A Fluorescent Probe Investigation of the Origin of Superselectivity in Perfluorinated Ionomer Membranes

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ABSTRACT: The fluorescent probes pyrene and $Ru(bpy)_3^{2+}$ were used to study the relative locations of cations and anions in microphase separated perfluorinated ionomers. After determining that these probes are located in the interfacial regions that separate the fluorocarbon phase from the ion and water-rich phase, cationic and anionic quencher ions were introduced into the system and changes in fluorescence monitored. Results show that Cs^+ is located on the aqueous side of the interfacial region, in close proximity to pyrene, while I^- is located deeper into the interfacial region and farther away from the aqueous phase. These differences are greater for carboxylate ionomers than for sulfonate ionomers, in close parallel to their relative abilities to discriminate against anion transport in practical membrane-based applications. These results show that the phenomenon of superselectivity is based on the differences in the average locations and therefore the transport pathways of cations and anions in perfluorinated ionomers.

Introduction

Perfluorinated ionomer membranes have become a well-studied class of polymers due in part to their highly unusual properties and in part to their technological importance in many separation applications. In addition to their good mechanical properties and superior chemical inertness, these ionomers provide an unusual degree of permeability selectivity in favor of cations over anions. This selectivity is in addition to the well-understood Donnan permselectivity which is based on differences in the equilibrium sorption of counterions and co-ions in an ion exchanging medium.[1] The term "superselectivity" was created by Reiss and co-workers[2−3] to designate this new, presumably kinetically based selective permeability.

This group, as well as other researchers,[4−6] has described possible origins of the phenomenon of superselectivity from theoretical and experimental grounds. Most of these relate, in one way or another, to the microphase separated morphology of the perfluorinated ionomers, itself a now well-studied feature of this class of polymers.[7] Generally, this phase separation is described as the clustering of water, exchange sites, and counterions (along with sorbed electrolyte for concentrated external solution environments) into a separate phase. The relatively high ionic conductivity of these materials which is accompanied by modest water sorption, as well as the low volume fraction of water at which the percolation threshold for conductivity is reached, indicates that these aqueous regions are highly interconnected. However, the exact details of this interconnectivity and its underlying cause are still a subject of study.[8]

Early ionic diffusion studies of these ionomers provided some important clues to the source of superselectivity.[4,6,9,10] The relationships among the ionic diffusion coefficients of small cations and anions in these polymers were found to be different from those seen for standard cross-linked ion exchange resins. In particular, the diffusion coefficients of the alkali metal ions are larger than those of halide ions in Nafion sulfonate and carboxylate membranes, even though the opposite is true for sulfonate ion exchange resins.[11] As well, for ions of the same charge but of different size such as sodium and cesium ions or chloride and iodide ions, the larger, more hydrophobic ion has a significantly smaller diffusion coefficient. This is in contrast to the relative diffusion behaviors both in ion exchange resins and in water. Interestingly, the activation energies of diffusion for these ions in the membranes are all similar and close to those seen for these ions in water. Thus, some specific barrier to diffusion which depends on charge type or ionic size would not seem to be the source of the diffusional differences.

An understanding of the underlying cause of these diffusional differences would be valuable and would potentially enable diffusional discrimination to be designed into future polymer membranes, perhaps for specific separation applications. It has been suggested that the interface between the hydrophilic and hydrophobic microphases might be at the source of this phenomenon,[4] in that it could act somewhat like a chromatographic stationary phase to selectively retard ionic diffusion based on charge type and hydrophilicity. In order to test this hypothesis, fluorescent probes have been used in this study to determine the relative equilibrium locations of cations and anions within the microphase separated structure of the polymer. The object is to establish the essential cause of superselectivity.

A number of fluorescent probes have proved to be useful in the study of these ionomer membrane systems.[12−24] The two fluorescent probes that are used most extensively (and which are used in this study) are pyrene (and pyrene derivatives) and tris(2,2′-bipyridyl)-ruthenium(II) ion. The polarity of the local environment of pyrene can be determined by examination of the relative intensities of the principal vibronic bands of pyrene's emission spectrum, since the symmetry-forbidden bands show marked intensity enhancements under the influence of solvent polarity.[25] If the principal vibronic bands observed at room temperature are numbered I−V, the intensity ratio of the III to I bands serves as a measure of polarity of pyrene's environment. Using this tool, it has been concluded that pyrene is located in the water−fluorocarbon interfacial regions of perfluorinated ionomers.[19−21] Lee and Meisel studied the interaction of Ag^+ and Pb^{2+} with pyrene and concluded that they are all in similar environments.[20] More recently, Blatt et al. have compared the quenching

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efficiencies of Pb^{2+} and I^- for pyrene in Nafion (Dupont) and Flemion (Asahi Glass Co.), relative to that in aqueous solution.[22] They found that the relative quenching efficiency of Pb^{2+} was much higher than that of I^-.

When tris(2,2′-bipyridyl)ruthenium(II) ($Ru(bpy)_3{}^{2+}$) is exchanged into these polymers, its fluorescence emission maximum shifts to a shorter wavelength compared to that found in water or sodium dodecyl sulfate micelles, but is similar to that in sodium perfluoroctanoate micelles.[20] Also, the quenching of the probe complex ion by several metal ions was found to be dynamic in all cases, but the quenching constant was reduced from that in aqueous solutions. The authors concluded that the probe molecule is located at the interface of the fluorocarbon and the water exchange site region. In a further study, Colon and Martin showed that the initial tris(2,2′-bipyridyl)ruthenium(II) ions to exchange into the ionomer occupy the sites of lowest water activity and that the probe molecule can take up to one month to reach an equilibrium environment within the polymer phase.[24]

In this study the fluorescent probes pyrene and $Ru(bpy)_3{}^{2+}$ are used to determine the location of ions within the polymer structure. The local environment of these probes in the ionomers is first examined to determine their location within the phase-separated structure and to note differences among the polymer types. Then these fluorescent probes are quenched by a number of ions (Cs^+, I^-, and Cu^{2+}), and from the ability of these ions to quench the probes the likely locations of the ions are inferred. Finally, the locations of these probe molecules and various ions are discussed in terms of the interfacial region between the ion/water-rich phase and fluorocarbon phase.

Experimental Section

Materials. Sulfonate and carboxylate forms of long and short side chain ionomers were kindly donated by E. I. du Pont de Nemours & Co. and the Dow Chemical Co., respectively. The Dupont and Dow carboxylate ionomers were received in the methyl ester form and the Dupont sulfonate ionomers in the sulfonyl fluoride form; they were both hydrolyzed using a solution of $KOH/DMSO/H_2O$, after which they were pretreated as previously reported.[26] The Dow sulfonate ionomers were received in the acid form and were pretreated in a similar fashion. The ionomers were used in the Na^+ form unless otherwise stated. Pyrene (Aldrich) was twice sublimed under vacuum prior to use. Tris(2,2′-bipyridyl)ruthenium(II) chloride ($Ru(bpy)_3{}^{2+}$) (Aldrich), $CuSO_4 \cdot 5H_2O$ (BDH), CsCl (G.F.Smith Chemicals), NaCl (BDH), and NaI (BDH) were used as received. Triply distilled water was used throughout this study. The radioisotopes ^{22}Na, ^{137}Cs, and ^{125}I were obtained as carrier-free radioisotopes (Amersham International).

Instrumentation and Procedure. Pyrene was incorporated into an ionomer by equilibrating the membrane in a 0.1 M solution of NaCl saturated with pyrene; fresh solutions were used at regular intervals. Other ionomer samples were equilibrated in 10 mL aliquots of 5×10^{-6} M $Ru(bpy)_3{}^{2+}$ solution to give a final membrane concentration of about 2×10^{-4} M, in order to give final absorbance of 0.08–0.1. The ionomers were left in the $Ru(bpy)_3{}^{2+}$ solution for at least one month to equilibrate. The uptake of pyrene and $Ru(bpy)_3{}^{2+}$ was monitored by measuring the absorbance of the incorporated probe in the membrane (average absorptivity of 5×10^4 M^{-1} cm^{-1} at 334 nm[12] and 1.46×10^4 M^{-1} cm^{-1} at 447 nm[20] for pyrene and $Ru(bpy)_3{}^{2+}$, respectively) using a Perkin-Elmer Lambda array 3840 spectrophotometer. Fluorescence emission spectra and intensities were collected at 25 °C on a Photon International Technologies Alphascan spectrophotometer. Pyrene was excited at 310 nm using slit widths of 4 nm (Ex) and 1 nm (Em). The $Ru(bpy)_3{}^{2+}$ was excited at 450 nm using slits widths of 6 nm (Ex) and 4 nm (Em). Samples were sandwiched between two quartz glass slides placed in a sample holder so that they were positioned at a 45° angle to the excitation source, and fluorescence emission was detected from the opposite side of the membrane at a 45° angle to the detector. Pyrene and $Ru(bpy)_3{}^{2+}$ fluorescence emissions were quenched using a number of ions. Ions were incorporated into an ionomer by placing a sample in a solution containing the ion and leaving to equilibrate for 8 h. The concentrations of Cs^+ and I^- ions in an ionomer were determined using radiotracer techniques. The solution was doped with the appropriate radiotracer and equilibrated for 8 h. The activities of the membrane and bathing solution were then measured, and the concentration of the ion in the membrane was calculated. The concentration of Cu^{2+} in a membrane was found by leaching the copper out of the membrane into 0.2 M NaCl bathing solution. The concentration of Cu^{2+} in the bathing solution was determined by flame atomic absorption spectroscopy using a Thermo Jarrel Ash Smith-Hieftje 1000 spectrophotometer. Equivalent weight determinations were carried out using a radiotracer technique described elsewhere.[27,28] The water content of a membrane was calculated from drying water swollen membranes at 120 °C under vacuum for 24 h and measuring the weight change.

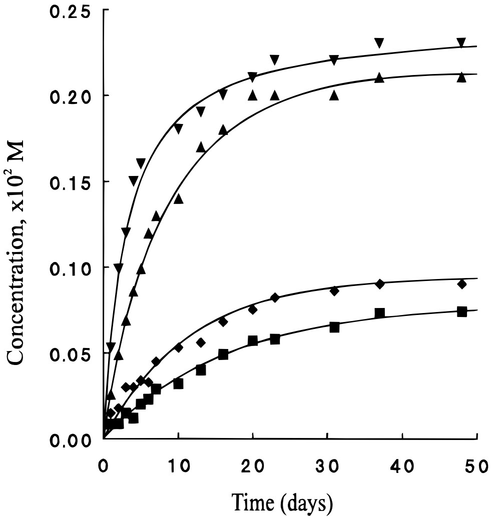

Figure 1. Pyrene uptake versus time in days for various membrane: ▲, 1220 EW Nafion sulfonate; ▼, 1020 EW Nafion sulfonate; ◆, 1290 EW Nafion carboxylate; ■, 1470 EW Nafion carboxylate.

Results and Discussion

Figure 1 shows the concentration of sorbed pyrene versus time for four of the ionomers studied. The results show that the equilibrium concentration of pyrene increases with increasing polymer ion content and that the sulfonate ionomer shows a higher saturated pyrene content than the carboxylate ionomer of similar ion content. Similar results were seen for all ionomers studied. The equilibrium concentrations of pyrene in the ionomers ranged from 2.3×10^{-3} M for a 960 EW Nafion sulfonate ionomer to 7.5×10^{-4} M for a 1470 EW Nafion carboxylate ionomer. These are in general agreement with that found by Lee and Meisel for the 1100 EW Dupont sulfonate ionomer.[20] The incorporation of pyrene into the perfluorinated ionomers showed that the maximum pyrene concentration is membrane dependent and that an equilibrium condition requires one month or more. Higher equilibrium concentrations were favored with the sulfonate ionomers and at higher ion contents (lower equivalent weights) in all cases. Even for the higher concentrations, there would be less than one pyrene molecule per "ion cluster", as estimated by other workers using observed Bragg

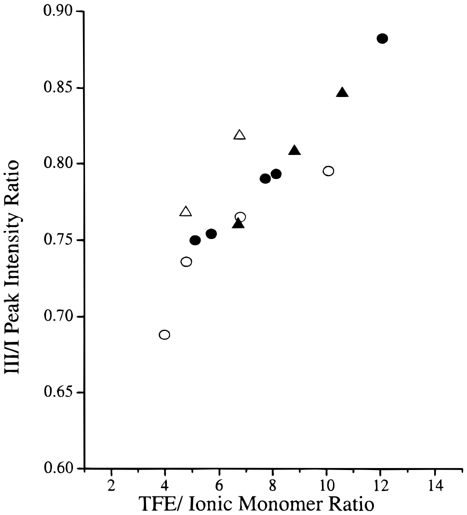

Figure 2. Pyrene III/I ratio vs TFE/ ionic monomer for perfluorinated ionomer membranes, equilibrated three months: ●, Nafion sulfonate; ▲, Nafion carboxylate; ○, Dow sulfonate; △, Dow carboxylate.

spacings and an assumed simple geometric arrangement of scattering entities.[20] It is possible that the differences in the equilibrium concentrations of pyrene for these ionomers reflect different microphase interfacial surface areas. Figure 2 shows the emission intensity ratio of the III/I vibronic peaks of sorbed pyrene as a function of decreasing ion content. The results show that the average environment of the probe changes with both ion content and type of ionomer. The pyrene appears to be located in a fairly hydrophilic environment in all cases. The III/I intensity ratio of pyrene ranges from 0.69 for the 680 EW Dow sulfonate to 0.85 for the 1660 EW Nafion sulfonate, compared to the measured values of 0.54 for water and 2.00 in perfluoromethylcyclohexane.[25] These results are in general agreement with the earlier studies which concluded that sorbed pyrene was located at the water−fluorocarbon interfacial region.[19−21] The variation in the III/I values of the pyrene suggests that the hydrophilicity of the interfacial region changes with ionomer type and ion content. The pyrene appears to be in the most hydrophilic environment in high ion content ionomers and in the most hydrophobic in the low ion content ionomers, not surprisingly. The values shown in Figure 2 are for samples which were equilibrated for three months. After another three months of equilibration, the III/I values were found to increase by a further 3−8%, indicating that the environments were becoming more hydrophobic with time. This suggests that pyrene very slowly continues to further diffuse into fluorocarbon material. The average fluorescence lifetimes of pyrene in the ionomers were found to range from 161 to 343 ns (deaerated), which is the range observed for pyrene in typical solvents. Rotational correlation times calculated from the depolarization lifetimes of pyrene here indicate that this molecule exists in a less restricted environment in the carboxylate ionomer (4−5 ns) compared to the sulfonate ionomer (38−95 ns). This suggests that although the environment of the carboxylate ionomer is more hydrophobic for pyrene, the environment of the pyrene is actually less rotationally restricted.

The values for the steady state fluorescence emission of $Ru(bpy)_3^{2+}$ are shown in Table 1. The λ_{max} values show little or no difference with changing polymer ion (and water) content for the same exchange group but do show a difference between the sulfonate and carboxylate polymers. The values for the carboxylate polymers show larger "blue shifts" compared to those for the sulfonate polymers. It has previously been proposed that the shift seen for $Ru(bpy)_3^{2+}$ is due to its interaction with the fluorocarbon material and not with the exchange group.[12,18] If so, these results suggest that, in the carboxylate form of the polymer, the $Ru(bpy)_3^{2+}$ may be exposed to a more fluorocarbon-like environment, perhaps as a result of a more defined interfacial region. Szentirmay et al.[19] have also shown that the when compared to pyrene, $Ru(bpy)_3^{2+}$ is less sensitive to its environment, and this may explain the very similar λ_{max} values seen with different ion contents. It should also be noted that for electrostatic considerations the $Ru(bpy)_3^{2+}$ must be located within the Coulombic fields of exchange groups. This environment is not expected to show large changes with ion content but would be expected to change with the length of side chain and especially with exchange group.

Table 1. Emission λ_{max} Values of $Ru(bpy)_3^{2+}$ in Membranes

membrane	λ_{max}, nm
680 EW Dow sulfonate	593
760 EW Dow sulfonate	593
960 EW Dow sulfonate	593
1290 EW Dow sulfonate	597
960 EW Nafion sulfonate	598
1020 EW Nafion sulfonate	597
1220 EW Nafion sulfonate	596
1260 EW Nafion sulfonate	596
1660 EW Nafion sulfonate	596
1080 EW Nafion carboxylate	582
1290 EW Nafion carboxylate	584
1470 EW Nafion carboxylate	585
720 EW Dow carboxylate	584
910 EW Dow carboxylate	584
Nafion 117	597[19]
H_2O	613[19]

It has been found from previous studies for these[12,22] and other heterogeneous systems[29,30] that the quenching of fluorescence for these fluorophores by the quenchers used is collisional (dynamic) in nature. The results from this study, both time resolved and steady state, also confirm that the quenching is dynamic in nature. The Stern−Volmer equation[31] for dynamic quenching of fluorescence is

$$I_0/I = \tau_0/\tau = 1 + k_q\tau_0[Q] = 1 + K_D[Q]$$

where I is the emission intensity in the presence of quencher, I_0 the the emission intensity in absence of quencher, τ the the average lifetime in the presence of quencher, τ_0 the the average lifetime in the absence of quencher, k_q the the bimolecular quenching constant, K_D the the Stern-Volmer quenching constant, and [Q] the the concentration of the quencher. A linear plot generally indicates (for a single class of fluorophore) that the fluorophore has total accessibility to the quencher. Figure 3 shows a typical Stern−Volmer plot of the quenching in the systems studied; the dotted line represents the behavior expected if the quenching followed the relationship given above. The plot, however, shows a deviation toward the quencher axis. If two fluorophore populations are assumed and one is not assessable to the quencher, then deviations from linearity as seen in Figure 3 can be expected. In this case the Stern−Volmer equation can be easily modified[32] to the form

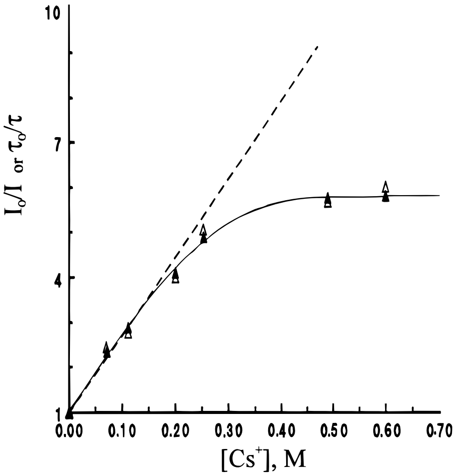

Figure 3. Quenching of pyrene in Dow sulfonate 760 EW by cesium ions: ▲, I_0/I; △, τ_0/τ.

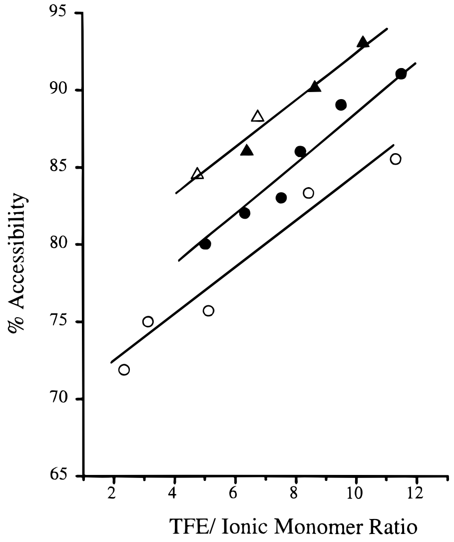

Figure 4. Accessibility of cesium ions for quenching of pyrene fluorescence: ●, Nafion sulfonate; ▲, Nafion carboxylate; ○, Dow sulfonate; △, Dow carboxylate.

$$\frac{I}{\Delta I} = \frac{1}{i_a K[Q]} + \frac{1}{i_a}$$

where i_a is the fraction of the initial fluorescence which is accessible to the quencher, $\Delta I = I_0 - I$ and $i_a = I_{0a}/(I_{0a} + I_{0b})$, and the subscripts a and b refer to the two populations of fluorophore and 0 again refers to intensity in the absence of quencher. The accessibility of the quencher for the fluorescent probe molecule then be found from a plot of $I_0/\Delta I$ vs 1/[Q].

Figure 4 shows the accessibility of the quenching ion Cs^+ to the pyrene molecules located within the cluster structure of the polymer. The results show that cesium ion has a generally high degree of accessibility to the pyrene probe molecule, the lowest being for the Dow 680 EW sulfonate with a value of 72%. Cesium ion and pyrene must therefore be in close proximity to each other in these polymer systems. As stated earlier, the pyrene is thought to reside on the aqueous side of the fluorocarbon–water interfacial region. Cesium ion must therefore be in or close to this region of the polymer structure. The degree of accessibility of the cesium ion to the pyrene molecule is higher for the carboxylate polymers and increases with increasing equivalent weight for both types of polymers. Membrane transport studies have shown that the diffusion coefficient of cesium ion in these polymers is generally lower than that for sodium ion, even at equal water contents, with the greatest difference seen for the sulfonate polymers. As well, the difference in the diffusion coefficients becomes smaller with increasing equivalent weight.[10] It has been suggested that cesium ion's relatively large size and low hydration enthalpy compared to those of sodium ion may generate a preferential distribution of this counterion into the interfacial region, but still in the vicinity of an exchange group to maintain electroneutrality.[4] The results of these cesium ion quenching studies indicate that cesium ion is in the interfacial region (close to pyrene), as indicated by the high accessibility values. Further, cesium ion would appear to be more localized on the aqueous side of the interface for the carboxylate polymers and with increasing equivalent weight for both polymer types. These results agree very well with the diffusional trends seen for sodium and cesium ions and their original interpretation.

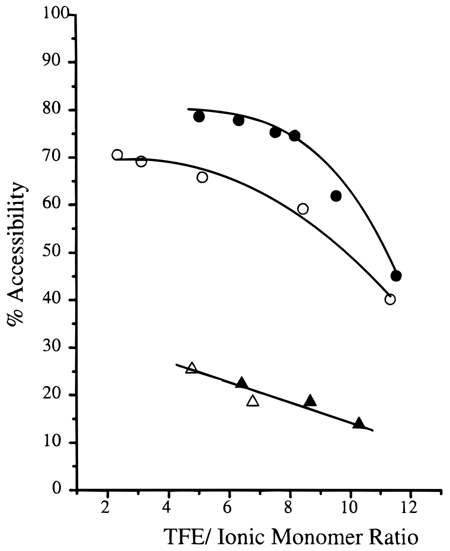

Figure 5. Accessibility of iodide ions for quenching of pyrene fluorescence: ●, Nafion sulfonate; ▲, Nafion carboxylate; ○, Dow sulfonate; △, Dow carboxylate.

The results for iodide quenching measurements are shown in Figure 5, and considerable differences are seen in the trends compared to those for cesium ion. Now quencher accessibility decreases with increasing equivalent weight and is lower for the carboxylate compared to the sulfonate polymers. These trends are opposite to those for cesium ion quenching. For each ionomer sample, iodide ion accessibility to pyrene is lower than that for cesium ion. Also noteworthy is the large difference in accessibility between sulfonate and carboxylate forms, unlike the cesium ion results. The position of the pyrene in the polymer is not expected to change with quencher. Therefore, iodide ion must be located in a different average location within the structure relative to that of cesium ion. Pyrene and iodide ion are less likely to be located in close proximity to each other with increasing EW and in the carboxylate membranes. Diffusion studies have shown that the diffusion coefficient of iodide is smaller than that of counterions such as sodium ion or cesium ion and that the difference is greater for carboxylate polymers and grows with increasing equivalent weight.[26] The iodide ion is relatively large in size and hydrophobic in nature, compared to chloride ion. Chloride ion may well therefore be located in the aqueous core region of the polymer

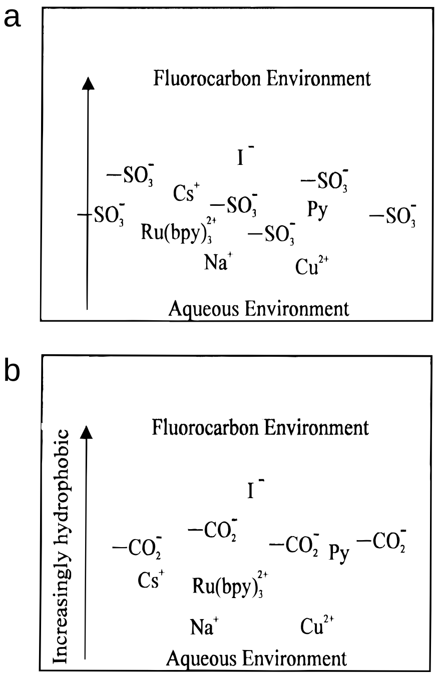

Figure 6. (a) Diagrammatic representation of the location of different ions within the sulfonate membrane structure. (b) Diagrammatic representation of the location of different ions within the carboxylate membrane structure.

system, which would account for its larger diffusion coefficient. The more hydrophobic iodide ion might be expected to be located in the more hydrophobic interfacial region. This would explain the difference in the diffusion coefficients for chloride and iodide ions. Iodide ion must not reside in the aqueous region, because its diffusion coefficient would then be expected to be similar to that of chloride ion. Iodide ion also shows less accessibility to pyrene than cesium ion and therefore may well be located on the fluorocarbon side of the fluorocarbon−water interfacial region or at least in regions where diffusion is very slow or restricted. The results of the quenching study suggest that the concentration of iodide ions in the vicinity of the pyrene decreases with increasing EW and in the carboxylate polymers. It is known that the spread in diffusion coefficients for iodide and chloride ion also increases at the same time.[26] This leads to the suggestion that iodide ion is more likely to be found on the fluorocarbon side of the fluorocarbon−water interfacial region with increasing EW and in the carboxylate polymers, thereby explaining the spread in diffusion coefficients. The form of the iodide ions in this fluorocarbon side of the interface can only be speculated at present; however, it is not unreasonable to expect that they might be ion paired. The rate constant of quenching pyrene by iodide ions is considerably reduced from that in water, probably due to the reduced diffusion coefficient of iodide and the average distance between the probe and quencher. The rate constant of quenching is reduced in the carboxylate membranes and with increasing EW. This is most probably due to the decreased water content which reduces the mobility of the iodide ions and pyrene, thereby reducing the efficiency of quenching of the accessible pyrene by iodide ion.

The quenching of pyrene and $Ru(bpy)_3{}^{2+}$ by copper(II) ions showed similar results. Copper ion (except for the two highest ion content polymers) showed complete accessibility to the probes. These two polymers showed accessibility above 77%. Copper ion is hydrophilic and would therefore be expected to be located in the aqueous region of the swollen polymer system. Copper ion must however be located close to an exchange group to maintain electroneutrality. This could explain the high accessibility to the pyrene and the $Ru(bpy)_3{}^{2+}$. Both probe molecules are thought to be located on the water side of the fluorocarbon−water interfacial region of the polymer, and therefore copper ion might be expected to have good access to them. The quenching constants of copper ion for both the pyrene and $Ru(bpy)_3{}^{2+}$ are reduced from those in water. This is most likely due to the lower diffusion coefficient of copper ion in these polymer systems. Diagrams of the relative positions of fluorescent probes and ionic quenchers in the two types of ionomers are shown in Figure 6.

Summary

The fluorescent probes pyrene and $Ru(bpy)_3{}^{2+}$ have been used to infer the relative locations of cesium and iodide quencher ions within the polymer structure. Evidence suggests that the probes are located in the interfacial regions between the fluorocarbon and ionic aqueous regions of these microphase separated polymers. Exact locations of the probes in the interface depend on both the inherent ion content of the polymer and the nature of the exchange site, not surprisingly. The relative abilities of cesium ion and iodide ion to quench these probes' fluorescence are different, and again the differences depend on both polymer ion content and exchange site identity. These trends closely parallel the previously determined ionic diffusional properties of these polymers, studied in membrane form, and provide a convincing explanation for the phenomenon of transport superselectivity. Thus, differences in the average locations of cations and anions within the interfacial regions of these polymers appear to result in different average diffusional tortuosities and observed macroscopic diffusion coefficients.

While these results correlate well with previous interpretations of the unusual ionic diffusional properties of these perfluorinated ionomers (and differences among different types of ionomers), they still must be considered to be somewhat speculative. The quenching of pyrene's fluorescence is a dynamic phenomenon and is affected by the diffusivity of the quencher ion. If cesium and iodide ions have different equilibrium distributions between the fluorocarbon−aqueous interface, then the rate at which they can approach and quench the probe will also differ in each microenvironment. Thus, the percent accessibility values which are determined by this application of the Stern−Volmer equation are not to be taken as precise values. However, the difference in the behavior of these ions remains significant, as does the differences seen with changing ion content and between the carboxylate and sulfonate types of ionomers.

This difference has considerable importance for practical uses of these ionomers, one example being their enormously successful application as membrane separators in the chlor-alkali industry. This technology now represents one of the largest current industrial applications of polymer membranes and relies on the selective retardation of hydroxide ion in favor of sodium ion.[6] It is likely that the success of this industrial technology (where the carboxylate membrane is superior in performance to the sulfonate form) has as its source the subtle differences in the way ions of different charge and hydration energy interact with the interfacial regions of these microphase separated ionomers.

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