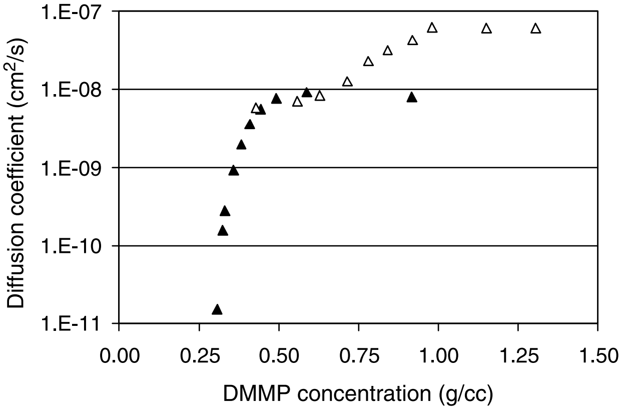

Fig. 8. DMMP diffusion coefficient versus concentration: Nafion, open triangle; DA, filled triangle.

intermediate concentrations. From a comparison of Figs. 5 and 6 it can be seen that the higher flux in Nafion compared to DA as a function of activity is a consequence of both higher concentrations and higher diffusion coefficients at all vapor activities.

4. Discussion

4.1. Water and methanol

This study has two main goals. First to determine the transport behavior of water and representative organic molecules in a sulfonated hydrocarbon triblock polymer; second to compare the transport properties with those determined for Nafion, in an attempt to understand how molecular transport is affected by the very different chemical composition and structural organization of these two types of ionomers. Transport properties determined from immersion solubility and liquid permeation with protic molecules, water and methanol, and with dipolar aprotic DMMP are a rich source of information about the effect of polymer composition and structure for the two classes of ionomers. The high water permeability of Nafion is due to a diffusion coefficient that is almost 20-fold higher than that in DA. The extremely high-water diffusion constant in Nafion requires that tortuosity is very low for ionic pathways. Given that two-thirds of Nafion consists of a fluorocarbon component, the impermeable phases must be small, dispersed regions to cause only minimal interruption of ionic pathways. In typical sulfonated-styrene triblock polymers, where styrene is present only in the endblocks, it is clear that the hydrocarbon midblock, present as a well defined continuous phase, interrupts ionic pathways and acts as an impedance to water transport. The situation is less certain in the DA and Kraton polymers, since 70 wt% of styrene occurs in the midblock, with a 2:1 mole ratio of butadiene to styrene. The implications of this compositional modification will be considered below in regard to water vapor sorption and diffusion.

Additional information critical to an understanding of the role of ionomer composition and structure is provided by measurements of sorption and permeability as a function of activity. Isotherms for acid, Ca and Cs forms of DA can be superimposed on the Nafion isotherm, normalized to 100 wt% at saturation, when the DA concentrations are divided by a factor, related to, but less than the saturation concentration. For DA–Ca and DA–Cs the scaling factors are only slightly lower than the saturation concentration, but the value for acid form of DA, 48 wt%, is less than half the saturation concentration of 107 wt% in Table 3. In vapor sorption measurements, sK64 reaches a concentration of only 34 wt% at a water activity equal to 0.9, far below the value of 240 wt% in immersion measurements. The contrast is even greater for sSIBS which attains 350 wt% saturation concentration in liquid, but only 26 wt% at activity 0.9. The saturation concentration is much higher than sK64 due to the higher extent of sulfonation of the styrene end blocks. These examples indicate that the isotherms for Nafion and the various sulfonated triblock ionomers can be superimposed by scaling factors that represent the saturation concentration for the initial, unrelaxed structure of the hydrocarbon ionomers. The structure is stable under most conditions of vapor exposure, but the extensive swelling that occurs at very high-vapor activity or upon contact with liquid causes reorganization of the polymer matrix.

The combination of immersion solubility and liquid permeability provides an average diffusion constant that can be related in a qualitative sense to aspects of polymer structure. A more detailed understanding of the effect of structure on transport properties can be obtained from the concentration dependence of the diffusion coefficient, derived from measurements of the steady state flux as a function of activity, in combination with the sorption isotherm. Nafion diffusion coefficients for water as a function of concentration, g/cm^3, are 20-fold higher than the DA values, but both sets of diffusion coefficients can be superimposed by a vertical shift. Moreover, diffusion coefficients for sSIBS, which are higher than DA values by a factor of about 2.5, can also be superimposed on Nafion values. Since, it has been shown that water diffusion in Nafion follows a free volume relation with standard parameters [5], it follows that this also holds for the sulfonated triblock polymers.

That the concentration dependence of diffusion is independent of ionomer composition implies that diffusion of water occurs exclusively in ionic pathways in the interphase volume between water-impermeable phases. The magnitude of the diffusion coefficient is dependent on ionomer structure, which determines the spatial distribution of sulfonate. High-water diffusion in Nafion, approaching the solvent self-diffusion coefficient of liquid water, requires well-connected pathways with little tortuosity. This is most likely due to the presence of small-scale rather than large-scale fluorocarbon phases, with hydrated sulfonate groups concentrated in the interfacial volume where transport occurs. In the case of the triblock ionomers, principal features of the original architecture are maintained following sulfonation, including the immiscibility of endblock and midblock, leading to polymer phases that are large compared to Nafion, but modified by incompatibility of sulfonated and hydrocarbon units.

The 2.5-fold higher diffusion coefficients for sSIBS compared to DA, even though the IEC is nearly the same for both ionomers, is an interesting example of the effect of compositional differences. The midblock accounts for 72 wt% of the DA polymer, with a 1:2 mole ratio of styrene to butadiene. At 38% sulfonation, there is less than one sulfonic acid unit for every seven units of the midblock. Thus, the dilute sulfonic acid units in the midblock might have difficulty in associating to provide effective continuity of ionic pathways. In sSIBS, sulfonic acid units are more concentrated, since, at 69% sulfonation, two out of three styrene units in the endblock are sulfonated. The relatively high-water diffusion coefficients in sSIBS require a redistribution of sulfonated styrene units to provide continuity of ionic pathways bridging the hydrocarbon matrix. This is likely promoted by phase incompatibility of sulfonated styrene units and residual unsulfonated styrene units, as observed in polystyrene homopolymer at levels approaching 5% sulfonation [26].

Methanol permeability in Nafion is somewhat higher than that of water, since the decrease in diffusion constant is offset by the marked increase in solubility. Although it might be expected that the increase in solubility is promoted by solvation of the fluoroether component, as well as the sulfonic acid, the low-methanol solubility for Nafion–Cs suggests that the methanol–fluoroether interactions are not favored and this conclusion is borne out in molecular modeling [27]. Methanol solubility in DA, is higher than that of Nafion but the diffusion constant is much lower, resulting in lower methanol permeability. Methanol solubility is lower in the salt forms of both ionomers but with marked differences. In Nafion both water and methanol solubilities are much lower in the cesium than calcium salts, whereas in DA water and methanol solubilities are nearly the same in the salt modifications. The contrast is highlighted by comparisons based on sulfonic acid content: 3.2 and 2.3 molecules of methanol per sulfonate in DA–Ca and DA–Cs, respectively, compared to 9.6 in Nafion–Ca. The other noteworthy effect is the large reduction in methanol diffusion constant from acid to salt forms of DA, in contrast with the near absence of an effect with water in DA. The low methanol diffusion constant in DA–Ca is largely responsible for the much lower methanol permeability compared to Nafion–Ca. Closer examination reveals that the diffusion constant is significantly higher for DA–Cs than for DA–Ca. One possible explanation is that diffusion in DA–Ca, is governed by an equilibrium between methanol associated with the sulfonate and methanol that is free to diffuse. All methanol is free to diffuse in DA–Cs, because strong cation shielding precludes methanol association with the sulfonate anion and solvation of the Cs–sulfonate salt is limited by the low-charge density of Cs.

4.2. DMMP

DMMP solubility in Nafion occurs primarily through solvation of the fluoroether component, as indicated by the equivalent solubility for acid and salt forms of Nafion, as well as by NMR measurements [28] and by molecular modeling [22]. The solubilities recorded for salt forms of Nafion in Table 2 are for times corresponding to the determination of liquid pemeabilities. Equilibrium solubilities require much longer time scales due to slow relaxation processes in the DMMP swelling of Nafion. Additional interactions are possible with the sulfonic acid since DMMP is a strong Lewis base, capable of acid–base interaction with the sulfonic acid. Also dipole–dipole interactions can occur with sulfonate salts between the PO dipole of DMMP and the strong dipole formed by the sulfonate–cation ionic bond, as predicted for the potassium sulfonate salt of Nafion [22]. These interactions might contribute to the rapid increase in DMMP solubility at low activity common to Nafion and its salt modifications but otherwise there is not evidence that interactions of DMMP with the sulfonate play a large role in the transport behavior of DMMP in Nafion. However, DMMP solubility in DA occurs primarily through interactions with sulfonic acid, since the solubility, determined under immersion conditions at 35 °C, is only 8 wt% in the unsulfonated precursor, but increases to 133 wt% in the acid form of DA. DMMP solubility is almost equally high in DA–Ca, probably due to dipole–dipole interactions but much lower in DA–Cs, as a result of the relatively weak dipole of the Cs salt, associated with the low-charge density of the Cs cation. The contrast with the high solubility of DMMP in Nafion–Cs, is a further indication of the primary importance of DMMP interactions with the fluoroether phase in Nafion.

DMMP liquid permeability is higher in Nafion than DA for all forms, due to higher solubility as well as a higher diffusion constant. As shown in Table 2, diffusion constants for Nafion are essentially unchanged in the salt and acid forms, whereas there is a large reduction in the diffusion coefficient in the two salt forms of DA. The contrasting solubility and diffusion behavior suggests that DMMP diffusion follows different pathways in the two ionomers, associated primarily with the fluoroether interphase in Nafion, but restricted to ionic pathways in DA. Significant differences are also observed in the results of vapor measurements. DMMP vapor permeabilities in DA are much lower than Nafion and increase by almost four-orders of magnitude over a small range of activity, compared with less than two-orders of magnitude increase in Nafion. Diffusion coefficients, calculated as the ratio of flux to effective concentration gradient, follow similar trends, but Nafion results are shifted to higher concentrations due to the higher density of Nafion. Measurements of flux are not available at low concentrations, corresponding to concentrations for DA, but Nafion diffusion coefficients are expected to increase with only modest slope, based on NMR solvent self-diffusion data, in contrast to the exponential rise for DA. The very different nature of the concentration dependence of diffusion in Nafion and DA membranes is a reflection of the difference in pathways for DMMP previously noted, but also dependent on the phase segregated morphology. DMMP vapor sorption kinetics in Nafion is usually non-Fickian, and includes a variety of secondary relaxations and irreversible changes.

These results are consistent with the suggestion that the structure consists primarily of small phases with intermixed fluorocarbon and fluroroether regions rather than large-scale fluorocarbon regions. DMMP sorption kinetics in DA is also non-Fickian, with curvature in the plot of weight gain against square-root of time. There do not appear to be distinct relaxation processes or irreversible changes with swelling by DMMP, but this cannot be ruled out based on the limited evidence in this study. The stability of structure in the DA membrane arises from the preexisting phase morphology that is only partially disrupted by the immiscibility of sulfonated styrene units with nonsulfonated components, and which have little effect on the immiscible phase formed by the midblock.

4.3. *Effect of cation substitution on diffusion constants*

The effect of cation substitution on the diffusion constant of the various liquids is dramatic, as noted in Table 3 and there are also examples of some marked differences in the effects for the two ionomers, as discussed earlier. Cation-mediated changes in ionomer morphology have received little attention in the literature compared to ion conductivity and the associated topic of ion mobility [29–31]. Cation substitution can be expected to have two effects that will lead to changes in solvent diffusion constants. The first is a change in the ionic pathways that are a consequence of the extent of association and degree of interaction of polar groups. Association of sulfonate–cations will be promoted by solvents of low-dielectric constant, in the present case DCH, as compared to methanol, and by poor solvation. Because of its low-charge density, cesium is poorly solvated and forms a contact ion-pair with the sulfonate anion, which is also poorly solvated. There are also differences in the environment of the sulfonate anion in Nafion and DA as indicated by the results of cation exchange in Table 2, which are stochiometric for calcium as well as cesium in Nafion, but result in one-third molar excess for calcium in DA, presumably due to a lower probability of finding two acid groups sufficiently close to react with a single Ca^{2+}. At present there is no independent evidence to indicate how the extent of ion association might affect the larger scale organization that controls the transport process.

The second effect of the cation on the diffusion constant arises from the role of ionic substitution in altering the segmental mobility, which supports solvent diffusion. Ion mobility as a function of solvent concentration has been fitted by a free-volume relation and ion mobility, where ions are present solely as part of the ionomer composition, has been successfully modeled by an extension of free-volume theory [32]. The diffusion of solvents in ionomers can also be treated by free-volume concepts, as indicated by the success of a free-volume analysis of water diffusion in Nafion [5]. Whether diffusion occurs along an ionic interphase, as for water and methanol in Nafion and additionally for DMMP in DA, or through the fluoroether phase, as for DMMP in Nafion, mobility is governed by polymer reptation to provide free volume for diffusion or fluctuations in the cross section of interphase ionic pathways. Segmental mobility and solvent diffusion will be promoted by the greater free-volume contributed by higher liquid solubility. Segmental mobility will also be affected by the extent of association of polar groups and by ionic crosslinks, but with results that differ for substitution on the styrene units of the main chain in DA as compared to the more mobile fluoroether side chain in Nafion. One example is the lower methanol permeability in the calcium salt of DA compared to Nafion, largely due to an unusually low diffusion constant for DA–Ca. An additional example of contrasting behavior is that substitution with Cs lowers the diffusion constant for water and methanol in Nafion compared to the calcium salt, but increases the diffusion constant in DA–Cs compared to DA–Ca. The difference might be due to an effect of the heavy Cs cation on the segmental mobility of the fluoroether side chain in Nafion, but much reduced effect with the sulfonate on the styrene unit on the main chain in DA.

5. Conclusions

Nafion is a fully fluorinated, nominally solvent resistant, phase-segregated polymer produced from a precursor without large-scale morphological differentiation of fluorocarbon and fluoroether regions. Phase segregation in Nafion results from the incompatibility of peripheral polar, sulfonic acid groups with the remainder of the perfluorinated polymer. The DA and Kraton membranes involve a sulfonated triblock with styrene endblocks and a copolymer styrene–hydrogenated butadiene midblock, exhibiting cylindrical morphology before sulfonation [13]. In contrast to Nafion, sulphonated units are distributed along the main chain of the hydrocarbon triblock ionomers with minimal spatial separation between polar and non-polar sites.

Analysis of liquid solubility and permeability data of Nafion and DA sulfonated triblock ionomers has revealed the effect of the differences in chemical composition and structure of these ionomers on the transport behavior of water and several organic solvents. The effect of sulfonic acid substitution on the styrene ring of DA compared to the terminal unit on the fluoroether side chain of Nafion is evident in the contrasting solubility behavior of water and methanol, which are both much lower in Cs than Ca forms of Nafion but comparable in the DA salts. The exceptionally high water and methanol permeabilities in Nafion are due primarily to high-diffusion constants, which require the presence of unimpeded ionic pathways. This implies that most of the hydrophobic perfluorinated polymer is distributed in small scale regions rather than a more regular, large-scale structure, as has also been suggested recently for hydrated Nafion based on SANS data [33]. In the sulfonated triblock ionomers the midblock forms a continuous phase that must be bridged by association of sulfonate groups to provide continuity of ionic pathways. In the acid form, the triblock ionomers also exhibit high water and methanol permeability. As distinct from Nafion, the Ca modification of DA results in a 100-fold reduction in methanol permeability compared to the acid, while the permeability of the Cs modification is higher than that of Ca. These results suggest that there are differences in the properties of the sulfonate substituted on the styrene unit of DA as compared to the fluoroether of Nafion.

The hydrocarbon and perfluorocarbon ionomers exhibit qualitative similarities in the sorption and permeation of water as a function of activity. Isotherms for the triblock ionomers can be superimposed on that of Nafion when the results for the triblock ionomers are rescaled by an appropriate factor. This factor is not arbitrary but represents the saturation concentration of the initial structure, which is lost at the very high degree of swelling under immersion conditions. Diffusion coefficients for water over a wide concentration range in DA and sSIBS can also be superimposed with that of Nafion by a vertical shift, a 20-fold factor for DA. This result indicates that diffusion of water is limited to ionic pathways for both types of ionomers, whereas the magnitude of the diffusion coefficients is determined by ionomer structure. An additional implication is that the free-volume dependence determined for water diffusion in Nafion [5] also applies to DA and sSIBS.

DMMP isotherms for Nafion and DA follow a similar form at intermediate concentrations, but with much lower slope for DA than DAIS. At low concentrations the diffusion coefficient in DA is smaller than that in Nafion, by more than two orders of magnitude, and rises exponentially, compared to a far more limited increase in Nafion approaching Nafion values at the highest accessible DA concentrations. The contrasting diffusion behavior is a result of the different environments for DMMP diffusion in Nafion and DA, involving primarily fluoroether regions of Nafion, and sulfonic acid containing regions of DA. It is interesting that there is substantial solubility of the moderately polar liquid DCH in the acid form of Nafion, but almost none in the salt forms. The contrast with DMMP which is equally soluble in the acid and salt forms, is due to the extensive solubility in the fluoroether phase, which evidently is not the case with DCH.

While the present work adds to a more detailed understanding of effects of composition and morphology on transport behavior in these two phase segregated ionomers, it only provides an indirect indication of the effect of sulfonation on the distinctive initial morphology of the triblock polymer and the phase reorganization that provides ionic pathways for water transport through the hydrocarbon medium. NMR studies to characterize dimensions and composition of the phases in triblock ionomers as a function of the extent of sulfonation, along with other analytical methods to characterize solvent interactions, are being pursued to answer these questions.

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