

THE UNIVERSITY OF CALGARY

ION DIFFUSION IN PERFLUORINATED IONOMER MEMBRANES

by

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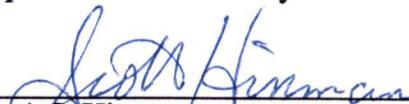
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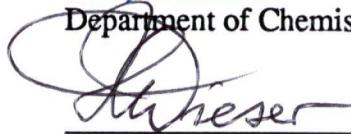
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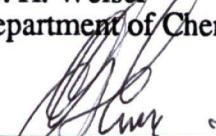
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ABSTRACT

Membrane sorption and self-diffusion coefficients for sodium ion, cesium ion, chloride ion, and iodide ion have been measured for four equivalent weights of the Dow PFSI'S. For the self-diffusion studies, values were determined as a function of temperature.

The diffusional behavior of the ions in the membranes is qualitatively explained in terms of a three regional diffusional model which is consistent with the spectroscopic studies of perfluorinated ionomer membranes. The self-diffusion coefficients of the ions in the Dow PFSI'S are compared with those in the 1050 EW carboxylate and the 1200 EW sulfonate Nafion polymers by an efficiency parameter E.

The proportion of the three types of water in the Dow PFSI'S and in the 1100 EW sulfonates, 1050 EW carboxylate and the 1250 EW carboxylate Nafion polymers were quantitatively determined by near-infrared spectroscopy. The strength of hydrogen bonding of water in the membrane relative to that of liquid water is used to explain why the ratio of self diffusion coefficients of sodium ion to cesium ion approaches the aqueous-like value for the Nafion carboxylates.

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To Akua Akomaa and the late E.K. Boakye

TABLE OF CONTENTS

Approval Page	ii
Abstract	iii
Acknowledgments	iv
List of Tables	viii
List of Figures	ix
I. INTRODUCTION	1
I.1 Perfluorinated ionomers	1
I.2 Morphology	7
I.2.1 Wide angle X-ray diffraction studies	9
I.2.2 Small angle X-ray diffraction studies	9
I.2.3 Differential scanning calorimetry	11
I.2.4 Infrared studies	14
I.2.5 Transmission electron microscopy studies	15
I.4 Structural models for perfluorinated ionomers	16
I.4.1 The cluster network model	16
I.4.2 The two and three phase models	17
I.4.3 A three region diffusional model for PFSI membranes	18
II. BACKGROUND OF SELF DIFFUSION STUDIES	21
II.1 Diffusion in ion exchange polymers	21
II.2 General trends in co-ion diffusion	22
II.3 General trends in counter-ion diffusion	22
II.4 General trends in diffusion in PFSI membranes	23
II.5 Donnan potential	24

III. EXPERIMENTAL	28
III.1 Materials	28
III.1.1 Salts	28
III.1.2 Radioisotopes	28
III.1.3 Membranes	29
III.1.4 Membrane pretreatment	30
III.2 Evaluation methods	30
III.2.1 Sorption	30
III.2.2 Ion exchange capacity	32
III.2.3 Membrane water content	32
III.3 Self diffusion experiment	33
III.3.1 Apparatus	37
III.3.2 Procedure and data treatment	38
III.4 Near-infrared studies	43
IV. RESULTS AND DISCUSSION	45
IV.1 Sorption studies	45
IV.1.1 Membrane water content	45
IV.1.2 Electrolyte sorption	47
IV.3 Self diffusion studies	52
IV.4 Self diffusion results of Dow PFSI'S	52
IV.4.1 Discussion of the self diffusion results	58
IV.5 Infrared studies	74
V. CONCLUSIONS	102
REFERENCES	106

LIST OF TABLES

I.1	Bragg Spacing for PFSI SAXS maximum Dow PFSI'S in Na ⁺ -form and Nafion in H ⁺ -form	12
IV.1	Water content of Dow PFSI'S in Na ⁺ and Cs ⁺ forms	46
IV.2	Polymer ionic concentration (M) in 0.2 M MX solution at 25° C	48
IV.3	Self-diffusion coefficients of Dow perfluorosulfonate ionomer membranes, 25° C	53
IV.4	Efficiency parameters (E) and volume fraction of water in Na ⁺ and Cs ⁺ forms, 25° C	61
IV.5	Efficiency parameters (E) and estimated volume fraction of water of PFSI membranes, 25° C	66
IV.6	Ratio of self-diffusion coefficients in perfluorinated ionomer membranes	68
IV.7	Activation energy of diffusion in Dow perfluorosulfonate ionomer membranes	72
IV.8	Near-infrared absorbance of water in perfluorinated ionomer membranes, Na ⁺ - form, 25° C	76
IV.9	Near-infrared absorbance of water in perfluorinated ionomer membranes, Cs ⁺ -form, 25° C	77
IV.10	Chi-square values for two and three peak fits	78
IV.11	Near-Infrared absorbance of water in 1100 EW Sulfonate polymer of different cationic forms	100

LIST OF FIGURES

I.1	Perfluorinated ionomer membrane as a separator	4
I.2	A graph of TFE units to perfluoroethersulfonate for Dupont's and Dow's polymers	10
I.3	A morphological model for perfluorinated ionomer membranes	20
II.1	Arrhenius plots of ionic diffusion in 1150 EW perfluorosulfonate and 1050 EW perfluorocarboxylate membranes	25
III.1	Schematic representation of concentration profile of tracer across films and membrane at study state	35
III.2	Cell arrangements used for membrane diffusion studies	39
III.3	Schematic diagram for the self-diffusion experiment	37
IV.1	Membrane ion concentration (molal) versus equivalent weight for the Dow PFSI'S	49
IV.3	Arrhenius plots of ionic diffusion in 680 EW perfluorinated sulfonate membrane	54
IV.4	Arrhenius plots of ionic diffusion in 760 EW perfluorinated sulfonate membrane	55
IV.5	Arrhenius plots of ionic diffusion in 960 EW perfluorinate sulfonate membrane	56
IV.6	Arrhenius plots of ionic diffusion in 1290 EW perfluorinated sulfonate membrane	57

IV.7	Arrhenius plots of ionic diffusion in quenched 960 EW perfluorosulfonated membrane	73
IV.8	Dow 680 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	80
IV.9	Dow 760 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	81
IV.10	Dow 960 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	82
IV.11	Dow 1290 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	83
IV.12	Nafion 1100 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	84
IV.13	Nafion 1050 EW perfluorocarboxylate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	85
IV.14	Nafion 1250 EW perfluorocarboxylate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	86
IV.15	Dow 1580 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit	87

IV.16	Dow 680 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	88
IV.17	Dow 760 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	89
IV.18	Dow 960 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	90
IV.19	Dow 1290 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	91
IV.20	Nafion 1100 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	92
IV.21	Nafion 1050 EW perfluorocarboxylate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	93
IV.22	Nafion 1250 EW perfluorocarboxylate ionomer membrane in cesium ion form, near-infrared	
	water stretch computer fit	94

Chapter I

Introduction

I.1 Perfluorinated ionomers

Perfluorinated ionomers are ion containing polymers which are uncross-linked. Ionomers consist of polymeric chains containing a relatively low percentage of ionizable monomers having enough large hydration capacity to give ionic conducting materials when used in aqueous conditions. Whereas ionenes have ionic groups as part of their backbone, ionomers have their ionic groups attached to a side chain. For perfluorinated ionomers, the ionic groups are anionic, either sulfonates or carboxylates. These materials have a tendency to form ionic domains called ion clusters (1), which contain the anionic groups and cations associated with them, and are microphase separated from the more hydrophobic portions of the polymer. The clusters are separated from one another by a medium of low dielectric constant, with hydrophilic channels connecting adjacent ionic clusters (2). The size of the ionic clusters depends on the nature of the cation, and the degree of solvation.

Perfluorinated ionomers form an important new class of synthetic membranes which are highly permselective. The unusual aggregation of ions coupled with the tetrafluoroethylene backbone makes this polymer important in many technological applications including the chlor-alkali industry. Thus it is important to study the relationships between ion diffusion and polymer structure.

Nafion ® is the trade name for Du Pont's perfluorinated ionomer. The self diffusion coefficients of sodium, cesium and iodide ions and water in dilute solution environments has been studied in Nafion (9). Several aspects of the results are unexpected compared to typical cross linked polystyrenesulfonate ion exchange polymers. Sodium ion has a higher self diffusion coefficient than cesium ion. The relative magnitude of self diffusion coefficients for cations are larger than anions. In

polystyrenesulfonate ion exchange polymers the self diffusion coefficients of anions are larger than cations. Further, in Nafion this unusual behavior is seen in concentrated solution environments at elevated temperatures (33), which is typical of anolyte and catholyte solutions in a modern chlor-alkali cell. These anomalies cannot be explained with the Donnan equilibrium, since at high concentrations there is electrolyte sorption. A three phase model (1) had been proposed to explain these anomalies. A detailed explanation of the three phase model is given in Section II.6.

The chemical structure of perfluorinated ionomers consists of a tetrafluoroethylene backbone and a vinyl ether side chain which has an ionic group attached to it. The hydrophobic fluorocarbon component and the ionic groups are incompatible, and so a phase separation occurs leading to the formation of ionic clusters. Since the side chain for the Dow PFSI'S is shorter than for Nafion it may be expected that the extent of microphase separation may be different from that of Nafion. The subject of this thesis is the study of ion diffusion in the Dow PFSI'S. The effect of equivalent weight on the self diffusion coefficients of sodium, cesium, chloride and iodide ions is studied. A comparison is made between the short side chain Dow perfluorinated ionomer membranes and Du Pont's long side chain perfluorinated ionomer membranes.

Since perfluorinated ionomers contain fixed anionic groups, they are permselective. The term "permselectivity" or "megapermselective" was first used by C. W. Carr and K. Sollner in their study of collodion membranes (55). It was found that cations of univalent strong inorganic electrolytes in solution were allowed to pass through the membranes, whereas the membranes were almost impermeable to anions. A discussion of this phenomenon is reserved for Section II.5. The perfluorinated nature of these polymers gives perfluorinated ionomers chemical inertness, thermal stability and mechanical strength. The above mentioned properties are desirable in some industrial

applications.

Nafion has many analytical and electrochemical applications. It is used as a bilayer membrane in chlor-alkali cells where it is desirable since it permits easy transport of sodium ions, while it acts as a barrier for chloride ions. It limits the hydroxide ion transport to about 2% in best cases and has good mechanical and chemical stability (3). The membranes are used to separate anolyte and catholyte solutions in the electrolysis of brine to produce caustic soda and chlorine gas. Figure I.1 is a schematic diagram of a PFSI membrane as a separator in a chlor-alkali cell.

Traditionally, chlorine and caustic are produced using diaphragm and mercury cells. In a diaphragm cell, brine is fed into the anode compartment where chlorine is formed. The sodium ions, water and an amount of chloride ions flow through a diaphragm made of asbestos into the cathode where water is reduced to form hydrogen gas and hydroxide ions. The diaphragm serves as a barrier to prevent hydrogen and chlorine gas from mixing which would create an explosion. The product from the cathode compartment is a dilute solution of caustic and brine which needs further separation by crystallization and filtration. In a mercury cell regeneration of mercury is necessary. The mercury amalgam is pumped to a separate reactor where sodium is reacted with water to form hydrogen and brine free caustic. Membrane based electrolytic cells do not require purification of the end products and are safe to operate (5).

Nafion is also used as a membrane in electro-purification. Disposition of waste has been a problem to electroplating companies. The chromic acid becomes contaminated with metal ions (iron, nickel, copper and aluminum). Some of the chromium is reduced from hexavalent form to trivalent form, resulting in the deterioration in the quality of chrome plating. Electrolytic cells using Nafion selectively remove the metal impurities through the membrane and simultaneously oxidize trivalent

Perfluorosulfonate Ionomer Membrane as a Separator

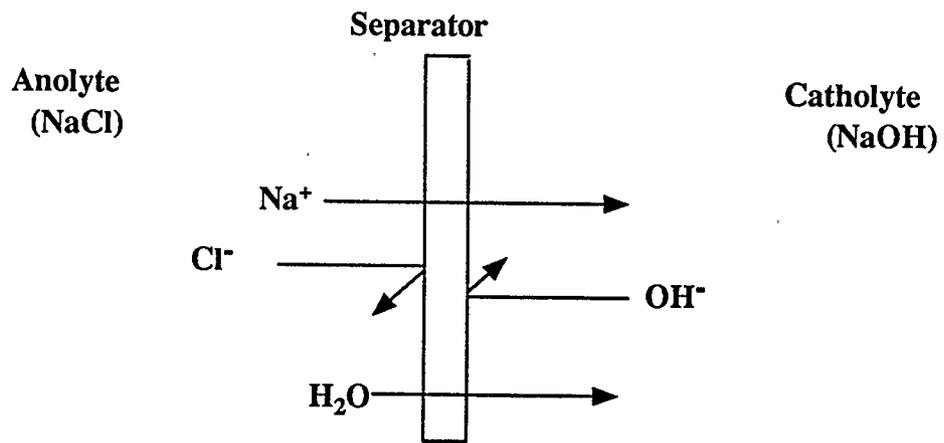
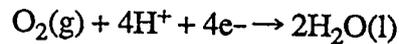


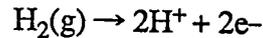
Figure I.1

chromium to hexavalent chromium.

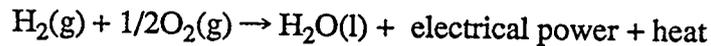
Perfluorinated membranes are also used in fuel cells. A fuel cell is a device which converts latent chemical energy of fuel to electricity (4). Fuel cells have found many applications in programs of space missions and military power sources. More recently fuel cells are considered in transportation (6, 13, 48). Nafion and more recently the Dow PFSA's are used as membranes in fuel cells (49). The electrochemical reaction that takes place at the cathode is;



and the anode is;



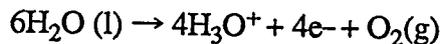
and the overall reaction is,



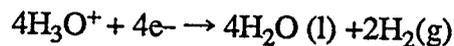
Hydrogen ion is the charge carrier

Nafion can also be used as membrane separator in water electrolyzers, which function in reverse to a fuel cell. Small scale water electrolyzers are commercially available for providing oxygen for space life-support systems in space crafts and submarines or as hydrogen generators for laboratories. As in fuel cells the charge carrier is the hydrogen ion.

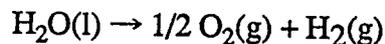
The anode reaction is



and the cathode reaction is,



The overall reaction is,



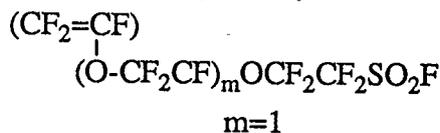
Among the analytical applications of perfluorinated ionomers is the hollow fiber suppressor in ion chromatography. The purpose of the fiber suppressor is to reduce

the conductance of the eluent before it reaches the conductivity cell detector since often the concentration of sample ion is orders of magnitude lower than the background eluent. The initially marketed suppressor column used a hydrogen form cation exchanger in the conversion of sodium carbonate to carbonic acid. Since the ionization of carbonic acid is minimal compared to sodium carbonate the conductance is low and the background noise is relatively low. The Nafion hollow fibre has an advantage over the cation exchange resin in that it does not need a separate regeneration step. Since Nafion is permselective only sodium and hydrogen ions diffuse through the fibre. Thus sodium ions are constantly exchanged with hydrogen ions to convert sodium carbonate to carbonic acid which has a lower conductivity.

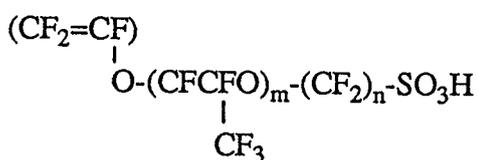
Nafion has been used in ion selective electrodes. Martin and Freiser (8) prepared electrodes by sealing a disc of Nafion 120 (1200 EW) to the end of a glass tube. The tube was then filled with an appropriate internal reference solution. They reported Nernstian response for cesium ions and tetrabutylammonium ions. Selectivity data for these ions were also reported.

I.2 Morphology

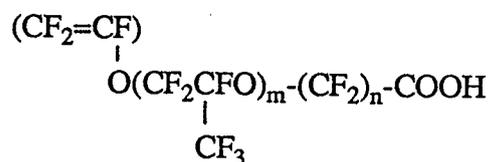
In 1962 the DuPont Company discovered a preparatory route for perfluorinated sulfonyl vinyl ether (PSFVE) monomers having the structure;



The Asahi Chemical Company started its development of perfluorinated ionomers for the membrane chlor-alkali process in 1970. They were mostly interested in short side chain vinyl ether comonomers which when polymerized with tetrafluoroethylene will produce an ionomer with high permselectivity and mechanical strength. They developed a new vinyl ether comonomer with $m=0$. The chemical structures of the monomers are ;

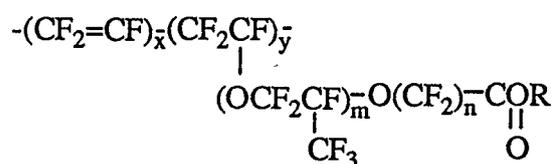


$m=0$ or 1 , $n=2-5$

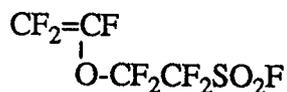


$m=0$ or 1 $n=1-4$

Flemion is a PFSI membrane developed by the Asahi Glass Co., Limited. It is a copolymer of tetrafluoroethylene and carboxylated perfluoro-vinyl ether as shown below.



In 1984 (14) the Dow Chemical Company announced a new synthetic route for a new vinyl ether having the structure;



In the production of a perfluorinated ionomer, a vinyl ether comonomer is copolymerized with tetrafluoroethylene (TFE) to form a melt fabricated precursor

polymer. The thermoplastic copolymer of vinyl ether comonomer and TFE can be extruded or molded into a film. After fabrication into the desired shape, the sulfonyl fluoride group is hydrolysed to the ionic sulfonate form SO_3Na , with NaOH (13,14). The Na^+ -form PFSI can be converted to the H^+ -form by ion exchange in HCl .

The amount of ions in the PFSI is expressed in terms of the equivalent weight of the polymer. Equivalent weight is defined as the weight in grams of dry polymer per millimole of exchange site. It is inversely proportional to the ion exchange capacity according to the relation

$$\text{EW} = 1000/\text{IXC}$$

where IXC is given in terms of milliequivalents per gram of polymer. It is a constant used for characterizing the ionomer. The desired equivalent weight is obtained by adjusting the ratio of vinyl ether comonomer and TFE units. The most important factor for mechanical strength is the TFE unit, while the vinyl ether comonomer is important in the transport of ions.

Generally membranes of high equivalent weights have low water contents. The use of a membrane of high water content results in a low current efficiency. The first attempt at improving the current efficiency for a sulfonate form functional polymer was to increase the equivalent weight. The limitation of this technique is an increase in the electrical resistance. The use of the carboxylate membrane which is low in water content, and which prevents back migration of hydroxide ion efficiently is also restricted by a high resistance and protonation of the carboxylic group since the anolyte is acidic (6). Thus for economical commercial operation it is highly desirable to employ a multilayer membrane containing both carboxylate and sulfonate layers formed by lamination.

Generally the Dow PFSI'S have lower water contents compared with Nafion (14). Nafion has a longer side chain than Dow's PFSI. For comparison purposes, it will

perfluoroethersulfonate. A graph of TFE units to perfluoroethersulfonate units versus equivalent weight is as shown in figure I.2 for such comparisons.

I.2.1 Wide angle X-ray diffraction studies

Since the wavelength of X-rays are comparable to the spacing of polymer chains in a crystal, X-ray scattering techniques are ideal for probing the structure of the crystalline domain in polymers. Gierke et al, and Moore and Martin have used wide angle X-ray diffraction (WAXD) to measure the intralamellar spacing in DuPont and Dow PFSI'S (2, 14). The integrated intensity of the crystalline peak was found to increase with equivalent weight for both Nafion and Dow PFSI'S (2, 14, 31). The dependence of crystallinity on equivalent weight is attributed to the side chains disrupting the lamellar ordering of the tetraethylene backbone segments. A comparison of the extent of crystallinity for 1100 EW Nafion, and 909 EW Dow was made (14). The Dow PFSI was found to be more crystalline than Nafion. Since the TFE to functional monomer ratio for these two membranes are the same a comparison could be made. Since the Dow PFSI has shorter side chains, they disrupt the TFE crystallization to a lesser extent than Nafion.

I.2.2 Small angle X-ray diffraction studies.

Small angle X-ray diffraction studies (SAXS) have also been used to study the morphology of Nafion and the Dow PFSI'S. Both PFSIS show a scattering maximum at ca $Q = 0.15 \text{ \AA}^{-1}$ and $Q = 0.05 \text{ \AA}^{-1}$ (2, 14, 31). Since the intensity and

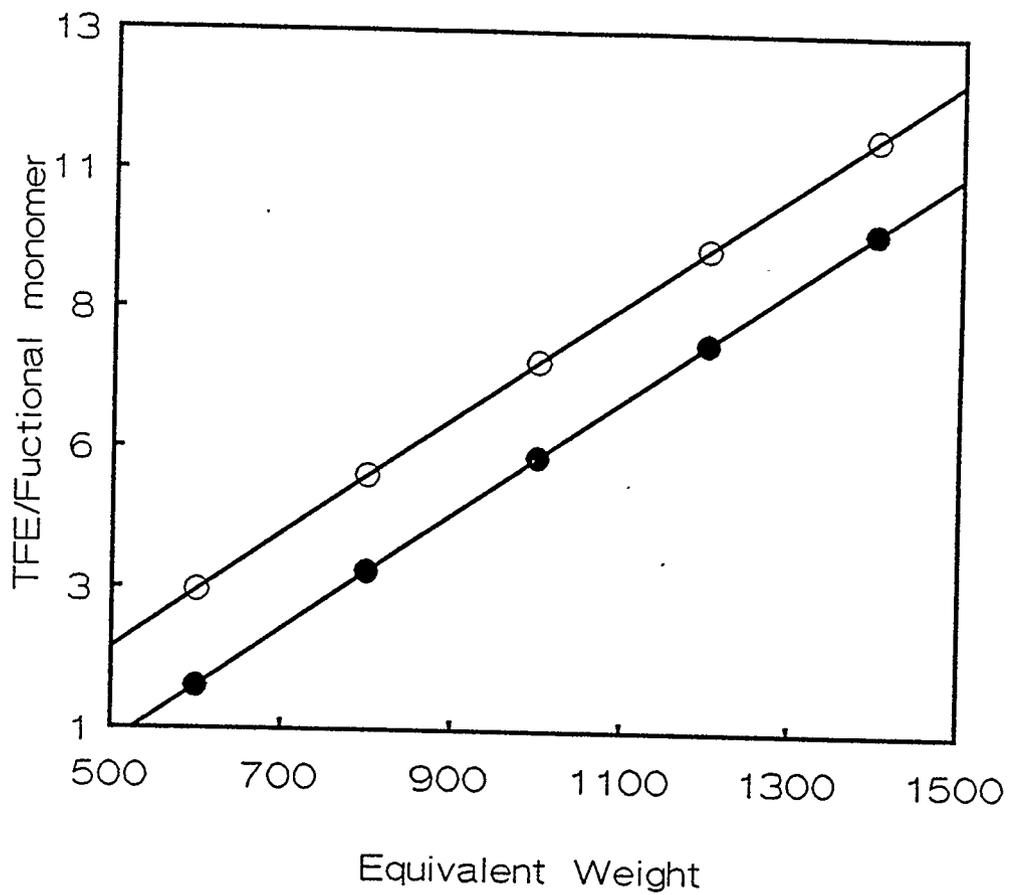


Figure I.2

A graph of TFE units to perfluoroethersulfonate for Dupont's and Dow's polymers. ● Nafion ○ Dow PFSI'S

position of the scattering maximum at $Q = 0.15\text{\AA}$ varied with PFSI water content and counter-ion, this SAXS peak is assigned to scattering from ionic clusters. The maximum at $Q = 0.05\text{\AA}$ is assigned to scattering from crystallites. Like the crystalline peak in WAXD scans, the intensity of this peak increases with increasing equivalent weight. The intensity of this reflection is related to the electron density contrast between crystalline and amorphous portions of the polymer. The intensity of the ionic scattering peak decreased with increasing equivalent weight for both Nafion and Dow's PFSI (2,14). As the water content decreases, the difference in electron density between the ionic clusters and the fluorocarbon matrix decreases (2,14,16). The intensity of the SAXS signal decreases as a result of the decrease in electron density contrast. Table I.1 lists the Bragg spacing for ionic cluster scattering maxima for Nafion and Dow PFSI. For both PFSI'S the diameter of the ionic clusters decreases with equivalent weight.

I.2.3 Differential scanning calorimetry

Moore and Martin have reported a differential scanning calorimetric study of the Dow PFSI'S (14). They state that depending on equivalent weight, two or three isotherms were observed. They assigned the endotherm at (150-180°C), to the matrix glass transition ($T_{g,m}$) on the basis that DSC and dynamic mechanical analysis of Na^+ -form Nafion has a glass transition at ca 150°C (17). They assigned the second endotherm at (270-300°C) to the ionic cluster glass transition ($T_{g,c}$) (14), on the basis that Na^+ -form Nafion shows a dynamic mechanical analysis relaxation at ca 240°C(18). The assignment of this peak is supported by the fact that the position of this peak is counter-ion dependent.

The third endotherm occurs at ca 335°C (14). This endotherm does not occur in non-crystalline 635 EW and quenched 995 EW polymers. This peak occurs at nearly the same temperature as the melting temperature of poly(tetrafluoroethylene) (14, 19).

Table I.1
Bragg Spacing for PFSI SAXS Maximum
Dow PFSI'S in Na⁺-form and Nafion in H⁺-form

Nafion		Dow	
EW	d (Å)	EW	d (Å)
944	43.2	635	77
971	43.0	803	46
1100	40.2	909	43
1200	36.6	1076	41
1600	32.4	1269	39
1790	30.8		

From references 14 and 16

For these reasons, they assigned this endotherm to the melting of PFSI crystalline regions.

For a random copolymer, the melting point depression induced by the introduction of non crystallizable comonomers may be expressed by Flory's equation;

$$\frac{1}{T_m} - \frac{1}{T_{m0}} = - \left[\frac{R}{\Delta H_m} \right] \ln n \quad \text{I.1}$$

where T_{m0} is the melting point of the homopolymer, poly(tetrafluoroethylene) T_m is the melting point of copolymer, R is the gas constant, ΔH_m is the heat of fusion per mole of crystallizable units and n is the mole fraction of crystallizable units. Moore and Martin concluded that the Dow PFSI'S are blocky due to the fact that equation 1 predicts that the T_m for the 909 equivalent weight should be 13°C lower than the T_m for the 1076 equivalent weight. Only a 2°C decrease in T_m was observed. Analogous data was obtained for vinylidene chloride - vinyl chloride copolymers (20). It was concluded that vinylidene chloride-vinyl chloride was blocky rather than random. Thus Moore and Martin (14) concluded that the Dow PFSI'S contain blocks of tetrafluoroethylene units that are larger than would be expected assuming a purely random distribution of monomers. Copolymerization theory predicts that PFSI'S are random copolymers (21), Starkweather found that the plot of $1/T_m$ versus $\ln n$ was a straight line which implies that the data followed Flory's equation (equation 1) and hence Nafion may be random (22). Starkweather also found a discrepancy between the heat of fusion by using Flory's equation and the Clausius-Clapeyron equation. As a result of the difference in the values of heat of fusion by the two methods he concluded that Flory's equation may not be applicable to the crystalline structure of Nafion. Mandelkern has found that using Flory's equation to measure the heat of fusion of copolymers can lead to fortuitous answers, since the value obtained by using Flory's equation is very dependent on the sensitivity of the method used to detect the disappearance of crystallinity. He used

Flory's equation to measure the heat of fusion for random type copolymers. The plots of $1/T$ versus $\ln n$ were straight lines with gradients which varied depending on whether 1, 2 or 5 percent of crystalline portions were at equilibrium with the melt when the melting point was measured. Thus the differences in values as reported by Starkweather may be due to the sensitivity in measuring the melting point of the crystals, and Nafion may be random.

I.2.4 Infrared studies

Falk reported an infrared study of water in the Na^+ -form of 1200 equivalent weight perfluorosulfonate membrane (24). Two forms of spectroscopically distinct types of water were found. The first makes up about 25% of the total sorbed water and does not participate in $\text{OH}\cdots\text{O}$ hydrogen bonds. This water is mainly found in the fluorocarbon environment. The remaining water is hydrogen bonded, but the average hydrogen bond strength is 62% of that of liquid water. According to Falk, the intrusion of fluorocarbon phase may be responsible for the weakness in hydrogen bonding. Falk concluded that most of the $\text{OH}\cdots\text{CF}_2$ interactions occur at the interface between the aqueous regions and the nonpolar fluorocarbon phase. This indicates a large surface to volume ratio for ion clusters and that clusters are nonspherical.

Yeager et al. measured the infrared spectra of water in 1050 equivalent weight perfluorocarboxylate and 1200 perfluorosulfonate membranes (25). The frequency of the non-hydrogen bonded water was the same for both membranes, the amount of non-hydrogen bonded water in the carboxylate being relatively smaller as compared to the sulfonate. Also the average strength of the hydrogen bond was found to be 92% of that in pure water for the carboxylates. They concluded that the interfacial region in the carboxylate polymer is less prominent, that intrusions of fluorocarbon are less frequent, and that phase separation is more complete compared to the sulfonate

polymer.

Barnes has confirmed the existence of non-hydrogen bonded water in the interfacial region close to the fluorocarbon phase using the near infrared method (26). A discussion of this study will be presented in Section IV.5

II.2.5 Transmission electron microscopy studies

Xue, Trent and Osseo-Asare have reported transmission electron microscopy studies (TEM) of Nafion 117 (EW = 1100) (13, 27). The TEM micrographs indicated the presence of three phases; an ionic cluster phase, an organic matrix phase and an interfacial phase. According to the report, spherical ionic clusters were surrounded by interfacial phase and were uniformly distributed across the membrane. The average size of the clusters were found to be between 25 and 50 Å.

Differential scanning calorimetry, infrared, X-ray diffraction, and transmission electron microscopy studies indicate the presence of three phases in perfluorinated ionomers. In the subsequent section four models which are consistent with the morphology of the ionomers will be discussed.

I.4 Structural models for perfluorinated ionomers

Several structural models of perfluorinated ionomer membranes have been proposed which are based on various transport and spectroscopic studies to explain the remarkable cation permselectivity (2, 16, 29, 30). Permselectivity is lost in concentrated solution environments in conventional ion exchange polymers, which is consistent with Donnan equilibrium (exclusion of co-ion from the polymer phase due to Donnan potential). This concept is discussed in Section II.5. Permselectivity however, persists in perfluorinated ionomer membranes in concentrated solution environments, which cannot be explained by the Donnan equilibrium. The above phenomenon had been designated by the term "superselectivity" by Reiss and Bassignana (57).

I.4.1 The cluster network model

Based on small angle X-ray diffraction studies Gierke has proposed a structural model for the ionic clusters in Nafion (29). The cluster network model assumes that ionic clusters are spherical in shape with a radii of about 4nm, with an inverted micellar structure. This assumption is supported by transmission electron microscopic studies with the observation of circularly stained regions in transmission electron micrographs of Ag^+ and Sn^{2+} form Nafion samples. However, based on infrared data, Falk (24) has suggested that the hydrated ionic clusters are either much smaller than Gierke estimated or are highly non-spherical with frequent intrusion of fluorocarbon phase.

Gierke also proposed that these clusters are interconnected by narrow channels with a diameter of about 1 nm. He also considered that the Bragg spacing of 5 nm estimated from SAXS data represents the distance between clusters. The ion exchange sites are fixed on the surface of the clusters and the channels. In this model the theoretical prediction of the intercluster channels is consistent with the observed

transport properties of Nafion (31). In a concentrated solution environment at elevated temperatures, a condition in which a membrane chlor-alkali cell is operated, 98% of the electrolysis current is carried by the sodium ions with the remaining current due to hydroxide ion transport. This so called "superselectivity", (a term designating kinetic permselectivity which was introduced by Reiss and Bassigna) can not be explained by conventional Donnan exclusion (31). According to the cluster-network model the hydroxyl ion transport is dramatically reduced by the high electrostatic potential barrier encountered when the anion transverses the narrow channels.

I.4.2 The two and three phase models

Hashimoto and coworkers (16, 30) used SAXS to study the morphology of perfluorinated ionomer membranes. Two basic models were considered in order to interpret the ionic scattering maximum.

The two phase model: In this model ionic clusters are dispersed in a matrix composed of fluorocarbon chains and nonclustered ions. The two phase model is based on a model proposed by Cooper et al for hydrocarbon-based carboxylated ionomers (32). The ionic scattering maximum is attributed to an intercluster interference reflecting an average intercluster distance.

The core-shell model: Macknight, Stein and coworkers proposed the core-shell model. In this model the ionic cluster is surrounded by a shell which is rich in fluorocarbon chains (32). The core shell particles are dispersed in a matrix composed of fluorocarbon chains and non-clustered ions. The scattering maximum arises essentially from intraparticle interference of the core-shell particle.

Hashimoto et al compared the two models by studying the effects of water content on the swelling of Nafion (30). These studies demonstrated that the microscopic degree of swelling (as determined by SAXS) is much larger than the macroscopic degree

of swelling. Based on these results, a core shell model for ionic clusters was proposed.

I.4.3 A three region diffusional model for PFSI membranes

Based on spectroscopic and self diffusion studies of perfluorinated ionomer membranes, Yeager et al. have proposed a model that explains the diffusional properties of perfluorinated membranes (1). A review of SAXS studies shows the presence of ionic clusters in PFSI membranes (2, 13, 30). These studies indicate that the majority of the sorbed water, ion exchange sites, and counter ions in the PFSI are microphase separated from the hydrophobic backbone of the polymer. Further studies by Fujimura and coworkers indicate that the microcrystalline domains in the PFSI membranes arise from the hydrophobic backbone (13, 30). These studies show that the perfluorocarboxylate polymer is more crystalline than the sulfonate, and that the sulfonate has a greater affinity for water than the carboxylate. Further they showed that the size of the ionic clusters depends on the anion exchange site, and the water content of the polymer, and that the sulfonate generates larger ionic clusters compared to the carboxylate. Also for a given equivalent weight, cluster size increases with water content.

Additional structural information is obtained from the studies of luminescence quenching of $\text{Ru}(\text{bpy})^{2+}$, where bpy is 2,2' bipyridine (23). This study was done with 1200 EW Nafion sulfonate polymer. The results indicate that the large size and low charge density cation interacts with the fluorocarbon portion of the polymer, and that a probable location of the cation is the interfacial zone between the ion clusters and the fluorocarbon backbone.

Other spectroscopic studies that show the presence of an interfacial zone are infrared studies and transmission electron microscopy studies which were discussed in Sections I.2.4 and I.2.5 (24, 25, 26).

Figure I.3 is a schematic representation of a three region structural model of

perfluorinated ionomer membranes (50). This model is consistent with the spectroscopic and self diffusion results. In this model the PFSI is considered to consist of three regions. These regions are labelled as A, B and C. Region A represents the crystalline and amorphous fluorocarbon phase. This region therefore contains backbone fluorocarbon material from which the X-ray crystalline peak arises. Region C contains the ion clusters, which are made up of the ion exchange sites, the majority of sorbed water, and the counter ions. Region B is located at the interface between the ion clusters and the fluorocarbon backbone. This region consists of side chain material, the non-hydrogen bonded water in the PFSI, which is small compared to the hydrogen bonded water in the clusters, and a few ion exchange sites with cations which were not incorporated into clusters. Thus region B is viewed as highly irregular with large fractional void volume and low ionic strength.

The relative proportion of cations in region C and B will depend on the size, charge density, and hydration energy of the cation. Large cations with a low charge density like $\text{Ru}(\text{byp})_3^{2+}$ and Cs^+ , will prefer region B relatively to region C, while small cations with large charge density and hydration energy like Na^+ will prefer region C. Further cations that diffuse through region B will have small diffusion coefficients since they diffuse through a diffusional path that is more tortuous and irregular. This model will be used to qualitatively discuss the results of the self diffusion experiment of the Dow PFSI'S in Chapter IV.

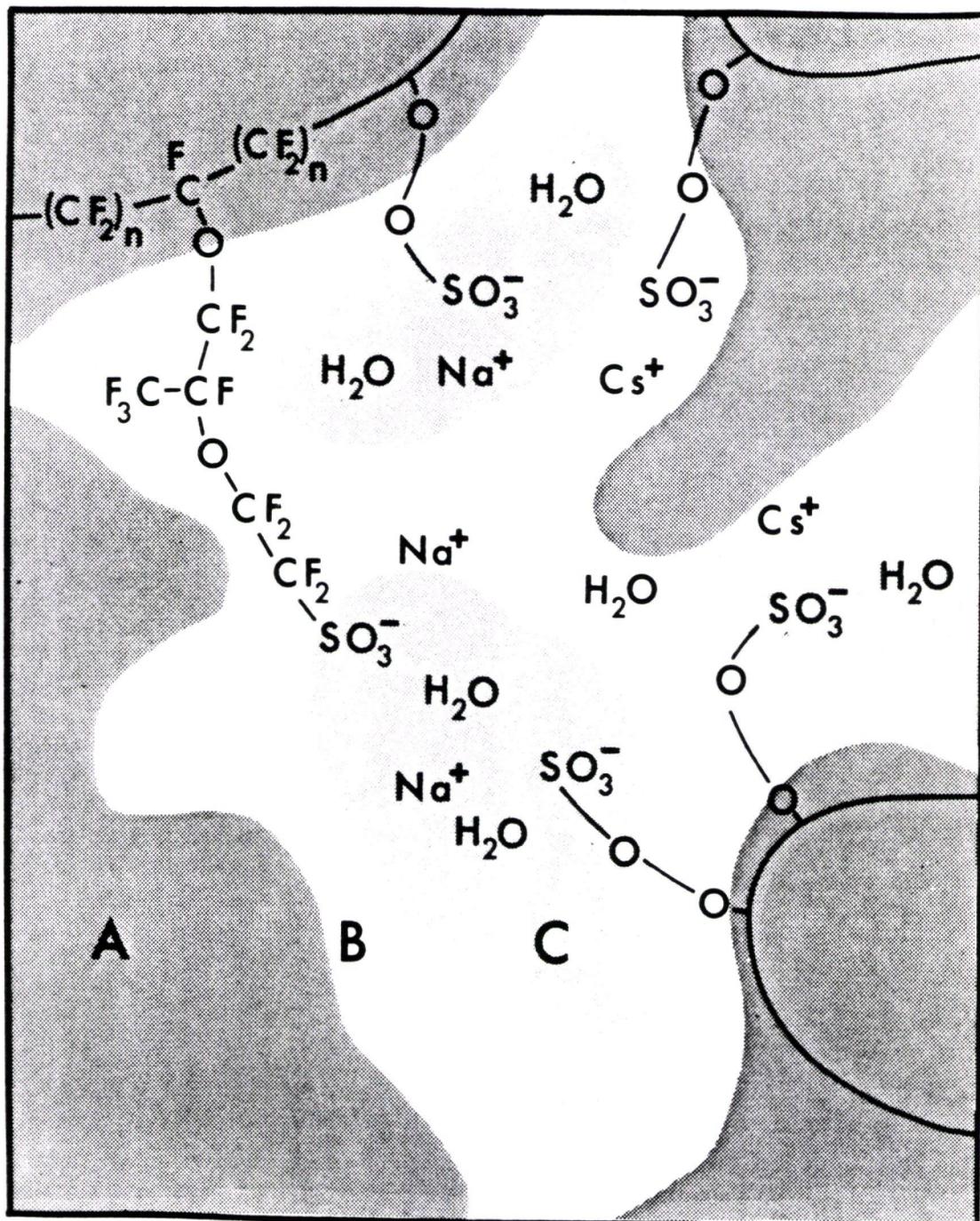


Figure I.3

A morphological model for perfluorinated ionomer membranes.

Chapter II

Background of Self Diffusion Studies

II.1 Diffusion in Ion Exchange Polymers

Among the important factors which determine the rate of diffusion in ion exchange polymers is the extent of swelling when immersed in a solution. The degree of swelling is dependent on the degree of cross-linking, the concentration of ion exchange groups, and the external solution concentration.

The first water molecules to enter the polymer hydrate the ions. As a result the strength of the electrostatic interaction between counter-ions and the fixed charged sites is reduced. The extent of swelling depends on the energy of hydration of the counter-ions. It is large for highly hydrated ions such as magnesium ion, and low for relatively weakly hydrated ions, such as cesium ion. In general the greater the concentration of ionizable groups in the polymer the greater the swelling. When a polymer is immersed in a concentrated electrolyte, the swelling is reduced.

Cross-linking provides resistance to swelling for the ion exchange polymers. In general a highly cross-linked polymer swells to a lesser extent, compared to a weakly cross-linked polymer.

The porous solid of a fixed structure is a model which had been used to describe cross-linked ion exchange polymers (44). This model has the advantage of simplicity and had been extensively used to discuss diffusion in conventional ion exchange polymers. In this model the polymer network is regarded as a rigid framework which is penetrated by interconnecting pores. These pores are filled with solvent and ions. Molecular transport takes place through the pores. The fixed ion exchange sites reside on the walls of the pores. The counter-ions and co-ions in the pores are subjected to the electrostatic field of the fixed charge sites.

II.2 General trends in co-ion diffusion.

The self diffusion coefficients of co-ions are generally greater than counter-ions in conventional ion exchange polymers. This is due to the difference in mechanism of transport for co-ions and counter-ions in these polymers. Co-ions are electrostatically repelled by the fixed charge sites, thus they are localized in regions of low fractional volume of polymer but high fractional volume of water. When the pore diameter of the polymer network is larger than the diameter of the co-ion, the co-ions diffuse in the centers of the pores to avoid frictional interaction with the polymer chains. As a consequence they diffuse through a shorter route, which results in relatively large diffusion coefficients. The activation energy of diffusion is also solution-like, suggesting a similar mechanism of diffusion to that in water. The relative order of co-ion diffusion coefficients are similar to those in solution.

II.3 General trends in counter-ion diffusion

The mechanism of diffusion in counter-ions is different compared to co-ions in ion exchange resins. Counter-ion diffusion is a complex process affected by many variables. The counter-ions are electrostatically attracted to the fixed charge sites. As a result they spend a high proportion of time in the vicinity of the polymer chains. The diffusion of counter-ions along polymer chains is called chain diffusion. In order to jump from one chain to the other, the counter-ion should have the necessary activation energy to overcome the electrostatic potential barrier in the direction of diffusion. This process is called volume diffusion. It becomes more difficult as the distance between the chains is increased due to swelling. Both chain diffusion and volume diffusion occur together in relative amounts depending on extent of swelling, ion exchange capacity and temperature. The tortuosity of the diffusional path is relatively larger than in co-ion diffusion. As a consequence the ion diffusion coefficients are reduced in comparison to

diffusion of co-ions. Also their activation energy of diffusion is larger.

In summary the diffusion coefficients of anions in a cation exchange polymer are larger than cations. Anions diffuse through the centers of pores, with a diffusional path which is less tortuous, resulting in low activation energies of diffusion as compared to cations. Cations diffuse by volume diffusion and chain diffusion. Since the diffusional path is more tortuous compared to the mechanism of diffusion of anions, the resulting diffusion coefficients are smaller and the activation energies of diffusion are higher compared to anion diffusion.

II.4 General trends in diffusion in PFSI membranes

Yeager et al. have reported self diffusion studies of sodium, cesium, chloride and iodide ions in dilute and concentrated solution environments for Nafion PFSI'S (1, 15, 16, 25, 28, 35, 44). Figure II.1 is the summary of published results for 1150 EW sulfonate and 1050 EW carboxylate membranes in 0.1 M solution. Here open symbols and closed symbols refer to sulfonate and carboxylate membranes respectively. The reported activation energies are 18.6 KJ mol^{-1} and 24.0 KJ mol^{-1} for chloride ion and 18.4 KJ mol^{-1} and 22.0 KJ mol^{-1} for iodide ion in the sulfonate and carboxylate membranes respectively.

The diffusion coefficient of sodium ion is larger than that of the anions. This result is unexpected compared to diffusion in conventional ion exchange polymers where anion diffusion coefficients are larger than cation diffusion coefficients. Further, the activation energies of diffusion for anions in conventional ion exchange polymers are less than those of cations. Similar trends were observed for the Nafion polymers when self diffusion coefficients were measured in concentrated solution environments (15).

Another interesting aspect of this report is the differences in spread between the self diffusion coefficients of sodium ion and the anions for sulfonate and carboxylate

membranes. While the self diffusion coefficient for sodium ion is slightly higher in the carboxylate membrane, the spread of diffusion coefficient between sodium ion and the anions is greater in the carboxylate than in the sulfonate.

An aspect which is also interesting with regard to ionic diffusion is observed for cesium ion. The previously obtained self diffusion coefficients for the 1200 EW sulfonate and 1050 EW carboxylate membranes at 25° C are 1.88×10^{-7} and 6.73×10^{-7} respectively (1, 25). The diffusion coefficient of sodium ion is five times larger than that of cesium ion for the sulfonate membrane. Also the activation energy of diffusion of sodium ions is relatively low compared to that of cesium ion for the same membrane. In solution the order of self diffusion coefficients for cesium ion and sodium ion is inverted with cesium ion having the larger self diffusion coefficient with a lower activation energy. A similar trend is present in conventional ion exchange polymers. For example in 8.6% divinylbenzene cross-linked sulfonate cation exchange resin, the order of diffusion coefficients of alkali metal ions is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ (43)

The perfluorocarboxylate membrane shows a larger self diffusion coefficient for sodium ion compared to cesium ion. The spread in self diffusion coefficient with respect to sodium and cesium ions in the carboxylate membrane is reduced compared to that of the sulfonate membrane. This suggests a greater organization of sorbed water and ion exchange sites into better diffusional pathways for the carboxylate membrane.

II.5 Donnan Potential

Electrolyte invasion can reduce current efficiency drastically. The sorbed electrolyte will participate in current conduction; as a result the current efficiency will decrease. Electrolyte sorption can be described by the Donnan potential. Consider a cation ion exchange polymer in dilute solution of a strong electrolyte. The polymer contains no sorbed electrolyte, and has immobile fixed anionic sites. Further the

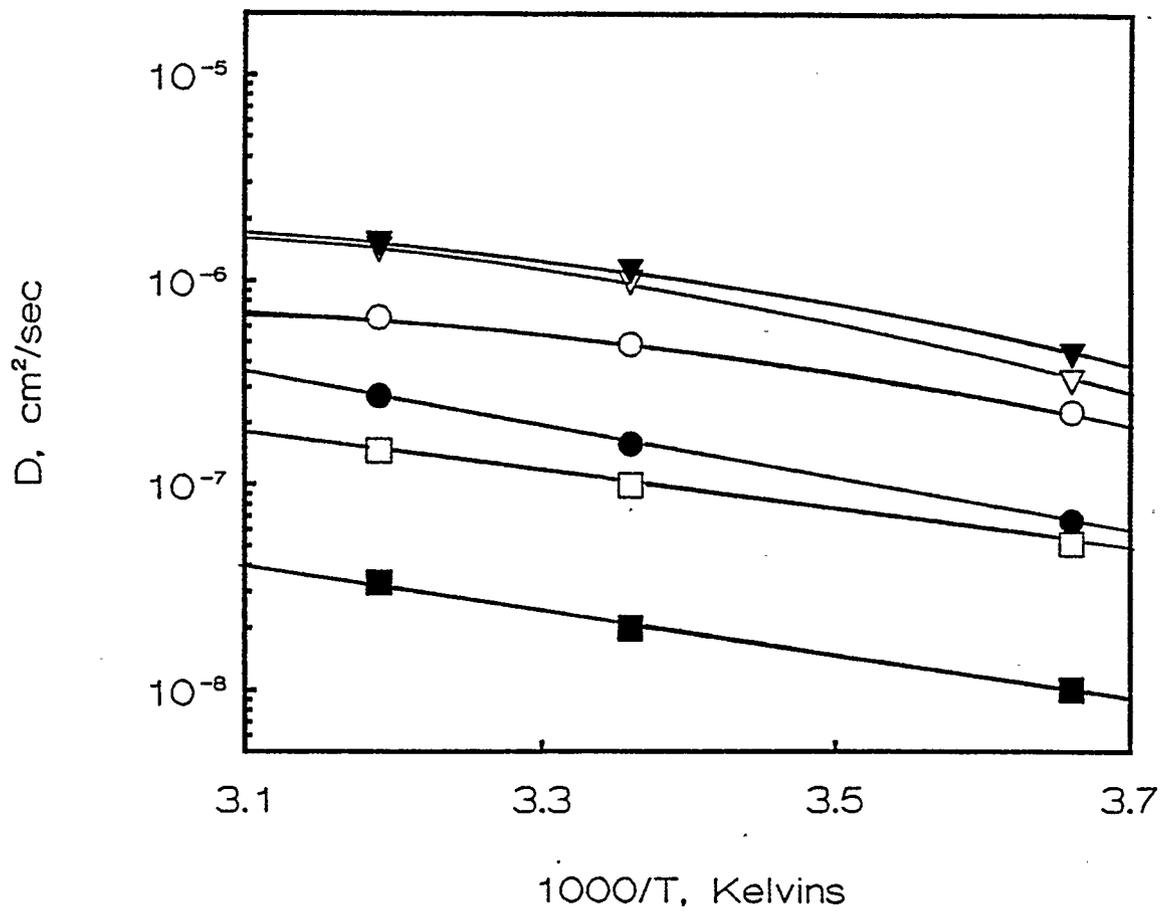


Figure II.1

Arrhenius plots of ionic diffusion in 1150 EW perfluorosulfonate and 1050 EW perfluorocarboxylate membranes. $\blacktriangledown, \triangledown$, Na^+ ; \bullet, \circ , Cl^- ; \blacksquare, \square , I^- . Reference 15.

polymer has a higher ionic strength than the solution phase. Thus there is a considerable concentration gradient between the solution and the polymer phase which results in the diffusion of small amounts of cations from the polymer into solution. Since the ions carry electric charges, such a process will disturb electrical neutrality. Migration of the first few cations into solution results in a net positive charge in the solution and a net negative charge in the polymer. As a result an electric potential is built between the two phases which opposes the tendency of the ions to level out the concentration differences between the two phases. This potential is known as the Donnan potential, and the equilibrium between ions in the polymer and the solution phase is known as the Donnan equilibrium.

Quantitatively, for a strong electrolyte solution MX, the Donnan equilibrium can be expressed as:

$$\frac{\bar{M}}{M} = \left(\frac{\bar{X}}{X} \right)^j \left(\frac{\gamma}{\bar{\gamma}} \right)^{i+j} \quad \text{II.1}$$

Where γ is a mean ionic activity coefficient. An osmotic pressure term has been neglected. The barred quantities refer to polymer phase, and non-bared quantities refer to the solution phase.

The co-ion concentration in the polymer phase corresponds to sorbed electrolyte. Such an electrolyte is excluded to a certain degree from the polymer phase by the Donnan potential. The Donnan potential depends on the external solution concentration, ion exchange capacity, and water content of the polymer.

The high charge of the polymer due to fixed ion exchange sites in the polymer phase acts as an effective barrier to co-ion uptake. This can be qualitatively discussed in terms of the Donnan potential. The internal counter-ion molal concentration

is high when the polymer has a high ion exchange capacity. The Donnan potential is high when the the ionic strength difference between the solution and polymer phase is large. The absolute value of the Donnan potential therefore is increased if the concentration of the external solution is low. In other words, when the external solution concentration is increased, the concentration gradient between the solution and the polymer phase is decreased, which results in a decreased Donnan potential and an increased electrolyte sorption.

The Donnan potential also depends on the water content of the polymer. The extent of swelling determines the effective ion exchange site concentration in the polymer. The concentration of ion exchange sites in the polymer is diluted if the water content is increased. As a result, the electrostatic exclusion of co-ions is decreased; thus the electrolyte sorption is increased.

CHAPTER III

Experimental

III.1 Materials

III.1.1 Salts

Sodium Chloride

Cesium Chloride

Sodium Iodide

All reagents used were Fisher certified. All salts were used without further purification. Salt solutions were prepared with distilled water.

All halide titrations were performed with 0.25 M AgNO_3 , which was standardized against NaCl. Iodide titrations were done manually. The titration results were checked with a potentiometric end point detection method. The equivalence point for the visual and the potentiometric methods were very close. The chloride titrations were done with an autotitrator, composed of Metrohm, 614 Impulsomat, 632 pH-Meter, 643 Control Unit and 655 Dosimat. The titration results were recorded with an Epson HX-20 computer.

III.1.2 Radioisotopes

The following radioisotopes obtained from Amersham International were carrier free and were used as received. ^{22}Na as NaCl in water, ^{125}I as NaI in dilute sodium hydroxide solution, pH 7-11, and ^{36}Cl as NaCl in water. Carrier free ^{137}Cs in CsCl was obtained from New England Nuclear

Sodium-22, Iodide-125, and Cs-137 are γ emitters; their activities were counted by using an LKB Wallac, model 1282 Compugamma counter. Chlorine-36 is a β^- emitter; its activity was counted by liquid scintillation, (LKB Wallac, model 1215 Rackbeta liquid scintillation counter) using Aquasol 2 (Universal liquid scintillation

cocktail for aqueous solutions, Biotechnology Systems, NEN Research Products, Boston Massachusetts). Cocktail samples obtained by using Aquasol 2 may be a clear solution, a clear gel, or two separate phases, depending on the percentage of water and Aquasol. It had been reported that the specific activity of a sample counted in each of the three forms differ considerably (15). Thus all the cocktail samples were prepared in the proportion of 15 cm³ Aquasol 2, 1 cm³ of radioactive sample and 1 cm³ of water. The resulting solution was clear and reproducibility was ensured.

For both γ and β emitters 1 cm³ of the radioactive sample was taken with a 2 cm³ Hamilton syringe and then weighed in a preweighed vial. The specific activity of a sample was calculated per gram of sample instead of per milliliter. This was done to ensure better accuracy.

III.1.3 Membranes

Four equivalent weights of the Dow perfluorosulfonate ionomer membranes were supplied by the Dow Chemical Company, Freeport Texas. The membranes had the following measured equivalent weights: 680, 760, 960 and 1290. The film thickness for the 680, 760, 960 and 1290 equivalent weights were 0.0300cm, 0.0100cm, 0.0100cm, 0.0200cm respectively. The 680 and the 1290 equivalent weight polymers were not uniform in thickness.

The 1290 EW sulfonate polymer had physical imperfections at some parts of the membrane. It was also brown in color.

III.1.4 Membrane pretreatment

A series of membrane pieces of about 5-10 cm² in area were pretreated by soaking in 95% ethanol for one hour, then successive soaking in 1 M NaOH and 1 M HCl for fifteen minutes. The membrane pieces were rinsed in distilled water between equilibrations. Finally the pieces were soaked in 0.2 M salt solution of interest for thirty minutes. The solution was replaced and thermally equilibrated in the salt solution overnight. In an attempt to remove the brown color the 1290 EW sulfonate polymer was soaked in concentrated nitric acid overnight. Although much of the color was removed by this method the membrane was not as colorless as the other equivalent weights after pretreatment. By boiling it in concentrated nitric acid the color improved, but this procedure was not used in sorption and self diffusion studies, since membrane morphology changes with temperature. After soaking the 1290 EW sulfonate polymer in concentrated nitric acid overnight, the membrane was pretreated by using the normal pretreatment procedure described for the other equivalent weights.

Quenched sodium form membrane samples (960 EW Dow sulfonate polymer) were prepared by heating in a furnace for twenty five minutes at a temperature of 340 °C, and then rapidly cooling in liquid nitrogen. The ion exchange capacity of the quenched samples decreased slightly as a result of the heating.

III.2 Evaluation methods

III.2.1 Sorption

The membrane sorption is expressed in molarity (moles of sorbed electrolyte per liter of wet membrane). Membrane ionic concentrations are expressed in molar units because self diffusion coefficients are calculated from flux measurements, using molar units instead of molal units. This quantity was measured by a radioactive method. The membrane volumes were calculated by using the individual measured dimension of

membrane samples. The length and width were measured with a ruler. Several measurements were taken and the average value used. The thickness was measured with a disc type micrometer. Several measurements at different portions of the membrane were done, and the average value used in calculating the membrane volume.

The moles of sorbed electrolyte, in the membrane was measured by soaking the membrane in a 0.2 M radioactive electrolyte solution and equilibrating for eighteen hours at 25°C. After the equilibration, a 2 cm³ sample of the solution was withdrawn for counting (donor sample). After background correction, the counts per minute was divided by the weight of the donor sample withdrawn to obtain the donor activity. The donor specific activity was obtained by dividing the donor activity by the concentration of the electrolyte in mol g⁻¹. The membrane was removed from solution and blotted with ashless filter paper to remove surface electrolyte solution. The blotting was done quickly to prevent desorption of sorbed electrolyte. The membrane was transferred into a vial, about 2 cm³ of non-radioactive electrolyte was then added. This was done to achieve the same counting geometry as the donor sample. In this way the radioactive ions were distributed within the same volume element in the vial as the vial containing the donor sample.

An automatic gamma counter, LKB Wallac Compugamma model 1285, was used to count gamma emitters. In the case of co-ion beta emitters, the sorbed electrolyte was leached out by rinsing the membrane with small portions of distilled water. The membrane was placed in a perfluorocarbon screw capped jar after blotting and was covered with about 20 cm³ of distilled water. The water was weighed before adding it to the jar. After one hour about 1 g of solution was sampled and counted. The remaining activity was taken out of the membrane by leaving it in another 20 cm³ of distilled water overnight. Most of the activity contained in the membrane came out in the first rinsing. However the total activity is the sum of the activities in the two rinsings. The volume

ion exchange capacity or the membrane ion concentration in terms of moles of sorbed electrolyte per liter of wet membrane in 0.2 M solution is calculated from the activity in the membrane and the donor specific activity:

$$\text{IXC} = \frac{\text{Activity in membrane (cpm)}}{1000 \text{ Donor specific activity (cpm/mol)} \times \text{Volume of membrane (cm}^3\text{)}}$$

III.2.2 Ion exchange capacity

The ion exchange capacity (IXC) is defined as the millimoles of exchange sites per gram of dry polymer. To determine this quantity, a procedure similar to the determination of membrane concentration was done. After equilibration of the membrane in 0.2 M radioactive NaCl solution, the membrane was rinsed with distilled water before blotting and counting. Moles of exchange sites were determined as described in the sorption experiment. The membrane was dried at 120°C under vacuum overnight. The Moles of exchange sites per gram of dry polymer gives the required ion exchange capacity.

III.2.3 Membrane water content

The water contents of the Dow PFSI'S were determined using the following procedure. After pretreatment, the membrane in a cationic form was quickly blotted with an ashless filter paper and weighed. The membrane was then dried under vacuum for eighteen hours. The dried membrane was weighed. Completeness of drying was monitored by drying to a constant weight. The percent water was calculated as follows:

$$\% \text{ water} = 100 \left(\frac{W_{\text{wet membrane}} - W_{\text{dry membrane}}}{W_{\text{dry membrane}}} \right)$$

Water contents in % water were converted to moles of water/ mole of exchange site.

III.3 Self-diffusion experiment

Diffusion is a universal process by which matter is transported from one point to another under a concentration gradient. By this process a diffusional flux is produced. In a solution containing a single solute, the solute moves from a region of higher to lower concentration, while the solvent moves in the opposite direction. All the molecules in the system will continually change place in a completely random manner. In the absence of concentration gradient, the molecular movements will not result in any net transport of dissolved particles in any direction. The term self-diffusion is used for a system in equilibrium, where there are no gradients of activity coefficients, electric potential, pressure and no convective currents. Self-diffusion of a species across a membrane is defined as the diffusion of ions or molecules from bulk solution from one side of the membrane, into the bulk solution on the other side of the membrane (7). For a system in equilibrium which consists of two identical solutions separated by a membrane, the above mentioned gradients do not exist. In our experimental system the diffusion experiment is treated in terms of a one dimensional model. The membrane surfaces are assumed to be planar and parallel to one another, and the membrane cross-section is uniform. All fluxes are then normal to the membrane surface and constant at steady state. This diffusional process can be described by Fick's first law of diffusion

$$J = -D \frac{dc}{dx}$$

where J is the flux and D is the diffusion coefficient given in units of moles cm⁻² sec⁻¹ and cm² sec⁻¹ respectively. Self diffusion is quantified if the system described above (system in equilibrium where two identical solutions are separated by a membrane) is perturbed by introduction of a trace amount of a radioactive isotope of the ion being studied, into one side of the membrane (donor solution) and monitoring its appearance at the other side of the membrane (acceptor solution). An ideal radioactive isotope should possess the

same diffusional properties as the naturally occurring species. In other words, isotope effects should be negligible or within accuracy of the measurements. Figure III.1 shows a concentration profile in steady state isotopic diffusion from donor solution across films and membrane to acceptor solution. At steady state the fluxes in the membrane, assuming Fick's first law, are equal to the fluxes in the films. Integration of equation III.1 leads to;

$$J = D \frac{C_A - C_A'}{\delta} = D \frac{\bar{C}_A' - \bar{C}_A''}{d} = D \frac{C_A''}{\delta} \quad \text{III.2}$$

where D is the self diffusion coefficient, δ and d are the film and membrane thickness, respectively, and C is the tracer concentration. Barred quantities refer to membrane phase and indices (') and (") refer to donor and acceptor film/membrane and membrane/film respectively. After a characteristic time lag t_a given by

$$t_a = 0.42 \frac{d^2}{D} \quad \text{III.3}$$

a constant concentration gradient of tracer is established across the membrane. The tracer concentration on the membrane surface adjacent to the donor solution \bar{C}_A' is larger than solution concentration C_A , since the ion exchange capacity of the membrane expressed as moles of exchange sites/liter of wet membrane, exceeds the external solution concentration.

At isotopic equilibrium the relationship between the isotopic and ionic concentration at the phase boundaries is given by;

$$\frac{C_A'}{C_A} = \frac{\bar{C}_A'}{\bar{C}_A} \quad \text{and} \quad \frac{C_A''}{C_A} = \frac{\bar{C}_A''}{\bar{C}_A} \quad \text{III.4}$$

$$\frac{\bar{C}_A}{C_A} = \frac{\bar{C}_A'}{C_A'} = \frac{\bar{C}_A''}{C_A''} \quad \text{III.5}$$

Combining equation III.2 and III.5 one obtains an expression for the self diffusion flux;

$$J = - \frac{\bar{DC}}{d \left[\frac{2\delta \bar{DC}}{d DC} + 1 \right]} \quad \text{III.6}$$

The flux equation is applicable to all mobile species. The rate determining step of self diffusion can be controlled by diffusion either across the membrane or across the film.

This can be analyzed by examining the denominator of equation III.6

$$\text{If } \frac{2\delta \bar{DC}}{d DC} \ll 1 \Rightarrow 2 \ll \frac{d DC}{\delta \bar{DC}}$$

then rate of diffusion is completely membrane controlled and the flux equation reduces to

$$J = - \frac{\bar{DC}}{d} \quad \text{III.7}$$

However when

$$\frac{2\delta \bar{DC}}{d DC} \gg 1 \Rightarrow 2 \gg \frac{d DC}{\delta \bar{DC}}$$

the rate determining step is film-diffusion controlled. The flux is given by

$$J = - \frac{DC}{2\delta} \quad \text{III.8}$$

Comparison of equations III.6, III.7 and III.8 shows that a membrane of thickness d , with adhering film of thickness δ , behaves as a membrane with a total thickness of

$$d \left[1 + \frac{2\delta \bar{DC}}{d DC} \right]$$

In general the rate determining step depends on the ratio $\frac{2\delta \bar{DC}}{d DC}$ which in turn depends on the ion content, thickness of the membrane, and the external concentration of the solution. This equation shows that a lower value of d (thin membrane), higher values of δ (thicker films resulting from poor stirring), high diffusion coefficients and large values of \bar{C}/C (low external solution concentration) highly favor film diffusion control.

III.3.1 Apparatus

A diagram of the diffusion cell used is shown in Figure III.2. It consists of two matched cells each of approximately 100 cm³ capacity. They are built with borosilicate glass, and have an inner diameter of 4 cm and a length of 10 cm. The two cells are provided with a double jacket for water circulation needed for temperature control of the solution during an experiment. An external thermostating bath was used to circulate water through the double jacket (Lauda circulator, Models MS and K-2/RD). Stirring is done with Teflon stirrer paddles mounted on a glass support. The paddles have four stirring blades at one end. They are rotated through magnetic coupling with tachometer-feedback DC motors, whose speed can be precisely regulated and maintained. The motors were calibrated and fixed at 900 rpm for all the experiments. Silicon rubber gaskets were used to seal the membrane between the two half cell compartments. Flux rates were decreased for sodium and cesium ion transport by reducing the exposed membrane area of 11 cm² to 1 cm². The area reduction was achieved by introducing a Teflon plate bearing an off-centre hole of an area of 1 cm² on each side of the membrane. The two cell compartments including the Teflon plates, membrane, and rubber gaskets were held in place by screwing together two metal rings placed on each side of the half cell.

III.3.2 Procedure and data treatment

Schematically the experiment is designed as in Figure III.3

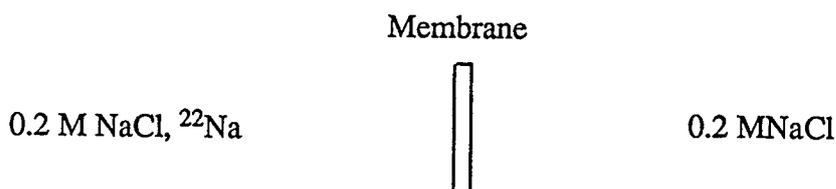


Figure III.3 Schematic Diagram for the Self Diffusion Experiment

Membrane samples of about 11 cm^2 were pretreated as discussed in Section III.1.4. Membranes were soaked overnight in 0.2 M electrolyte solution of interest. The membrane was then placed in the cell assembly. Both sides of the cell were filled with 0.2 M electrolyte solution. The experiment was initiated by adding approximately $10 \mu\text{L}$ of appropriate radioisotope. (The quantity added depends on the activity of the source of radioisotope). Therefore an initial assessment of the activity of the radioisotope was done for all the experiments. A 1 cm^3 sample from the donor solution was immediately withdrawn for counting after the radioisotope was added. At periodic intervals 1 cm^3 samples were withdrawn from the acceptor solution with a calibrated 2 cm^3 Hamilton syringe. A maximum of ten 1 cm^3 samples were withdrawn, to monitor the flux. To ensure steady state behavior each run was terminated before 2% of the donor radioactivity had been transferred.

STIRRED CELL

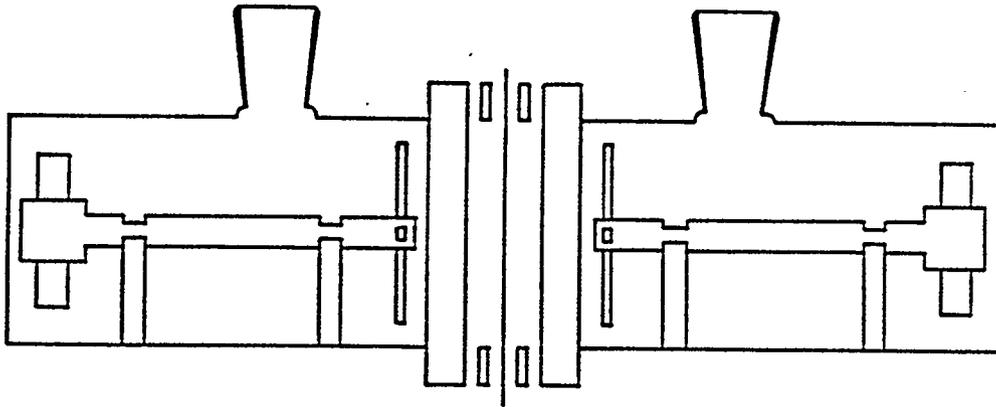


Figure III.2

Cell arrangement used for membrane diffusion studies.

The samples from each experiment were counted in sequence. This procedure was followed to avoid half life corrections, especially for self diffusion studies of anions which were run for long durations.

The steady state flux is calculated from the experimental data using the following equation:

$$J = \frac{MC \frac{dA_{\text{corr}}}{dt}}{\rho S A_d} \quad \text{III.9}$$

where,

M = initial acceptor weight (g)

S = membrane surface area (cm²)

C = concentration of donor solution (moles cm⁻³)

ρ = solution density (g/cm³)

A_d = specific activity of donor solution (cpm/g)

dA_{corr}/dt is the slope of the A_{corr} versus time in cpm g⁻¹ sec⁻¹

After background correction, two additional corrections were done for the measured activity of the acceptor solution. One of these compensates for the activity loss due to sample withdrawal from the acceptor solution which would otherwise be distributed in the acceptor solution. The other normalizes the decreasing weight of the acceptor solution back to its initial weight. The true specific activity of the ith sample is therefore calculated taking into consideration these three activity corrections;

$$A_{i,\text{corr}} = \left[A_{i,\text{net}} + \frac{\sum_{j=1}^{i-1} A_{j,\text{net}}}{M - (i-1)} \right] \left[\frac{M - (i-1)}{M} \right] \quad \text{III.10}$$

where,

A_{i,corr} = true specific acceptor activity for the ith sample

$A_{i,\text{net}} = A_i$, measured - background count

M is the weight of acceptor solution

The self diffusion coefficient for a purely membrane controlled diffusion is

$$\bar{D} = \frac{Jd}{\bar{C}} \quad \text{III.7}$$

Where,

d = membrane thickness (cm)

J = flux in moles $\text{cm}^{-2}\text{sec}^{-1}$

\bar{C} is the membrane concentration (moles cm^{-3})

For sodium and cesium ions, the overall rate of diffusion was partially influenced by the unstirred film; corrections were made accordingly. After calculation of \bar{D} , obtained from equation III.7, which is an apparent value, the true membrane diffusion coefficient was then calculated from the equation;

$$\bar{D}_{\text{true}} = \frac{\bar{D}}{1 - \frac{2\delta\bar{D}\bar{C}}{dDC}} \quad \text{III.11}$$

where

δ = film thickness of the unstirred film. Quantities without bars refer to values in solution.

The thickness of the unstirred film was determined by measuring the steady state flux of tracer concentrations ranging from 0.05 M to 0.2 M solutions. The stirring was fixed at 900 rpm. The film thickness was obtained from a plot of $1/J$ versus $2/DC$. This can be shown by rearranging equation III.6;

$$J = - \frac{\bar{D}\bar{C}}{d \left[\frac{2\delta\bar{D}\bar{C}}{dDC} + 1 \right]} \quad \text{III.6}$$

By taking the reciprocal of this equation and rearranging, one obtains;

$$-\frac{1}{J} = \frac{2\delta}{DC} + \frac{d}{DC}$$

III.12

Thus the slope of the plot of $1/J$ versus $2/DC$ gives the film thickness. A film thickness of $13 \mu\text{m}$ was obtained for experiments done at temperatures of 25°C and 40°C . A film thickness of $16 \mu\text{m}$ was obtained for experiments done at 0°C . All the other experiments were done in 0.2 M electrolyte solutions using the mentioned film thickness, since the stirrer was fixed at 900 rpm for all the experiments.

III.4 Near infrared studies

In order to study the forms of water reported to be present in the mid-infrared region (24,25), near infrared measurements were done for membranes in sodium and cesium ion forms. A Nicolet 8000 FT-IR spectrometer with indium antimonide (liquid N₂-cooled) detector was used for these measurements. By means of two rubber gaskets the membranes were clamped on a cardboard support which was then placed in the sample beam. Two hundred scans were collected and stored as spectra. The spectra were imported into Spectra Calc and decomposed into three peaks with the program "Curvefit". The peak center and area percent of water in non-hydrogen bonded, weakly hydrogen bonded and strongly hydrogen bonded forms were calculated using the program, "Curvefit. The program works by first asking the operator to make a guess of the number of bands present, peak centers, peak heights and peak widths. The software further requires the operator to choose the peak type, that is, whether the peak area is a mixture of Lorentzian and Gaussian or Gaussian. The program then asks for the number of passes and iterates a number of times using the starting guesses, to find the combination of band heights, positions and widths which best fit the data file. After iterating the program reports the peak centers and areas of the peak. The software also reports the chi-square value which reflects how well the frequencies of the computer generated curve correspond to the actual curve being analysed. The chi-square value therefore is a reflection of the "goodness" of the fit, the smaller the value the better the fit.

According to the above mentioned procedure, the system was optimized, by using the spectra of sodium ion form Nafion 1100 sulfonate. Firstly the system was optimized by assuming that the spectra consisted of two peaks. Secondly it was optimized by assuming three peaks. It was found that the calculated chi-square value was significantly better if three peaks were assumed rather than two peaks. The fitted

curves for both assumptions will be presented in chapter IV for comparison purposes. Thus the envelope was decomposed by assuming that it consisted of three peaks.

Further, after assuming that there were three peak areas, the percent Lorentzian was varied in an attempt to get the best chi-square value, and hence the best fit. It was realized that the best chi-square value is obtained only when all three peak areas are assumed to be Gaussian. After optimization, the spectra for the other membranes were decomposed in the same manner.

Chapter IV

Results and Discussion

IV.1 Sorption Studies

IV.1.1 Membrane Water Content

Membrane pretreatment and cationic form have an influence on the water content of perfluorinated membranes. Pretreatments in which the perfluorinated membrane is boiled in water have been reported (11, 12). The boiled membranes sorb more water than the room temperature pretreated membranes. Moreover the resulting water content after the membrane has been boiled in water remains constant for weeks (16).

Table IV.1 lists the water content of Dow PFSE'S for four equivalent weights in sodium and cesium ion forms. Previously reported water contents of 1200 EW sulfonate Nafion in sodium and cesium ion forms have been added for comparison purposes (47). The water content of the 680 EW is significantly higher than the Nafion membrane and the other Dow membranes. As a result the cluster size of the 680 EW sulfonate polymer is significantly larger than the other polymers as in Table I.1. The water content of the 1200 EW Nafion sulfonate is higher as compared to the water content of the 960 EW sulfonate Dow polymer. These two polymers have about the same TFE to functional monomer ratio. This implies that the Dow PFSE'S have a lower water content as compared to their Nafion analogs. The membrane pretreatment procedure discussed in Section III.1.4 was used. The membranes in sodium ion form have a greater water content than those in cesium ion form. This is because the hydration energy of sodium ions is greater than that of cesium ions.

Table IV.1

Water content of Dow PFSI'S in Na⁺ and Cs⁺ forms

Equivalent Weight	Moles of water / mole of SO ₃ ⁻	
	Na ⁺	Cs ⁺
680	53.0	25.0
760	19.2	7.54
960	10.6	4.40
1291	8.61	4.30
Nafion 1200 Sulfonate	11.9	6.6

IV.1.2 Electrolyte Sorption

Results of the electrolyte sorption of four equivalent weights of Dow PFSI'S in 0.2 M solution are listed in Table IV.2. Volume capacities were recorded in molarity units. This is needed in the calculation of self diffusion coefficients. Also there is the need to calculate electrolyte sorption in molal units, because it represents the effective electrolyte concentration in the polymer. It also allows us to evaluate the extent of Donnan exclusion for the membranes (7). Thus, in this study the water content of the membranes were taken into consideration in the calculation of the concentration of sorbed electrolytes. Volume capacity decreases with increasing equivalent weight for sodium and cesium ion forms. This is because the ratio of functional monomer to TFE units is increased as equivalent weight is decreased. Thus as the number of exchange sites increases the number of cations required to obtain electrical neutrality is increased. The volume capacity of the 680 EW polymer is quite low. This is because of its large water content. The polymer swells to a larger extent than the other polymers. As a result the increased volume due to swelling decreases the volume capacity. An aspect of this result that is interesting is the difference between the volume capacities of the membranes in sodium and cesium ion forms. For all the membranes volume capacities of cesium ions are slightly larger than sodium ions. This is due to the high selectivity of cesium ion for the membranes compared to sodium ions. Also interesting is that the volume capacities for iodide ions are larger than for chloride ions for all the membranes. This may be due to the fact that the larger and more polarizable iodide ion may be further interacting with the interface between the fluorocarbon backbone and the ion clusters.

Figure IV.1 is the summary of the results of membrane ion concentration in molar units, obtained for chloride and iodide ions. Also shown in the figure is the

Table IV.2

Polymer Ionic Concentration (M) in 0.2M MX Solution at 25°C

EW	Ions			
	Na ⁺	Cs ⁺	Cl ⁻ *	I ⁻ *
680	0.843	0.880	0.0561	0.0588
760	1.73	1.94	0.0334	0.0530
960	1.56	1.72	0.00950	0.0455
1290	1.15	1.28	0.00824	0.0361

* Determined in 0.2M NaX Solution

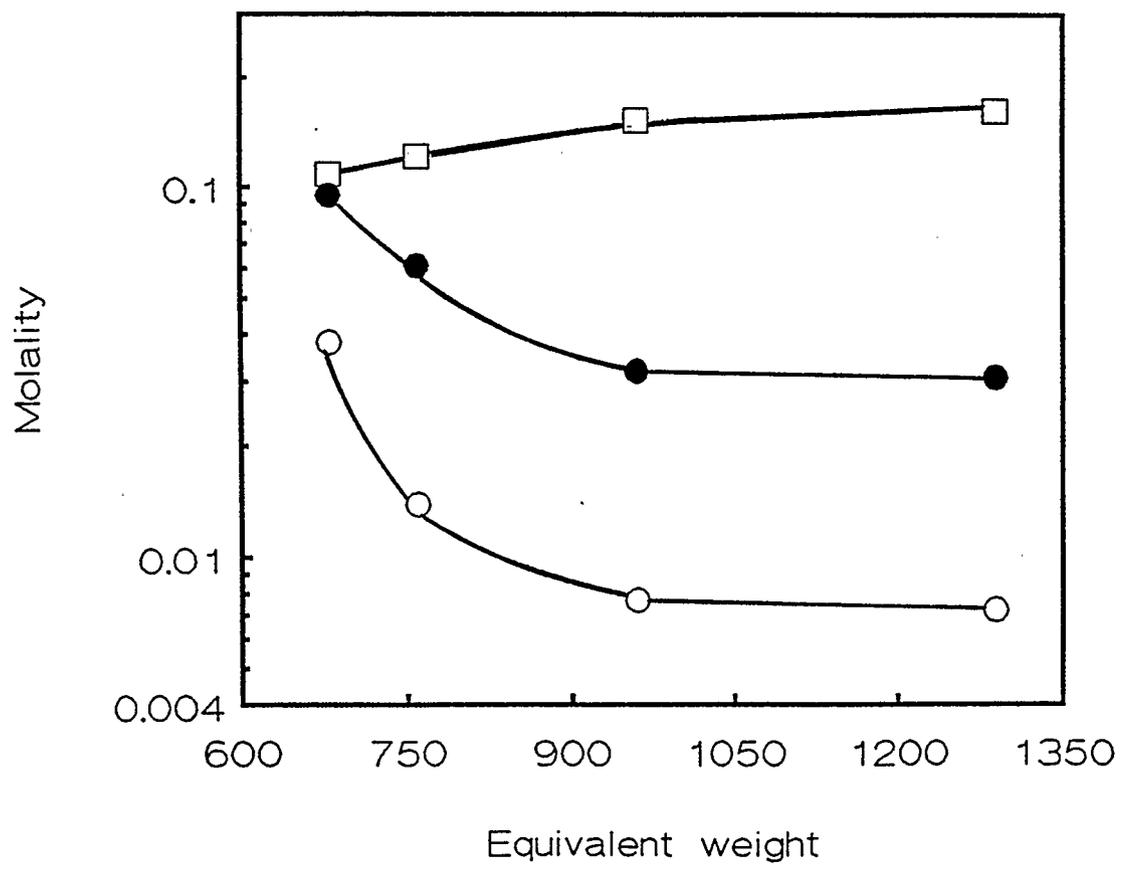


Figure IV.1

Membrane ion concentration (molal) versus equivalent weight for the Dow PFSI'S. ○ DONNAN ● CHLORIDE □ IODIDE

"ideal" Donnan sorption curve, calculated using Equation II.1. Here the activity coefficients for the solution and membrane phases are assumed to be the same for simplicity. The electrolyte sorption results show a distinct difference between chloride and iodide ions. While the sorption curve for chloride corresponds to the predicted Donnan equilibrium, the iodide curve does not.

The sorption of chloride ion is explained by considering the moles of water per exchange site. A decrease in moles of water per exchange site of the polymer will cause an increase of the concentration of ion exchange sites. This will result in an increase in the Donnan potential. It is therefore not surprising that the exclusion of co-ions increases with equivalent weight, as the Dow PFSI'S water content decreases with increasing equivalent weight.

The work of Mauritz and Gray demonstrates how the co-ion exclusion is dependent on the water content of the polymer (20). They reported hydroxide ion sorption studies for 1100 EW sulfonate Nafion. The experiments were done in sodium hydroxide solution in the concentration range 7.5 to 17.9 M. They found that electrolyte sorption is characterized by a relatively constant $\text{NaOH}/\text{SO}_3\text{Na}$ molar ratio of about 0.27. The constancy of the molar ratio was explained by using the Donnan equilibrium theory. The volume capacity of the ion exchange sites is increased by dehydration, i.e. increasing the external solution concentration of sodium hydroxide decreases the membrane water content. As a result the polymer deswells causing an increase in ion exchange charge density. This leads to an increase in Donnan exclusion. The constancy of $\text{NaOH}/\text{SO}_3^-$ can be reconciled if the rate of increase of external solution concentration is equal to the increase of volume capacity.

Electrolyte sorption studies have been done by Herrera and Yeager for chloride and iodide ions (33). The membranes used were 1050 EW perfluorocarboxylate and 1150 EW perfluorosulfonate. The carboxylate membrane was found to show less

sorption compared to the sulfonate. This was attributed to lower water content of the carboxylate membrane. In a similar study in dilute solution environments the electrolyte sorption was about the same in both perfluorinated ionomers (33).

The sorption curve of iodide ion is distinctively different from the sorption curve of chloride ion. Sorption for iodide ion increases with increasing equivalent weight. The larger, more polarizable iodide ion seems to further interact with the polymer to increase its concentration in the polymer. This interaction may be taking place in a hydrophobic region of the polymer which is the interface between the ionic clusters and the fluorocarbon backbone. The formation of compact clusters in the high equivalent weight polymer might imply the creation of a larger fractional void volume in the interface. Since iodide ion may be sorbing in the interface, sorption will increase with equivalent weight.

IV.3 Self Diffusion Studies

Ion diffusion in Dow PFSI'S was studied in this research to obtain information on how permselectivity changes with equivalent weight. Results of ion diffusion in the Dow PFSI'S will be presented. Also a comparison of the results of the Dow PFSI'S are made with those of Nafion to obtain information on the effect the short side chain and crystallinity have on ion transport. Further, ion diffusion in perfluorinated ionomer membranes is compared to ion diffusion in conventional ion exchange polymers. The mechanisms of diffusion for both polymers are discussed.

IV.4 Self diffusion results of Dow PFSI'S

Self diffusion results for the Dow PFSI'S are listed in Table IV.3. The results are also presented in Figures IV.3 - IV.6 in the form of Arrhenius plots where ionic self diffusion coefficients are plotted versus the inverse of absolute temperature. The activation energies were obtained from the tangents of the Arrhenius plots at 25° C. The membranes employed in this study have different ion exchange capacities, water contents, and extents of crystallinity. Diffusion coefficients for all ions generally decrease with increasing equivalent weight and crystallinity. The spread between the diffusion coefficients of cations and anions decreases with decreasing equivalent weight. This provides indirect evidence that as equivalent weight increases the ions increasingly tend to diffuse through different paths depending on their charge type and hydration energy.

The diffusion trends for the 1290 EW as well as 960 EW polymer are similar to both the carboxylate and sulfonate versions of Nafion. They are different to the trend of diffusion in conventional ion exchange polymers. The self diffusion coefficients of

Table IV.3
 Self-Diffusion Coefficients in Dow
 Perfluorosulfonate Ionomer Membranes, 25° C

EW	Diffusion Coefficient x 10 ⁷ , cm ² sec ⁻¹			
	Na ⁺	Cs ⁺	Cl ⁻	I ⁻
680	79.1	54.0	66.6	25.7
760	23.4	14.8	24.9	12.2
960	20.9	4.09	6.72	0.767
1290	16.8	3.70	5.19	0.599
*Nafion 1200 Sulfonate	9.83	1.88	4.89	0.99
*Nafion 1050 Carboxylate	11.1	6.73	1.58	0.20

* Adapted from references (1, 25, 33)

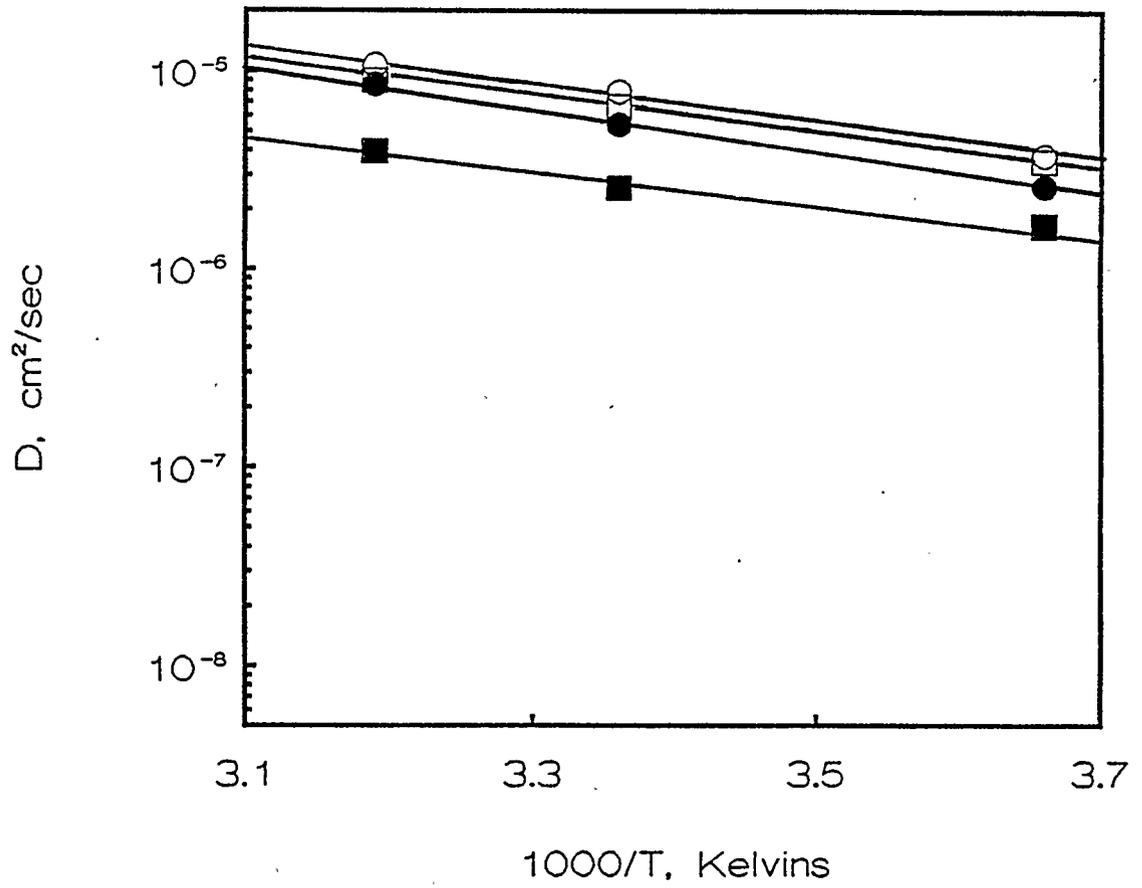


Figure IV.3

Arrhenius plots of ionic diffusion in 680 EW perfluorinated sulfonate membrane. \circ Na^+ \bullet Cs^+ \square Cl^- \blacksquare I^-

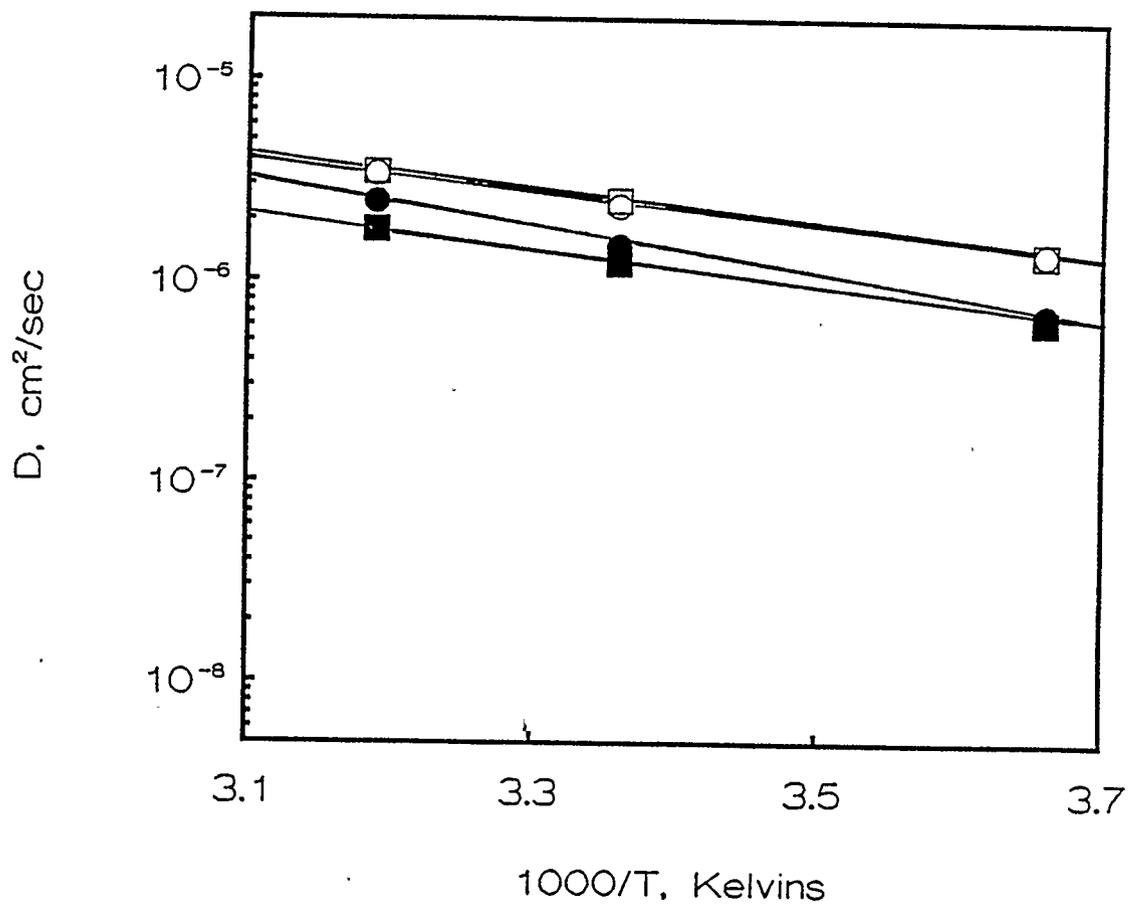


Figure IV.4

Arrhenius plots of ionic diffusion in 760 EW perfluorinated sulfonate membrane. ○ Na⁺ ● Cs⁺ □ Cl⁻ ■ I⁻

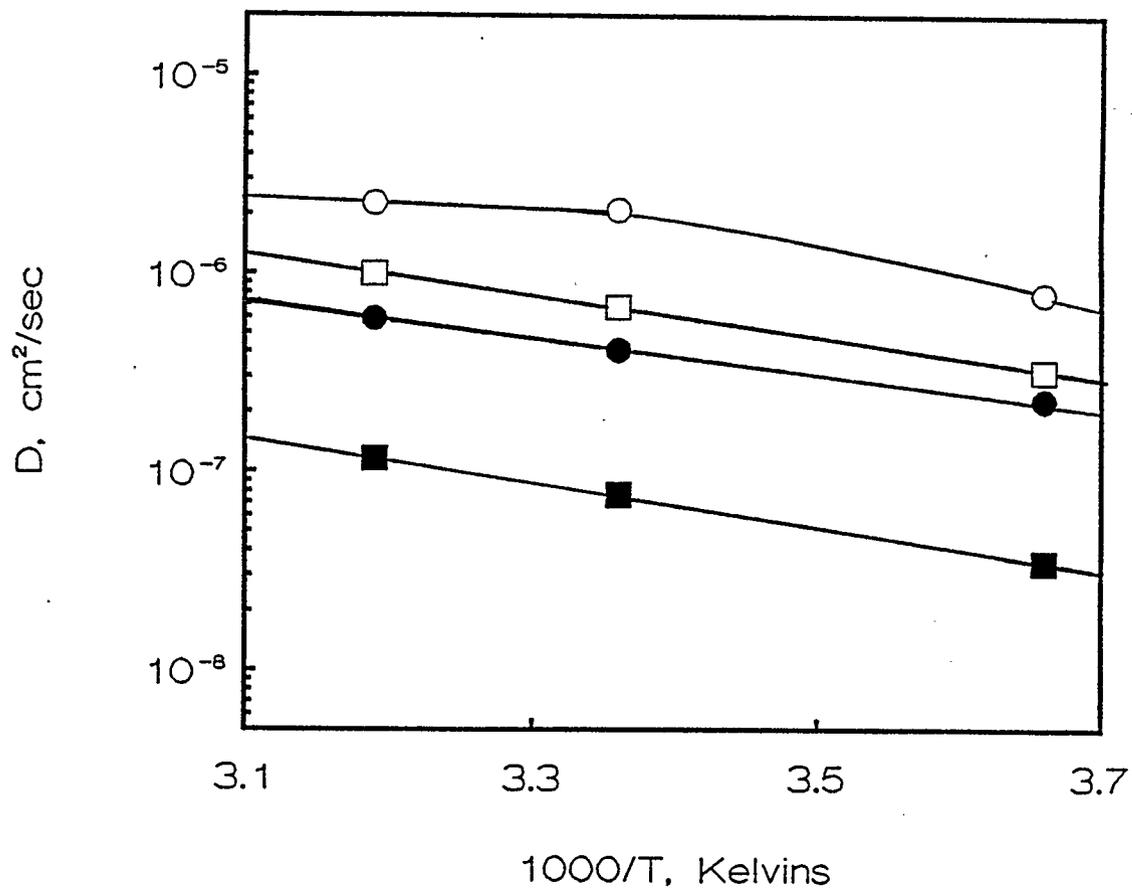


Figure IV.5

Arrhenius plots of ionic diffusion in 960 EW perfluorinated sulfonate membrane. ○ Na⁺ ● Cs⁺ □ Cl⁻ ■ I⁻

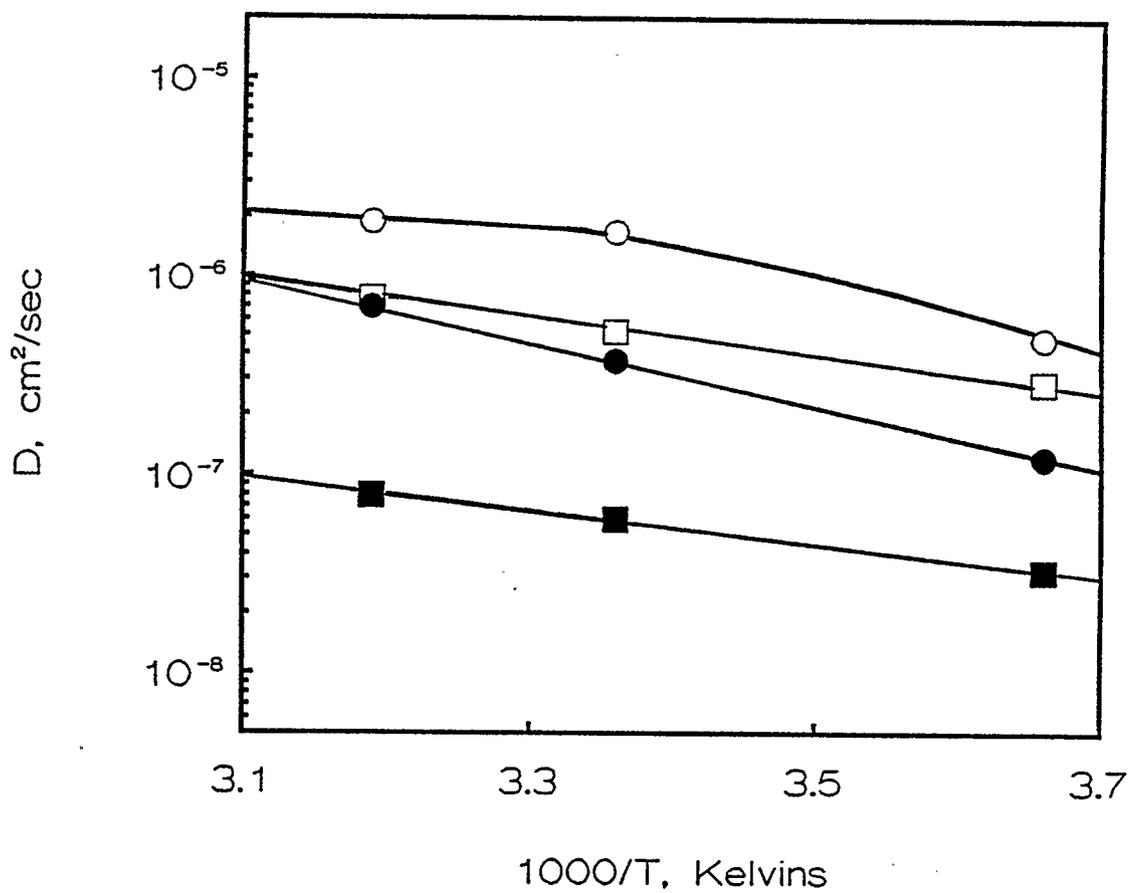


Figure IV.6

Arrhenius plots of ionic diffusion in 1290 EW perfluorinated sulfonate membrane. \circ Na^+ \bullet Cs^+ \square Cl^- \blacksquare I^-

iodide, chloride and cesium ions are now lower than sodium ion, which is the reverse observed for conventional ion exchange polymers. Activation energies of diffusion of cesium ion and the anions are slightly higher than that of sodium ion.

Kinetic permselectivity is significantly reduced for the 680 and 760 EW membranes. The self diffusion coefficients of all ions are higher in these membranes as compared to the higher equivalent weight polymer. However, the activation energy of diffusion for the cations and the anions are all solution-like. The diffusional behavior of the ions in these membranes may be due to the high water content and low crystallinity. This finding is not surprising, since permselectivity measured by current efficiency values is reported to depend on the water content of the membrane (34). The carboxylate version of Nafion, which has a lower water content and which is more crystalline, is more permselective than the sulfonate analogue (15, 33).

IV.4.1 Discussion of the self diffusion results

The self diffusion coefficient of sodium ion is in general higher than the self diffusion coefficients of the other ions. An exception is for the 760 EW sulfonate polymer where the self diffusion coefficient of chloride ion was about the same as sodium ion within experimental error. Further, the self diffusion coefficient of sodium ion increases with decreasing equivalent weight. The value for the 680 EW sulfonate polymer is significantly higher than for the other Dow polymers. The large values of self diffusion coefficient of sodium ions in the membranes are consistent with the three region diffusional model discussed previously. The ion clusters with their associated sorbed water represented by region C of this diffusional model are interconnected. This network of aqueous regions would provide sodium ions with a highly efficient diffusional path, and it is likely that sodium ions are delocalized throughout these regions, within the limitation of overall charge neutrality. As the water content of the

membrane is increased this region may become more solution-like and more interconnected. As a result, the self diffusion coefficient of sodium ion increases as the equivalent weight decreases. This has been illustrated with percolation theory (35). If the clusters are assumed to be conductive media through which sodium ion transports, then the conductivity will increase if the cluster concentration and sizes increase (29). This results in clusters interconnecting to form a pathway that is less tortuous. As a consequence, there is an increase in the self diffusion coefficient of the sodium ions, since they reside mainly in region C (35). The 680 EW sulfonate polymer has a very high water content (53 moles of water per mole of exchange sites). As a result the size of ionic clusters deduced from the Bragg spacing in Table I.1 is significantly larger than for the other polymers. Hence, the self diffusion coefficient of sodium ion in the 680 EW sulfonate polymer is distinctly larger than those of the other polymers.

An interesting aspect of these results is to compare the differences between the self diffusion coefficients of sodium ions in the Dow PFSI'S and in the 1050 EW carboxylate and 1200 EW sulfonate Nafion polymers. The diffusion results can be explained with an efficiency parameter E:

$$E = \frac{\bar{D} / D_{\text{water}}}{V_{\text{f,water}}} \quad \text{IV.1}$$

The parameter $V_{\text{f,water}}$ is the volume fraction of water in the membrane. It is calculated from the weight percent of sorbed water, the molecular weight of water, the density of the wet polymer and the estimated partial molar volume of water in the polymer, which is 17 mL mol⁻¹ (50). \bar{D} is the experimentally determined self diffusion coefficient in the membranes tabulated in Table IV.3 and D_{water} is the diffusion coefficient in 0.2 M electrolyte solution of interest.

Listed in Table IV.4 are the efficiency parameters E of sodium and cesium ions with their corresponding volume fraction of water. The parameter E reflects the

overall degree of organization of sorbed water in the polymer. The inherent assumption to this evaluation is that diffusion only occurs in aqueous regions of the polymer, and that diffusion of ions through the fluorocarbon regions is negligible. A secondary assumption is that all the water molecules act as solvent and that water of hydration participates in the diffusion process. One will expect that the efficiency parameter E will approach unity if the aqueous microphase is "perfectly" organized to enable one-dimensional diffusion across the membrane. There are several reasons as to why the efficiency parameter is less than unity. Firstly some isolated water molecules and some water of hydration may not be available for diffusion. Secondly due to differences in mechanism of diffusion of ions in perfluorinated ionomer membranes, there would be differences in the E value depending on the tortuosity of the pathway of diffusion.

Not only are the diffusion coefficients of sodium ions in the Dow PFSI'S larger as compared to Nafion but the E values are as well. The efficiency parameter E for the 680 EW sulfonate polymer in the sodium ion form is significantly higher suggesting a highly organized aqueous medium in the membrane for diffusion of sodium ions. Due to the high water content of this polymer, the size of the ion cluster is large compared to the other Dow PFSI'S. As a result, the clusters may be more available for diffusion compared to the other Dow PFSI'S whose E values do not differ to a large extent. Although the volume fraction of water in the 960 EW Dow polymer and in the 1200 EW Nafion sulfonate are about the same, the efficiency parameter of the 960 Dow polymer is about twice as large as that for the 1200 EW Nafion sulfonate. One possible explanation of this feature is that for the Dow PFSI'S the volume elements between clusters are more available for diffusion. Another possible explanation is that for the Dow PFSI'S the interconnecting channels are structured in a way that reduces the tortuosity of the diffusion path as compared to Nafion.

The self diffusion coefficients of cesium ion are lower than those of sodium

Table IV.4

Efficiency Parameters (E) and Volume Fraction
of Water in Na⁺ and Cs⁺ - Forms , 25° C

Equivalent Weight	Efficiency Parameter (E)		Volume fraction of water	
	Na ⁺	Cs ⁺	Na ⁺	Cs ⁺
680	0.731	0.516	0.770	0.507
760	0.602	0.283	0.304	0.254
960	0.573	0.126	0.274	0.157
1290	0.546	0.153	0.236	0.127
*Nafion 1200 Sulfonate	0.263	0.061	0.280	0.150
*Nafion 1050 Carboxylate	0.361	0.300	0.231	0.109

* Adapted from references (1, 25, 33)

ion in both the Dow PFSI'S and Nafion. In dilute solution of an electrolyte at 25° C, the self diffusion coefficients of cesium ion are larger than those of sodium ion. This implies that the mechanisms of diffusion in solution and in the membranes are quite different. Due to the large size and low hydration energy of cesium ion, it may reside in region B of the three region diffusional model (within the limits of electrical neutrality in the clusters). This region has a relatively low ionic strength as compared to region C. Since region B has a large fractional void volume and is very irregular, cesium ion would follow a more tortuous diffusional path compared to sodium ions which diffuse through region C. As a result, the self diffusion coefficient of cesium ion is smaller than sodium ion for all the Dow PFSI'S and Nafion polymers. On the basis of the same volume fraction of water, the diffusion coefficient of cesium ion for the 760 EW sulfonate polymer and that for sodium ion in the 1290 EW sulfonate polymer can be compared. Although the volume fraction of water for the 760 EW sulfonate polymer in the cesium ion form is slightly higher than that for the 1290 EW sulfonate polymer in the sodium ion form, the efficiency parameter of sodium ion in the 1290 EW sulfonate is twice as large as that for the corresponding value of cesium ion in the 760 EW sulfonate polymer. This implies that the diffusional path of sodium and cesium ions in perfluorinated ionomer membranes are quite different. Whereas diffusion of sodium ions are aqueous-like those of cesium ions are not. The cesium ions therefore may be diffusing along a diffusional path that is longer as compared to sodium ions which may be diffusing through an interconnected pathway which results in solution-like diffusion coefficients.

The self diffusion coefficient of cesium ion for the 680 EW Dow sulfonate polymer is significantly higher than for the other Dow PFSI'S. For the Dow PFSI'S the self diffusion coefficients decrease with increasing equivalent weight, and decreasing water content. Also the efficiency parameter E decreases with increasing equivalent

weight. An exception is for the 1290 EW sulfonate polymer which has a higher E value compared to the 960 EW sulfonate polymer. This may be due to the fact that the 1290 EW sulfonate polymer might be more phase separated than the 960 EW membrane. The E value is even higher for the 1050 EW Nafion carboxylate, and lowest for the 1200 EW Nafion sulfonate. Yeager et. al, using mid-infrared studies measured the hydrogen bond strength of water in the membranes relative to liquid water (25). They found that the strength of hydrogen bonding in the 1050 EW Nafion carboxylate is 92% of that in water while in the 1200 EW sulfonate it is 62%. This means that the carboxylate is more phase separated and that intrusion of fluorocarbon material into the ion clusters is less frequent in the 1050 EW Nafion carboxylate than in the 1200 EW Nafion sulfonate polymer. From the values of the efficiency parameters of the Dow PFSI'S and the Nafion sulfonate and carboxylate polymers it can be inferred that for the Dow PFSI'S, phase separation increases with equivalent weight. Thus the 1290 EW sulfonate polymer has an E value that is higher than the value for the 960 EW sulfonate polymer, although the 960 EW sulfonate polymer has a higher volume fraction of water. Also it can be inferred from the values of the efficiency parameters that the 960 EW sulfonate Dow polymer is more phase separated than the 1200 EW Nafion sulfonate polymer. This comparison is made on the basis of the same TFE to functional monomer ratio, and about the same volume fraction of water. The value of the efficiency parameter of the 960 EW sulfonate Dow polymer is about twice as large as that for the 1200 EW Nafion sulfonate polymer. This suggests that since the Dow polymer has a shorter side chain, it has less polymer material in the interface compared to the Nafion polymer. The value of the efficiency parameter for the 680 EW sulfonate polymer is quite higher than for other equivalent weights of the Dow PFSI'S. This suggests that as the water content is increased it is likely that region C may be partially contributing to the transport of cesium ions, and that cesium ions may be partitioning between regions B and C as they

diffuse through the membrane.

Although the self diffusion coefficient of chloride ion is lower than that of sodium ion, for all the Dow PFSI'S except for the 760 EW sulfonate polymer, it is higher than that of iodide ion. Due to the electrostatic repulsion of the anions from region C, they diffuse mostly through region B. Also, since region B has a large fractional void volume and is irregular, the anions would follow a tortuous path compared to sodium ions which diffuse through region C which is more interconnected. The self diffusion coefficients of the anions are therefore relatively lower than those of sodium ions. The self diffusion coefficients of the anions in the 680 EW sulfonate polymer are significantly larger than in the other equivalent weights of the Dow PFSI'S. Also the self diffusion coefficients of the anions in the membranes decrease as the equivalent weight is increased, and as the water content of the membranes decreases. The high values of self diffusion coefficients in the 680 EW and the 760 EW sulfonate polymers are due to their large water content, and the possibility of anions partitioning between regions B and C. As the water content is increased, the effective concentration of ion exchange sites decreases (20). As a consequence the exclusion of co-ions from region C decreases, resulting in a simultaneous diffusion of the anions in regions B and C. A disadvantage in this feature is that the lower equivalent weight of the Dow PFSI'S will show reduced permselectivities for practical applications.

Listed in Table IV.5 are the efficiency parameters E for the halide ions and the estimated volume fractions of water in the polymers. The E values for the 680 EW and the 760 EW sulfonate polymers are significantly higher than those for the 960 EW sulfonate and 1290 EW sulfonate polymers. This suggests that the mechanism of diffusion of the anions in the low and high equivalent weight polymers are quite different. While diffusion of the anions in the 680 EW sulfonate and the 760 EW sulfonate polymers are solution-like, diffusion in the 960 EW sulfonate and 1290 EW

sulfonate polymers are not solution-like. The E values of for the 960 EW sulfonate Dow polymer and 1150 EW Nafion sulfonate polymer are 0.121 and 0.0857 respectively. The higher value for the Dow PFSI implies that diffusion of chloride ions in this polymer is more solution-like as compared to the 1150 EW Nafion sulfonate polymer. These two polymers have about the same ratio of TFE to functional monomer and volume fraction of water. However the overall permselectivity in terms of the ratio of sodium to chloride ions is better for the Dow polymer since the diffusion coefficient of sodium ion in this membrane is about twice as large as that for the 1150 EW Nafion sulfonate polymer.

The membrane self diffusion coefficient of iodide ion decreases as equivalent weight is increased. Also chloride and iodide ion self diffusion coefficients in the 960 and 1290 equivalent weight membranes are dramatically smaller than those of the other Dow PFSI'S. The iodide ion self diffusion coefficient is relatively smaller than that of the chloride ion. The larger more polarizable iodide ion seems to interact more with the interface than chloride ion. Further, the values of the estimated efficiency parameters for iodide and chloride ions show that the mechanism of diffusion of iodide ions is somehow different from that of chloride ions in the Dow polymers. The difference in the E values is greater in the 960 EW and the 1290 EW sulfonate polymers than in the 680 EW and the 760 EW sulfonate polymers. Thus the behavior of iodide ion in interacting with the polymer increases with equivalent weight and extent of crystallinity. This was also observed in the sorption studies of sodium halides. While chloride ion followed the predicted Donnan equilibrium, iodide ion showed an increase of sorption with equivalent weight which was not Donnan-like. While the E value for iodide ion in the 1150 EW Nafion sulfonate polymer is 0.017, it is 0.014, and 0.012 for the Dow the 960 and 1290 EW sulfonate membranes, and is 0.0042 for the 1050 EW Nafion carboxylate membrane. The extent of phase separation as deduced from mid-infrared studies by Yeager and coworkers shows that the 1050 EW Nafion

Table IV.5
Efficiency Parameters (E) and Estimated
Volume Fraction of Water of PFSI Membranes, 25° C

Equivalent weight	Efficiency Parameter (E)		Volume Fraction of Water	
	Cl ⁻	I ⁻	Cl ⁻ , I ⁻	
680	0.404	0.178	0.770	*0.703
760	0.403	0.196	0.304	
960	0.121	0.0137	0.274	
1290	0.108	0.0124	0.236	
Nafion 1150 Sulfonate	0.0857	0.0173	0.280	
Nafion 1050 Carboxylate	0.0337	0.00424	0.231	

* The volume fractions of water in the membranes in sodium iodide and sodium chloride solutions are the same; a difference was found for the 680 EW sulfonate polymer.

carboxylate is more phase separated than the 1150 EW Nafion sulfonate (25). Also from X-ray studies it is deduced that the 1050 EW carboxylate is more crystalline than the 1150 EW sulfonate polymer (16, 30), and that the Dow PFSI'S are more crystalline than their Nafion counterparts when the comparison is made on the basis of the same ratio of TFE to functional monomer (14). Thus it is deduced that the smaller ratio for the 960 EW sulfonate Dow polymer, compared to 1150 EW sulfonate Nafion polymer may be due to the Dow polymer being more crystalline, and that this interaction increases with equivalent weight and extent of phase separation.

The effect of equivalent weight on permselectivity is shown in Table IV.6. Previously reported values for Nafion 1050 EW carboxylate and 1150 EW sulfonate polymer have been added for comparison (1, 25, 33). The ability of the polymer to discriminate among the diffusion of sodium, cesium, chloride and iodide ions is seen for all samples, and this increases with increasing equivalent weight. Permselectivity is low for the 680 and 760 equivalent weight polymers. This may be due to the high water content and to a highly aqueous pathways for diffusion. Cesium ion and the anions therefore may be partitioning in regions B and C in the course of diffusing through the polymer. As the equivalent weight increases diffusion through the interface is increased, which result in low values of diffusion coefficients due to the tortuous nature of this path.

Another interesting aspect of the results is to compare the ratio of Na^+ to Cs^+ diffusion coefficients in the 1050 EW Nafion carboxylate, 1150 EW Nafion sulfonate, 960 EW Dow sulfonate and 1290 EW Dow sulfonate polymers. The Na^+ to Cs^+ self diffusion coefficient ratio in water is 0.65. The ratio from the reported values for the 1050 EW carboxylate polymer is 1.65, which implies that the diffusion of the cesium ion in the carboxylate is relatively aqueous-like, and that sodium and cesium ions are more or less diffusing through the same route. This is supported by the evidence that

Table IV.6

Ratio of Self Diffusion Coefficients in Perfluorinated Ionomer Membranes, 25° C				
Equivalent Weight	Na ⁺ /Cl ⁻	Na ⁺ /Cs ⁺	Na ⁺ /I ⁻	Cl ⁻ /I ⁻
680	1.19	1.46	3.08	2.10
760	0.95	1.58	1.92	2.04
960	3.11	5.11	27.3	8.76
1290	3.24	4.50	28.1	8.66
*1150 Nafion Sulfonate	1.93	5.55	9.53	4.92
*1050 Nafion Carboxylate	7.03	1.65	55.5	7.90

*Adapted from references (1, 25, 33)

the hydrogen bond strength of water associated with the ion clusters in the carboxylate membrane is 92% compared to the hydrogen bond strength in ordinary water, while that in the 1200 EW sulfonate polymer is 62% (24, 25). This together with the diffusion studies of Na^+ and Cs^+ show that the carboxylate is more phase-separated. Thus one would expect that the ratio of Na^+ to Cs^+ self diffusion coefficient in the 1200 EW sulfonate polymer which is less phase separated compared to the carboxylate will be more than 1.65. The measured ratio from previous studies is 5.55, which means that diffusion of Cs^+ ions in the 1200 EW sulfonate is mainly along the interfacial region of the polymer. The ratio of self diffusion coefficient of Na^+ to Cs^+ for the 960 and 1290 equivalent weight polymers are less compared to the 1200 EW Nafion sulfonate. This implies that the extent of phase separation in the 960 and 1290 equivalent weight polymers may be slightly higher than in the 1200 EW Nafion sulfonate, and that phase separation in the Dow PFSI'S may be increasing with equivalent weight.

Another feature of Table IV.6 that is interesting is the ratio of self diffusion coefficients of Cl^- to I^- , for the 960 EW and 1290 EW Dow sulfonate polymers and the Nafion polymers. It is inferred that as crystallinity is increased, iodide ion tends to interact with the polymer, which reduces its self diffusion coefficient, compared to the self diffusion coefficient of chloride ion. The ratios of self diffusion coefficients of Cl^- to I^- , for the 960 EW and 1290 EW Dow sulfonate polymers, are slightly higher than the value reported for the 1050 EW Nafion carboxylate polymer. However the value of the 1150 EW Nafion sulfonate polymer is very low compared to the 960 EW and 1290 EW Dow sulfonate polymers and the 1050 EW Nafion carboxylate polymer. Fujimura and coworkers have reported that the carboxylate version of Nafion is more crystalline than the sulfonate (16, 30). Also Moore and Martin have shown that the Dow PFSI'S with the same ratio of TFE to functional monomer are more crystalline than the Nafion analogs. Hence it may be concluded that this feature of iodide ion interacting with the interface

increases with crystallinity.

Listed in Table IV.7 are the activation energies of diffusion calculated from the tangents of the Arrhenius plot at 25° C. The activation energies of sodium, cesium, chloride and iodide ions in the Dow PFSI'S are all similar and solution-like. Further the activation energies of cesium, chloride and iodide ions are less than previously reported values for Nafion 1150 sulfonate (1, 23, 25). High activation energies of anions in Nafion polymers are said to be due to some anions following dead end pathways and others being attracted to cations that are present in a relatively low dielectric medium. The relatively low values of activation energies of cesium ion and the anions for the Dow PFSI'S suggest that in the Dow PFSI'S there might be fewer isolated pockets of aqueous regions not available for diffusion. The Dow PFSI'S having a shorter side chain, might have less polymer material in the interface as compared to Nafion, as a result the volume elements between clusters may be more aqueous-like and more available for diffusion. Also the activation energies of cesium, chloride and iodide ions are slightly higher for the 960 EW and 1290 EW Dow sulfonate polymers compared to the 760 EW and 680 EW Dow sulfonate polymers. As the water content increases, there is the possibility that region C may be contributing to the transport of the anions and cesium ions. This feature will depend on the water content of the polymer. Since the 960 EW and 1290 EW sulfonate polymers have less water content, the concentration of exchange sites are high. Thus the exclusion of the anions occurs to a greater extent than in the 680 EW and 760 EW sulfonate polymers. Also due to the large size and low hydration energy of cesium ion it tend to diffuse mainly in region B of the three region diffusional model. As a result the activation energies in the high equivalent weight polymers are slightly higher than those in low equivalent weight polymers.

The diffusion results of sodium and chloride ions for the quenched 960 EW Dow sulfonate polymer is shown in Figure IV.7. Although the self diffusion coefficient

for the sodium ion decreased slightly compared with that for the virgin 960 EW sulfonate polymer, permselectivity increased. This result is unexpected since permselectivity was found to increase with equivalent weight. Also after quenching the polymer the ion exchange capacity changed which makes it very difficult to make a direct comparison with the virgin polymer.

Table IV.7

Activation Energy of Diffusion in Dow
Perfluorosulfonate Ionomer Membranes

Equivalent Weight	Activation Energy, KJ mol ⁻¹			
	Na ⁺	Cs ⁺	Cl ⁻	I ⁻
680	18.7	21.0	18.2	17.3
760	18.2	22.2	18.9	18.3
960	17.8	18.2	23.4	24.7
1290	20.9	26.9	21.0	20.1

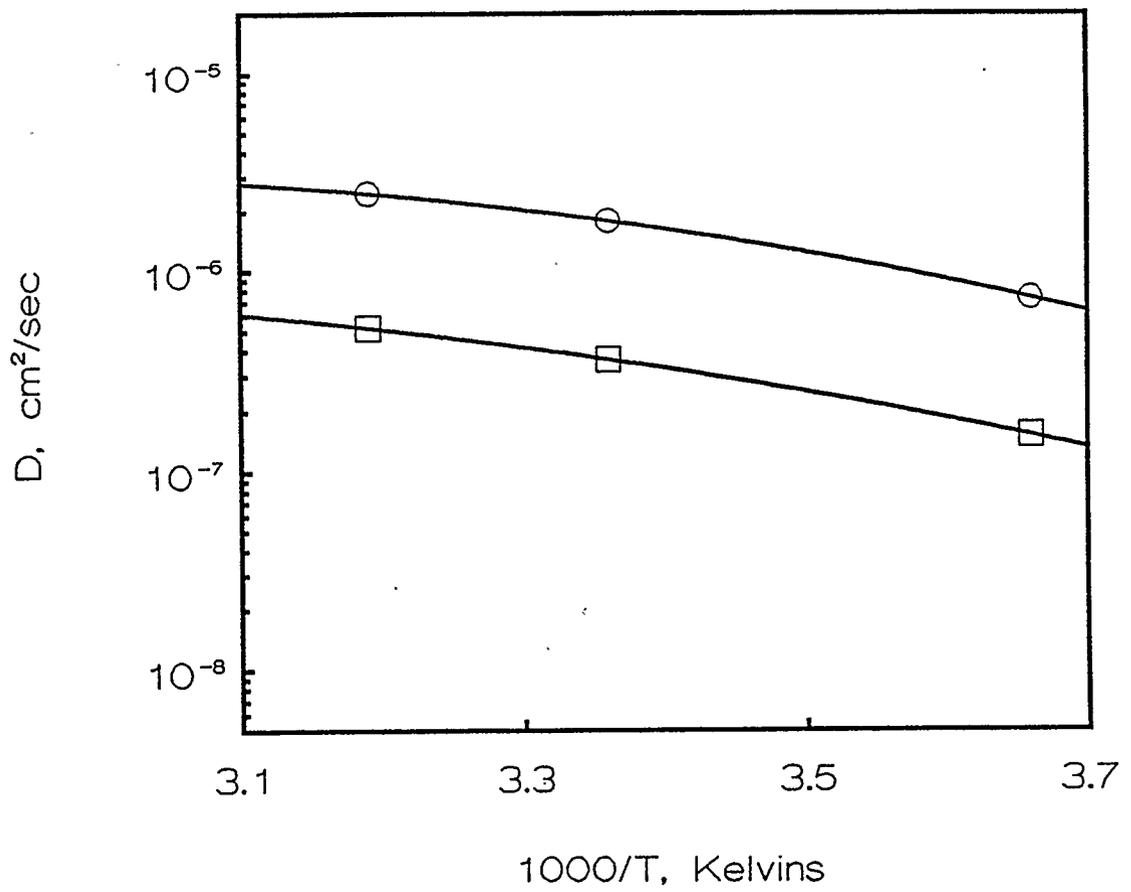


Figure IV.7

Arrhenius plots of ionic diffusion in quenched 960 EW perfluorinated sulfonate membrane. \circ Na^+ \square Cl^-

IV.5 Infrared Studies

Infrared studies have been used to study perfluorinated ionomer membranes at the molecular level (24, 25, 36-39). These have included studies of backbone vibrations and the characteristics of sorbed water molecules. Using the mid-infrared region, Yeager and coworkers measured the extent of hydrogen bonding of sorbed water in the 1050 EW carboxylate and the 1200 EW sulfonate Nafion membranes (25). Values of 92% and 62% of the intermolecular hydrogen bond strength in liquid water were obtained for the 1050 EW carboxylate membrane and 1200 EW sulfonate membrane respectively. The membranes contained 90% and 95% deuterated water respectively, to reduce the absorbance of the OH group in HDO in the membranes to a measurable value. Falk has also used the mid-infrared region to estimate the amount of non-hydrogen bonded water in a 1200 EW Nafion sulfonate membrane (24). The membrane was first dried over sulfuric acid. As a result the water content was substantially lower, 9% by weight as compared to a fully hydrated Nafion which has a water content of about 20% by weight.

In the present study, however, the near infrared region was used to measure the extent of hydrogen bonding, and the proportion of non-hydrogen bonded water in the Dow PFSI'S and some Nafion membranes. The near infrared region was used for the following reasons. Firstly, the combination overtone bands have lower molar absorptivities compared with the fundamental region; therefore no special pretreatment procedure was used in order to reduce the absorbance of water in the membranes to scale. Secondly, the frequency shift of the peak center due to hydrogen bonding is greater in the near infrared region than in the mid-infrared region. Thirdly, whereas the molar absorptivity of the fundamental band through hydrogen bonding is variable by a factor of 20 or more, the molar absorptivity of hydrogen bonded water and non-hydrogen bonded water in the near infrared region are about the same (40). (For example in Falk's

work the amount of non-hydrogen bonded water was calculated to be roughly 25% by assuming that the molar absorptivity of hydrogen bonded water was four times higher than that of non-hydrogen bonded water in the membranes.) In this study the molar absorptivity for the hydrogen bond water and the non-hydrogen bonded water are taken to be the same.

Listed in Table IV.8 and IV.9 are the results for perfluorinated ionomer membranes in the sodium and cesium ion forms. The frequencies of absorption and the area percent of the three component peaks represent three distinct forms of water found in the membranes. These are type I, non-hydrogen bonded water; type II, weakly hydrogen bonded water; and type III, strongly hydrogen bonded water such as found in water clusters and in ice. The assignment of these types is made in order to compare our results to Luck's work on pure water and water in cellulose acetate (53). The relative proportion of the peak areas in pure water as found by Luck are 13%, 42% and 45% respectively. Also shown in Figures IV.8 to IV.22 are the original spectra and the computer fitted curves. A description of how the computer fitted curves were obtained is given in section II.4. Both two component and three component decomposed spectra are presented. The chi-square values for the two and three component fits are listed in Table IV.10. The lower the chi-square value the better the fit. Fitting the curve with three peak areas gives a much better fit than fitting it with two peaks. Even though a three parameter fit is expected to generate some improvement, the degree of the change is seen as significant.

In order to understand these results a brief review of the mode of attachment of water molecules to the exchange sites and counter-ions in a nearly dry membrane is given. In a nearly dry membrane, water molecules may either be inserted between a cation and an anion as in Figure 23 (a) or they may be attached to a cation and an anion without disrupting the cation anion bond as in Fig 23 (b) and (c). At a very high water

Table IV.8
Near-Infrared Absorbance of Water in
Perfluorinated Ionomer Membranes, Na⁺-form, 25° C

Equivalent Weight	Component Peak Position, cm ⁻¹ (Area Percent)		
	Non H-Bonded (Type I)	H-Bonded (Type II)	H-Bonded (Type III)
Water	5297 (13)	5200 (42)	5038 (45)
680	5288 (7)	5224 (41)	5132 (52)
760	5289 (13)	5235 (34)	5154 (52)
960	5293 (12)	5237 (35)	5153 (53)
1290	5294 (13)	5242 (30)	5159 (57)
1580	5294 (13)	5242 (31)	5158 (56)
Nafion 1100 Sulfonate	5291 (13)	5235 (34)	5153 (53)
Nafion 1050 Carboxylate	5293 (11)	5224 (32)	5114 (57)
Nafion 1250 Carboxylate	5295 (12)	5227 (31)	5115 (57)
*Dried Nafion 1100 Sulfonate	5297 (32)	5200 (68)	-

*Approximate, reference 26

Table IV.9

Near-Infrared Absorbance of Water in
Perfluorinated Ionomer Membranes, Cs⁺-form, 25° C

Equivalent Weight	Component Peak Position, cm ⁻¹ (Area Percent)		
	Non H-Bonded (Type I)	H-Bonded (Type II)	H-Bonded (Type III)
Water	5297 (13)	5200 (42)	5038 (45)
680	5292 (2)	5215 (44)	5116 (54)
760	5293 (7)	5226 (49)	5143 (44)
960	5295 (8)	5227 (49)	5143 (43)
1290	5296 (7)	5226 (46)	5145 (47)
Nafion 1100 Sulfonate	5296 (3)	5221 (51)	5131 (46)
Nafion 1050 Carboxylate	5289 (9)	5225 (34)	5117 (57)
Nafion 1250 Carboxylate	5291 (13)	5219 (35)	5106 (52)

Table IV.10

Chi-Square Values for Two and Three Peak Fits

Equivalent Weight	Two Peak Fit		Three Peak Fit	
	Na ⁺	Cs ⁺	Na ⁺	Cs ⁺
680	0.010	0.0050	0.0020	0.0016
760	0.0051	0.0019	0.00049	0.00024
960	0.0067	0.0014	0.00061	0.00028
1290	0.0066	0.00075	0.00079	0.00030
1580	0.0079	—	0.00081	—
Nafion 1100 Sulfonate	0.010	0.013	0.00091	0.010
Nafion 1050 Carboxylate	0.010	0.023	0.0013	0.0024
Nafion 1250 Carboxylate	0.0067	0.0033	0.00040	0.00024

content the insertion mode prevails, whereas at very low water content, all the three possible situations can occur depending on the water content of the membrane and the relative affinities of cations and anions in the membrane (51).

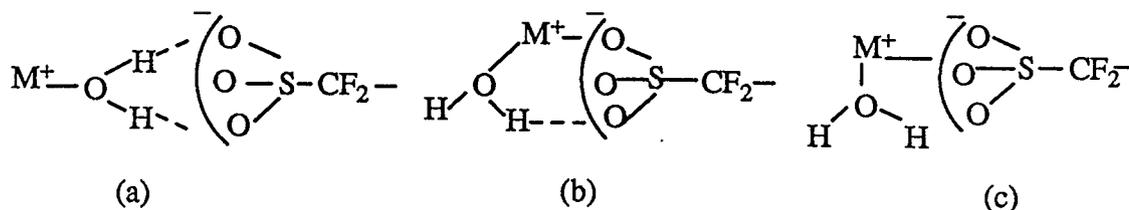


Figure 23

Modes of attachment of water to cations and anions in Nafion membrane
(from reference 51)

Barnes used the near infrared region to study water in the 1100 EW sulfonate Nafion polymer. In contrast to the present study he found two forms of water, non-hydrogen bonded type I at 5297 cm^{-1} and hydrogen bonded type II water at 5200 cm^{-1} . The difference in the types of water between the two studies is due to the difference in the pretreatment procedure. In contrast to the pretreatment procedure given in Chapter III this present study, Barnes heated the membranes at $120\text{ }^{\circ}\text{C}$ for 70 hours (26). In the study of Barnes, the mole ratio of water to sulfonate site in the membrane was 1.2 or less. Thus virtually all the water in these dried membranes would be expected to either be water of hydration for the exchange sites or counter ions, or possibly be isolated water molecules which are not hydrogen bonded. Hence, when membranes of this type are dried from their equilibrium water contents, clustered water with the strongest hydrogen bonding desorbs first. This is also seen for cellulose acetate membranes, where the relative peak areas for the types I, II and III water are 19% : 45% : 36% at a relative humidity of 98% and 33% : 50% : 17% at a relative humidity of 11% (53). Further, the peak centers for the types II and III water are shifted to lower

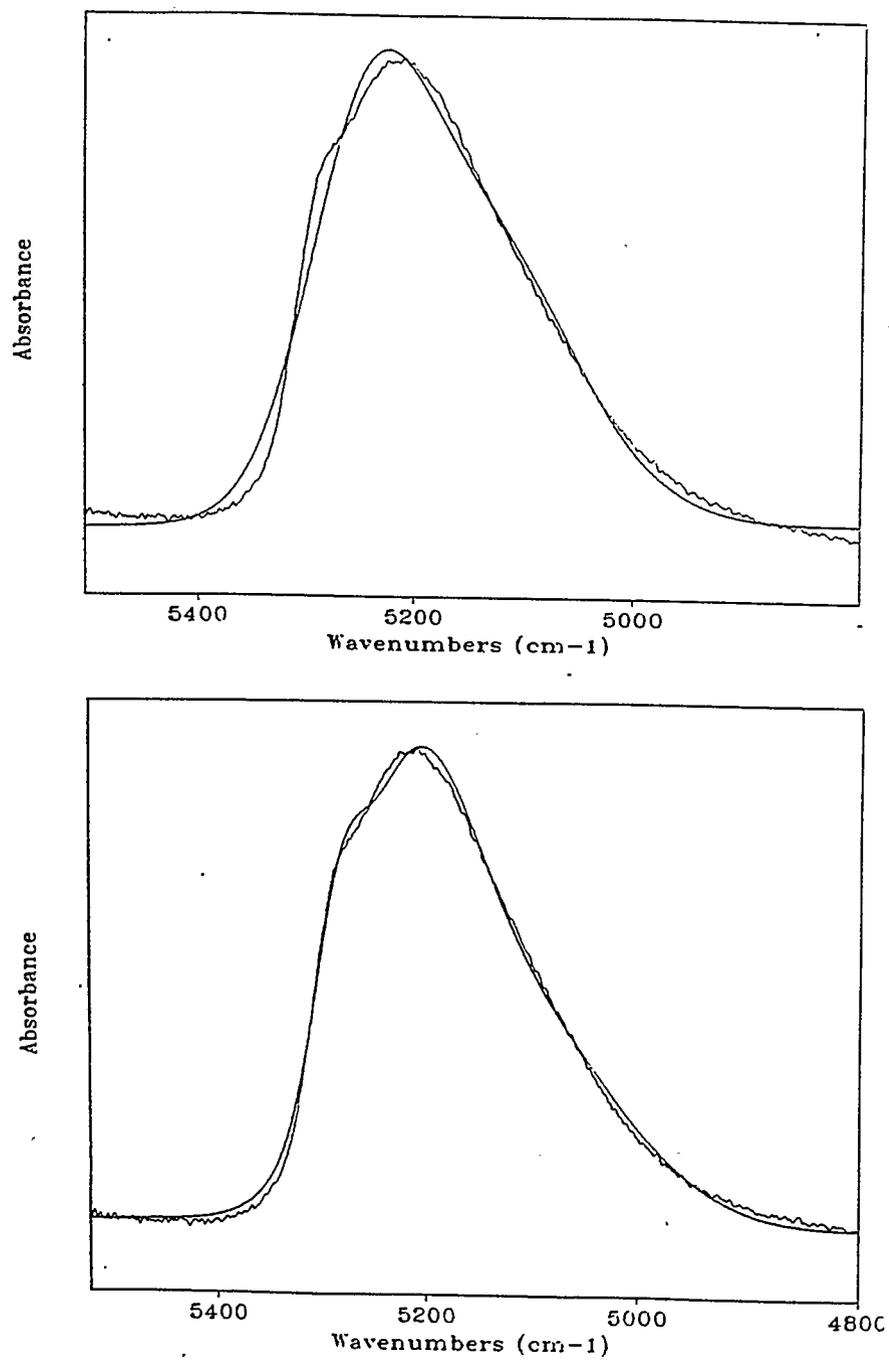


Figure IV.8

Dow 680 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

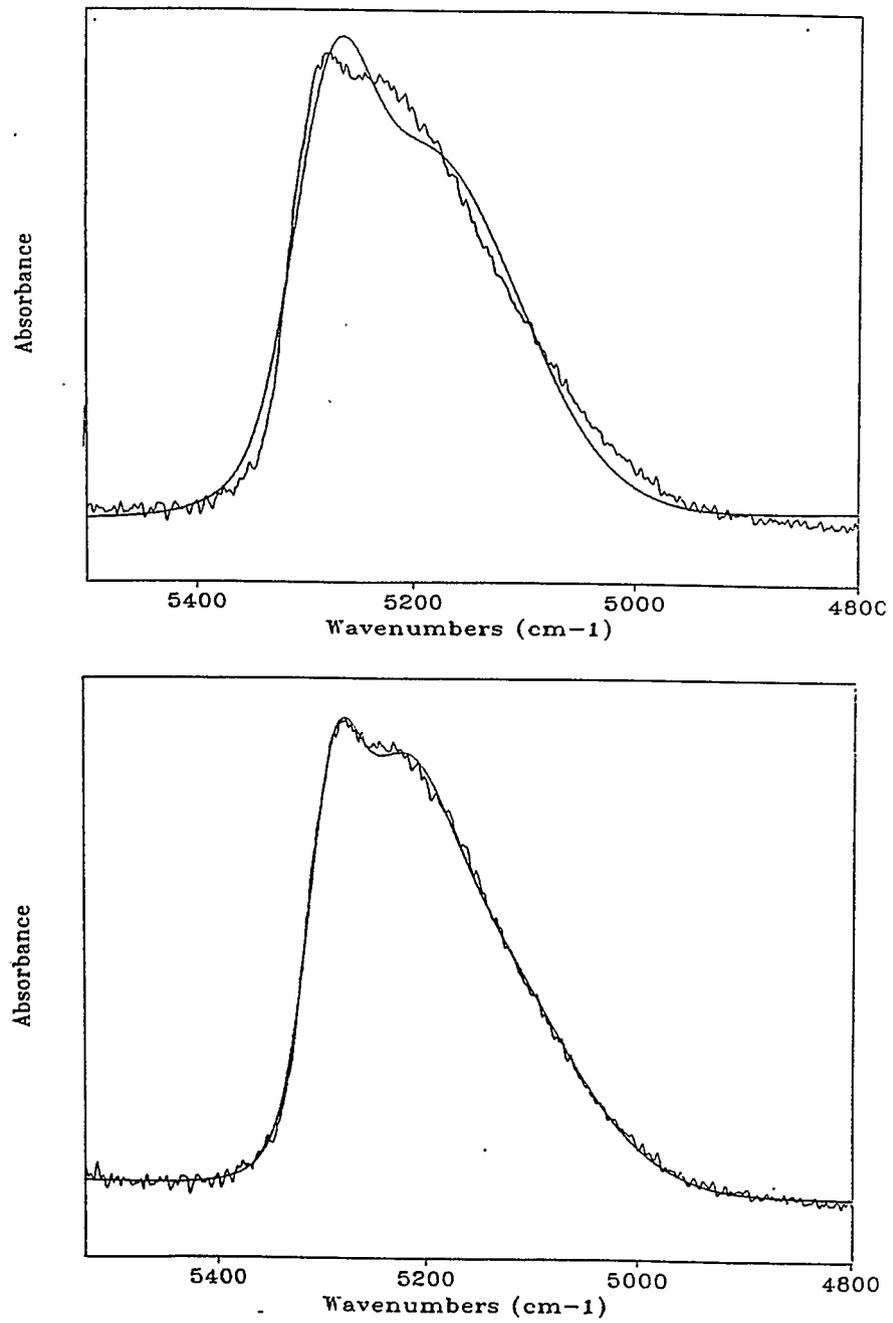


Figure IV.9

Dow 760 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

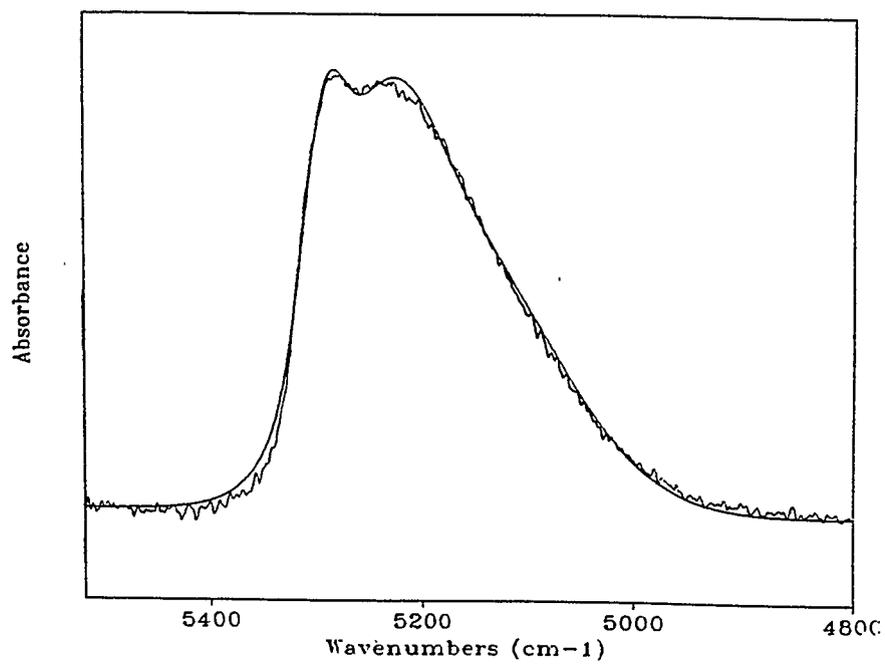
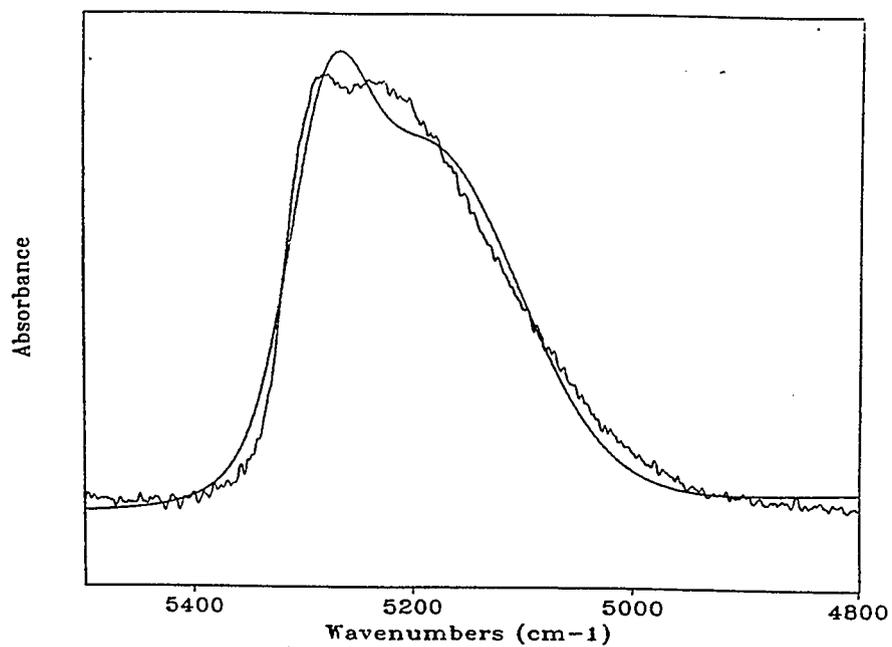


Figure IV.10

Dow 960 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

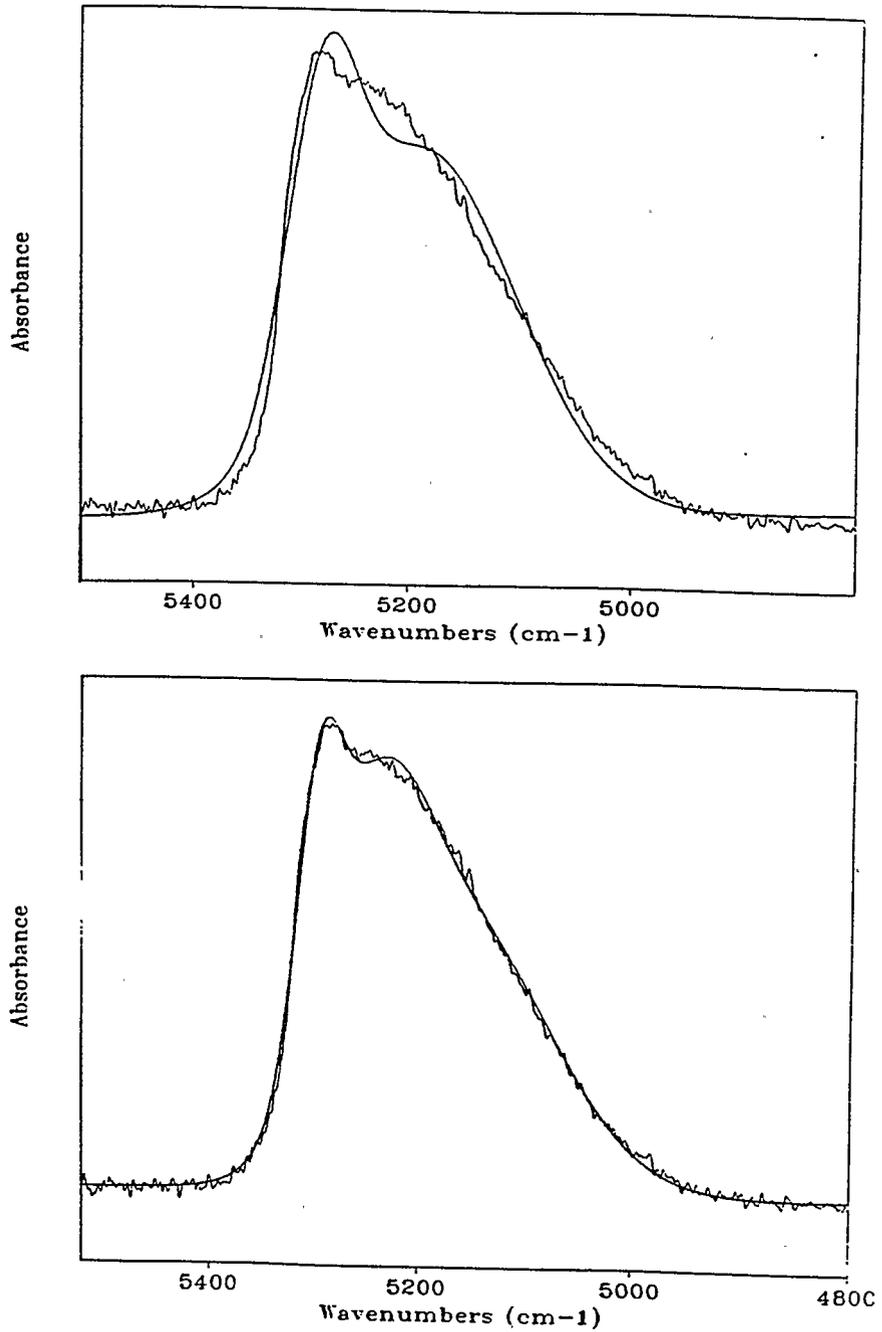


Figure IV.11

Dow 1290 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

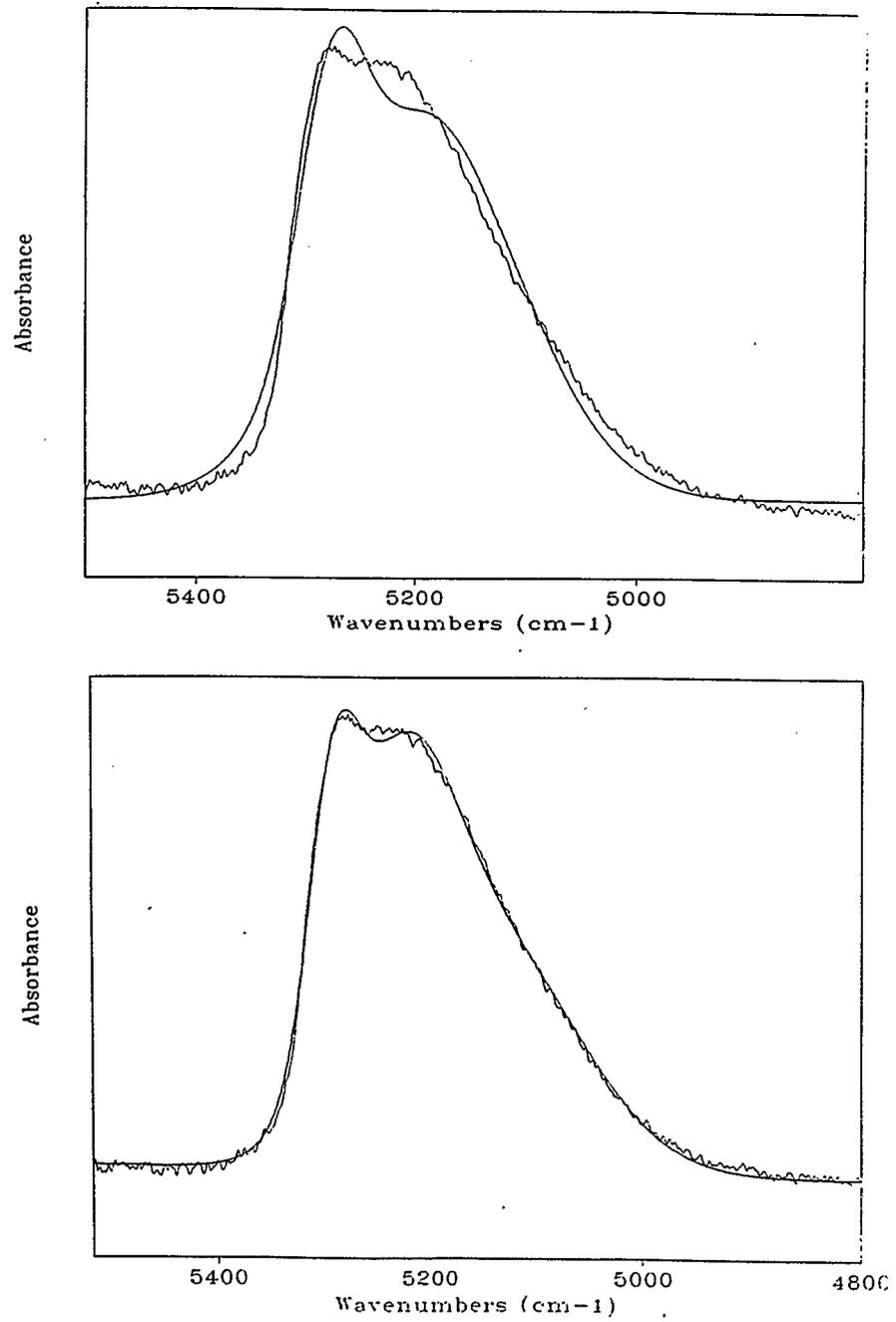


Figure IV.12

Nafion 1100 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

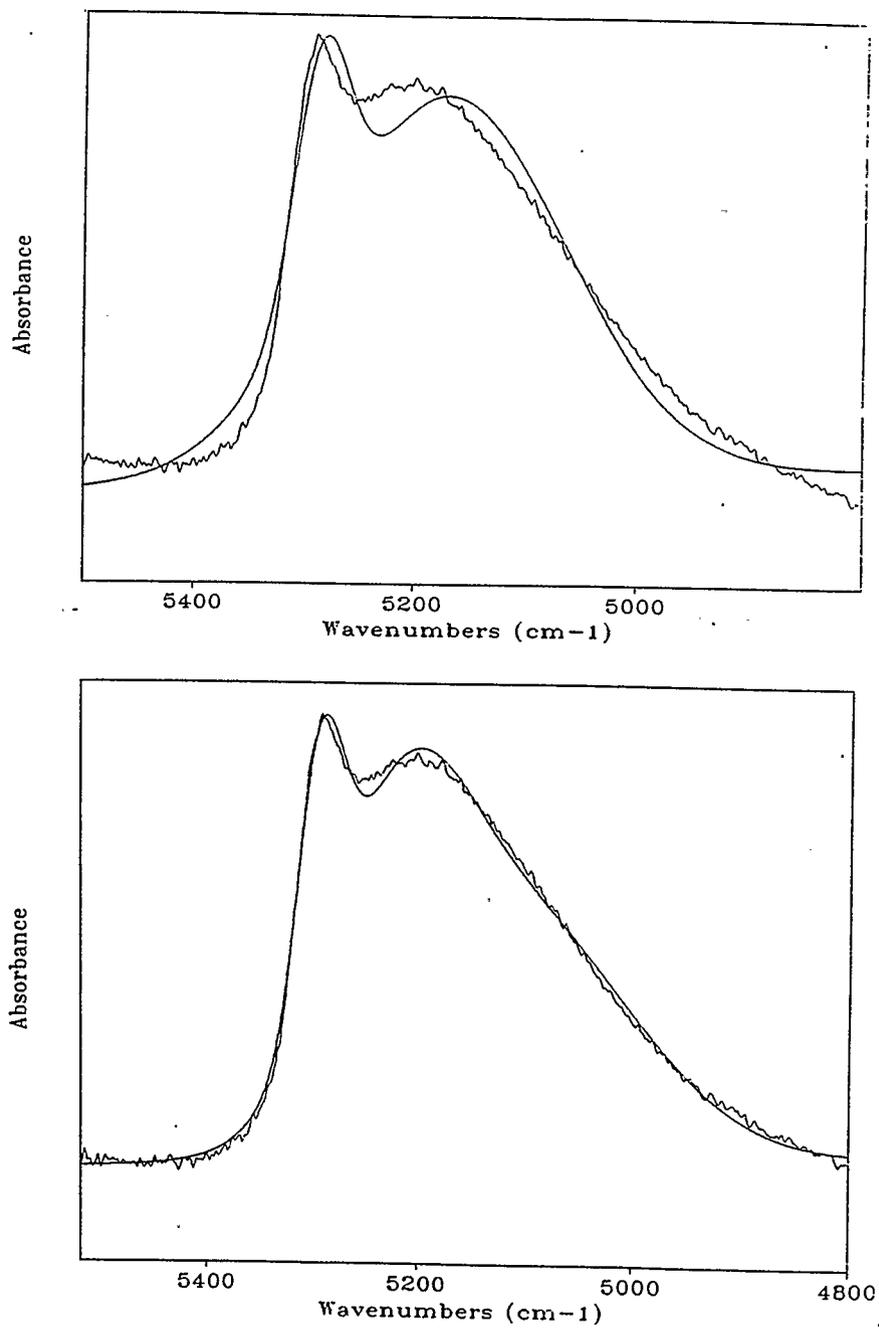


Figure IV.13

Nafion 1050 EW perfluorocarboxylate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

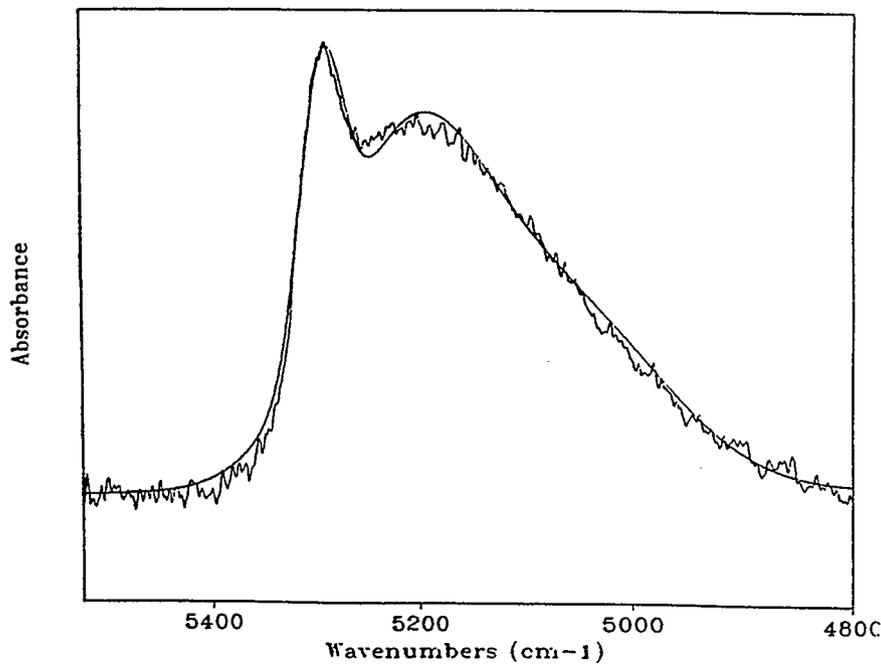
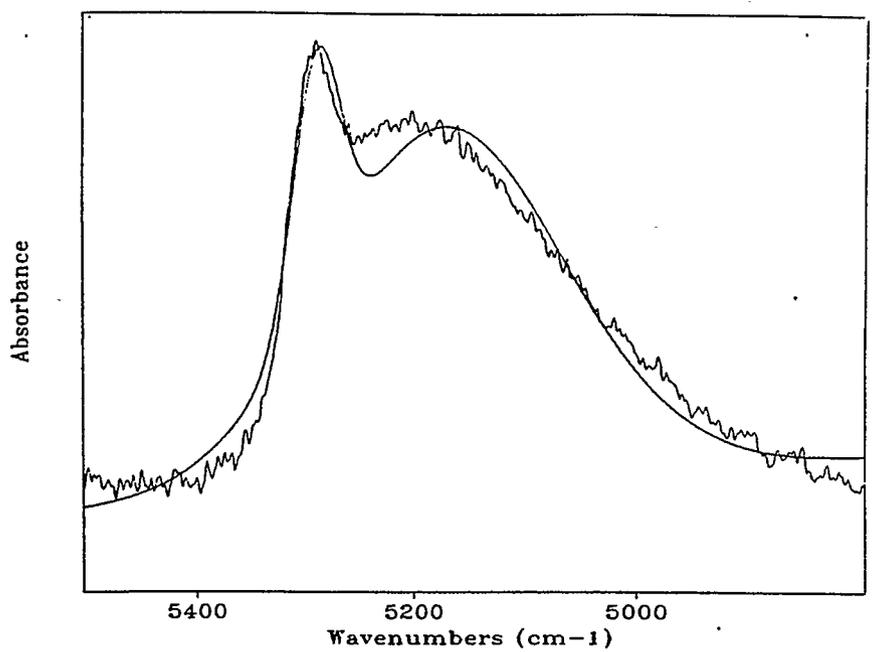


Figure IV.14

Nafion 1250 EW perfluorocarboxylate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

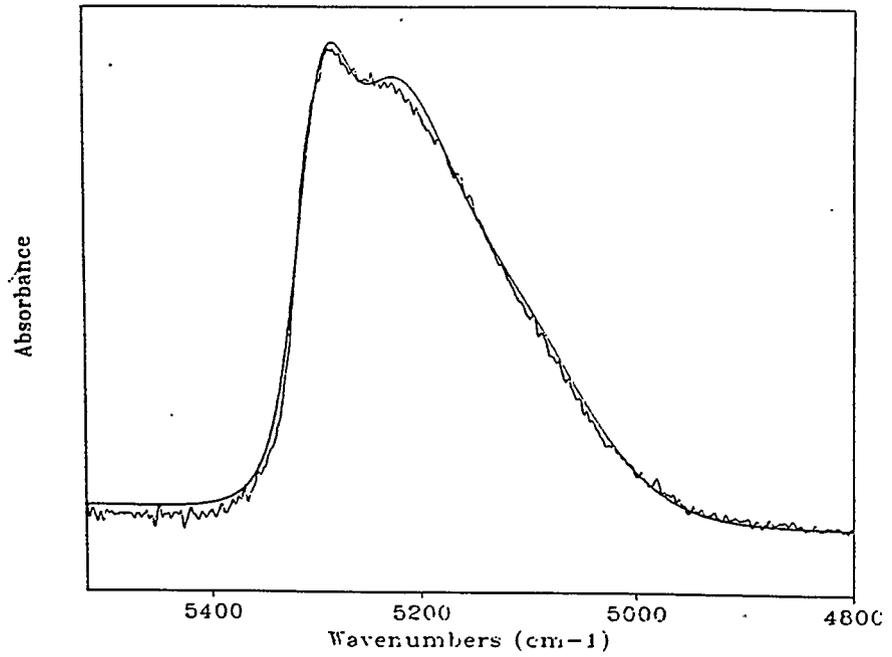
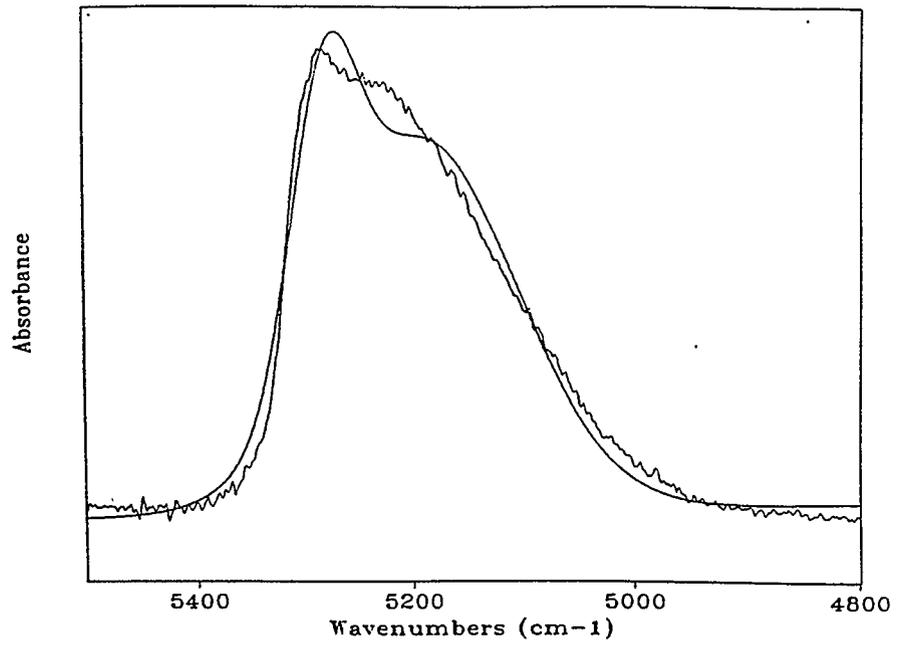


Figure IV.15

Dow 1580 EW perfluorosulfonate ionomer membrane in sodium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

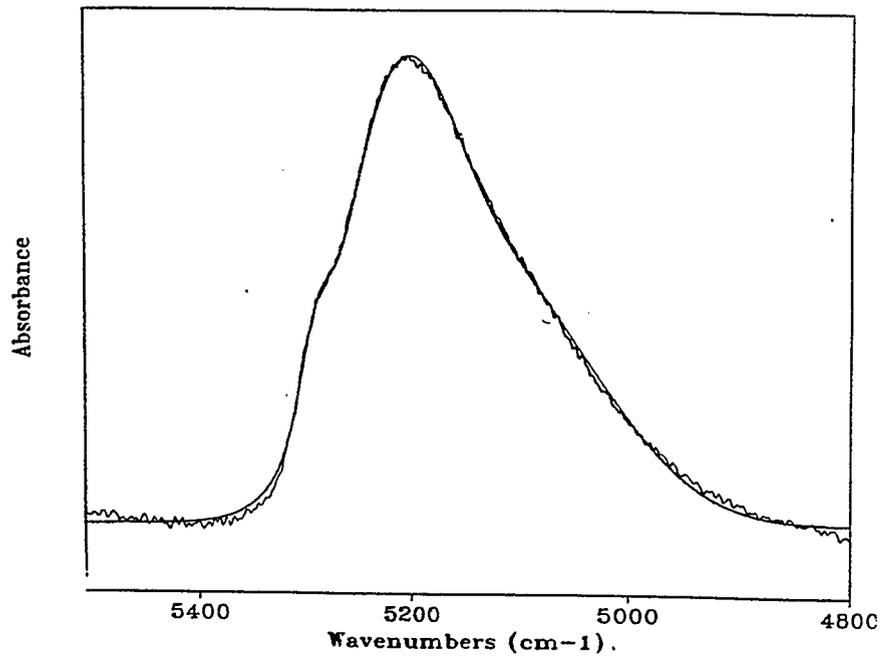
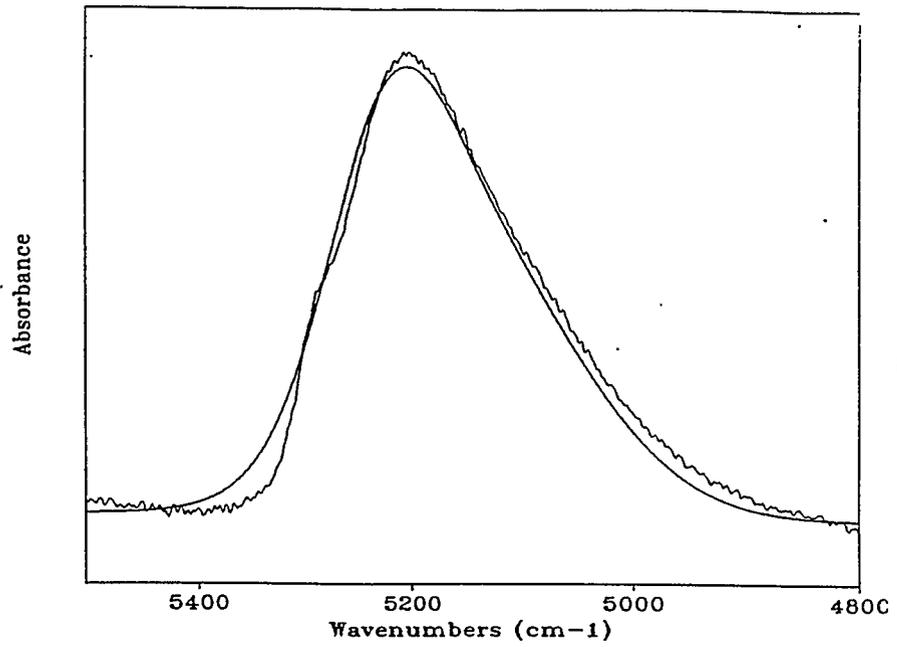


Figure IV.16

Dow 680 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

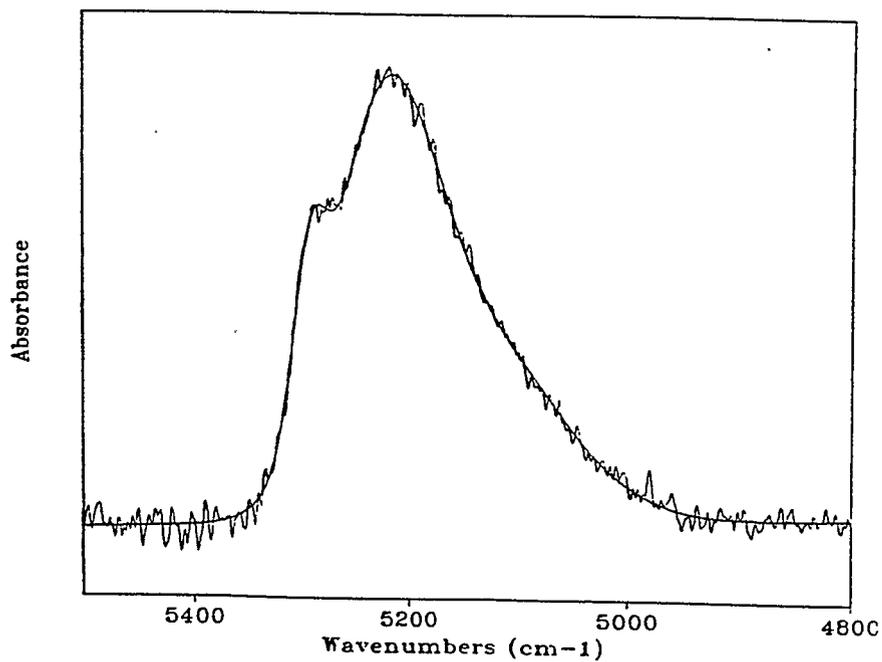
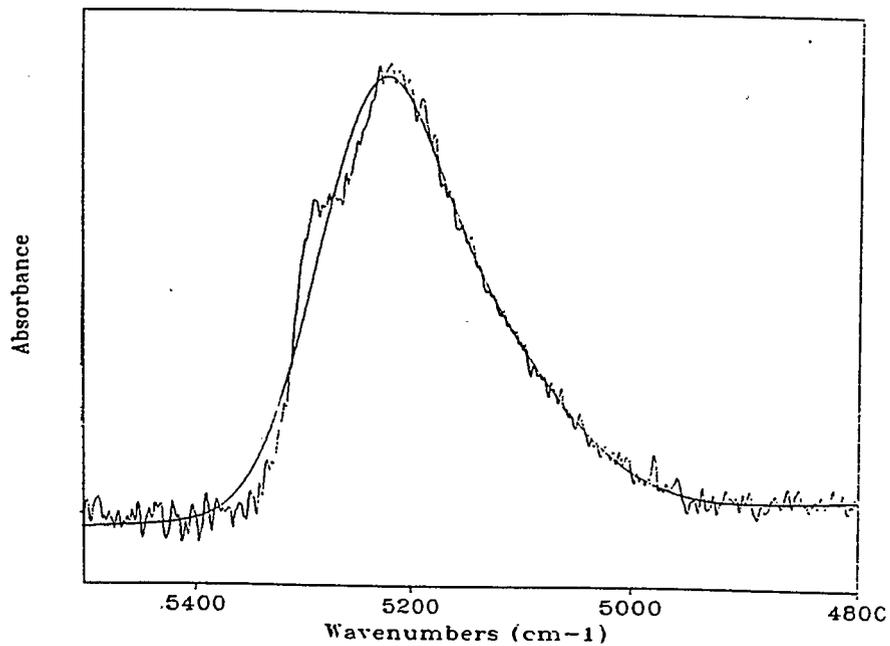


Figure IV.17

Dow 760 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

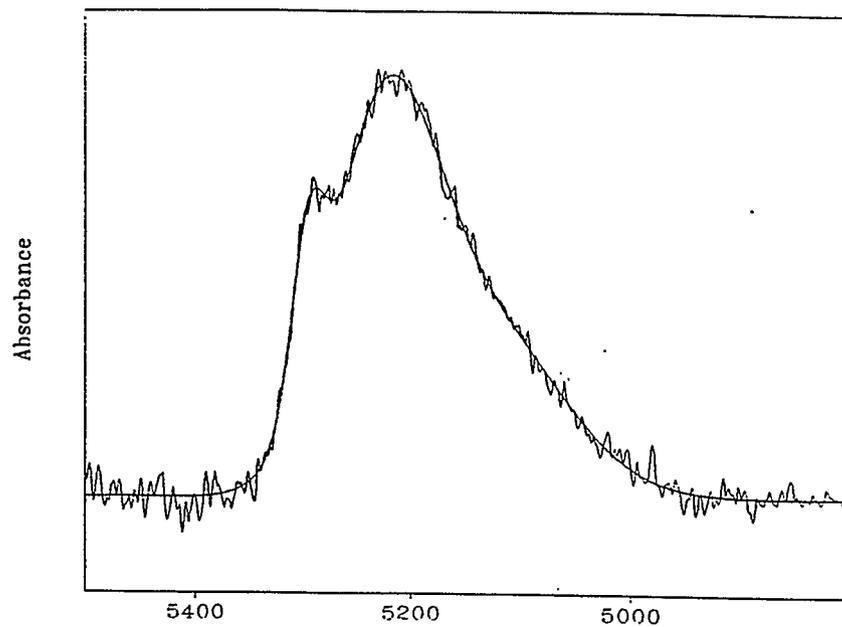
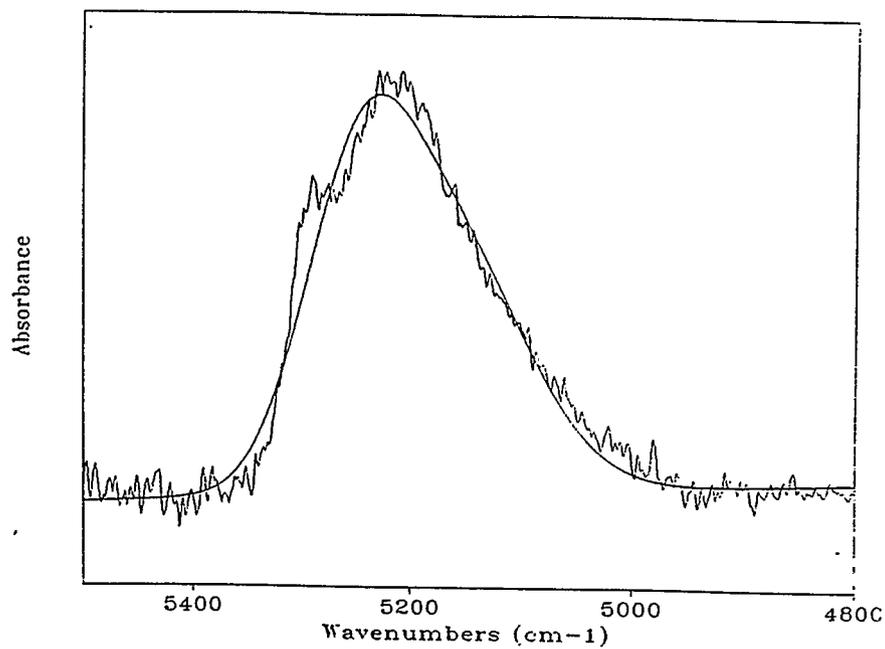


Figure IV.18

Dow 960 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

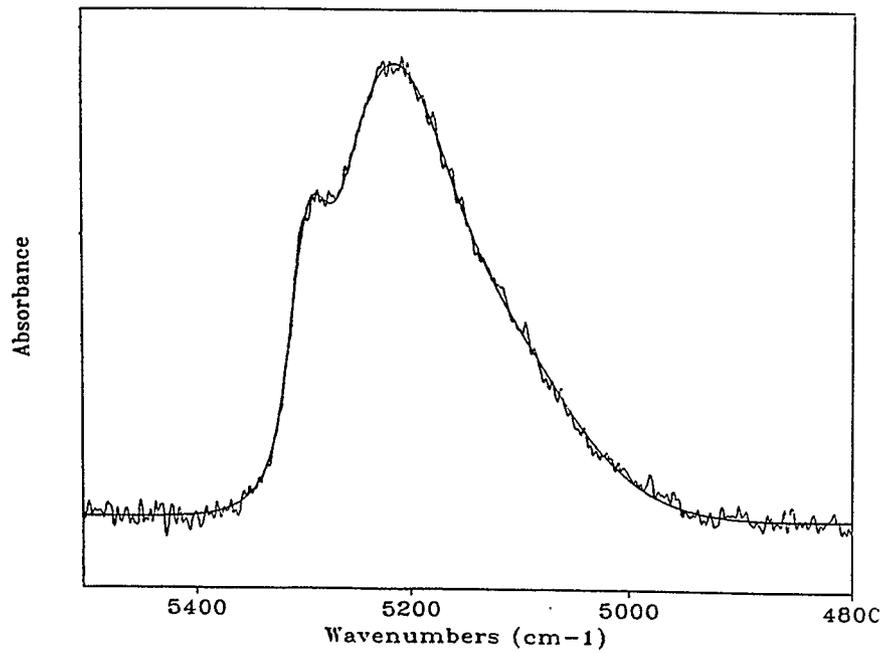
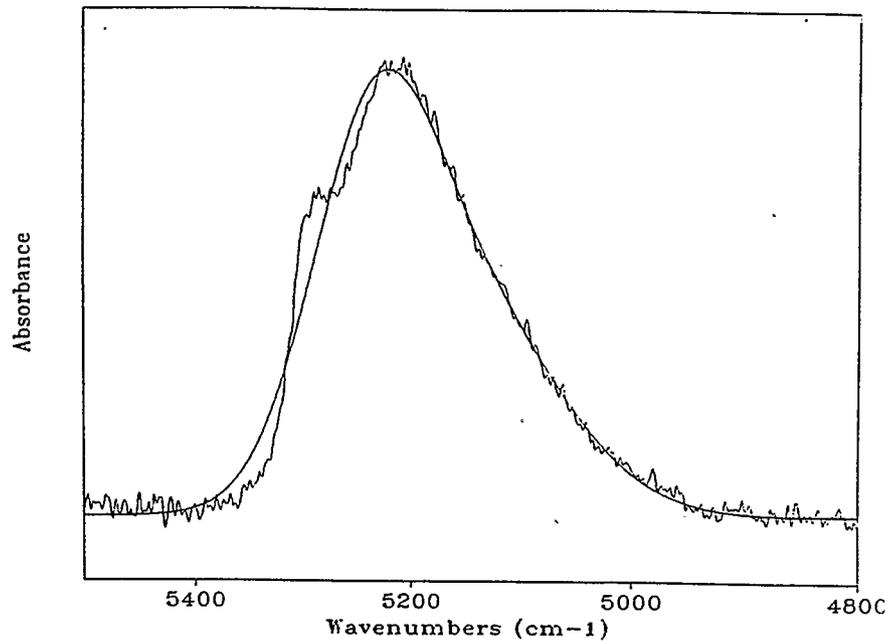


Figure IV.19

Dow 1290 EW perfluorosulfonate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

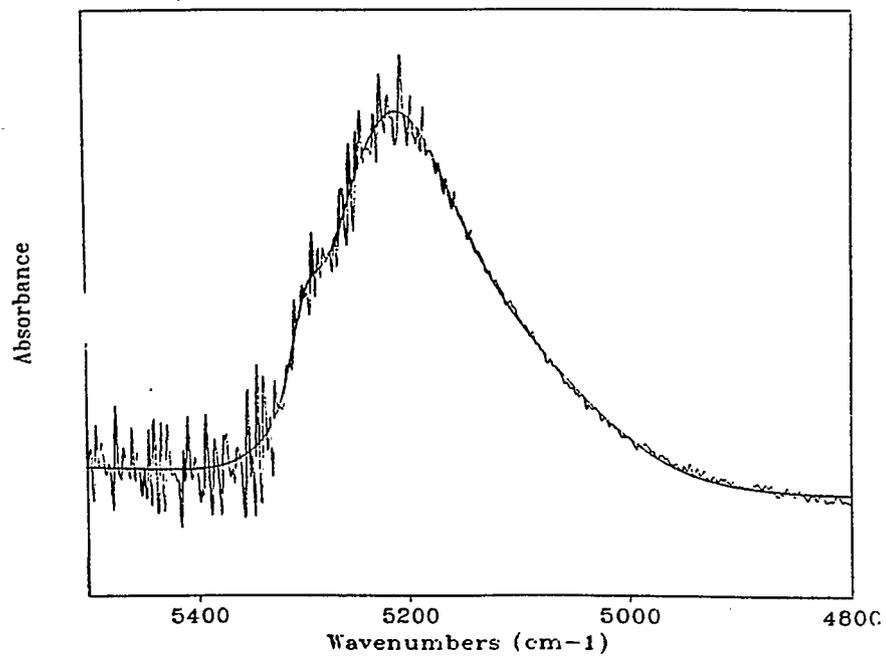
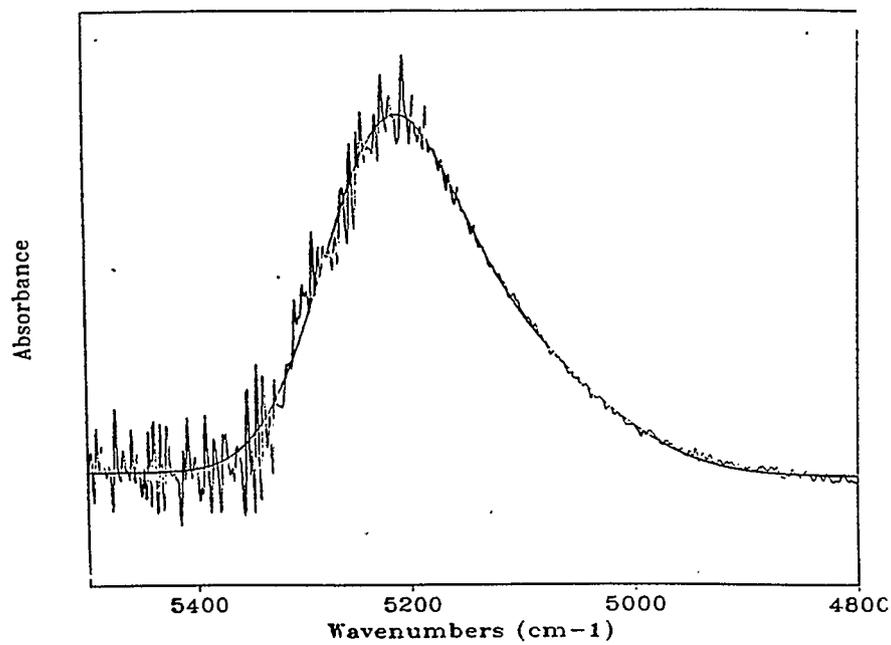


Figure IV.20

Nafion 1100 perfluorosulfonate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

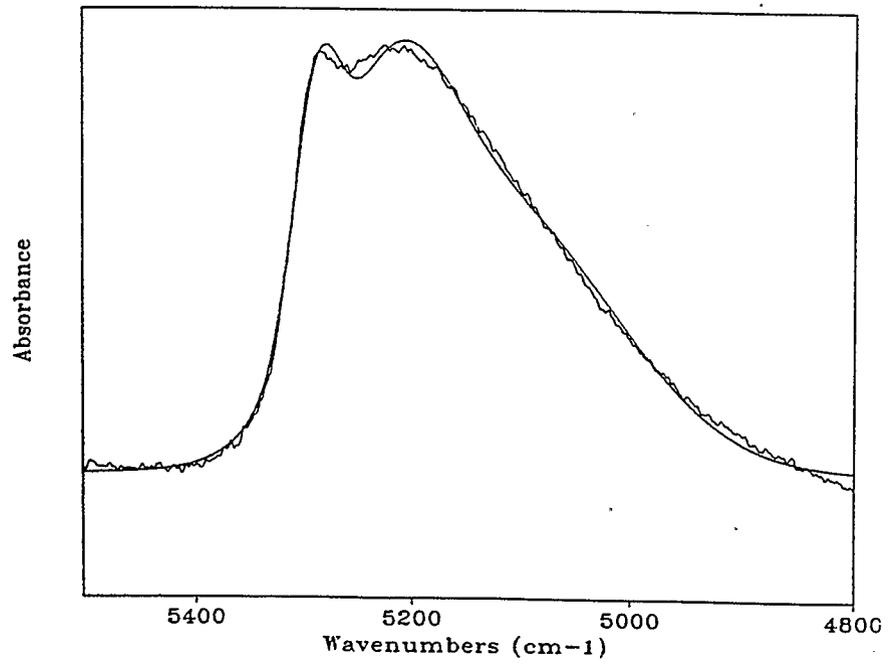
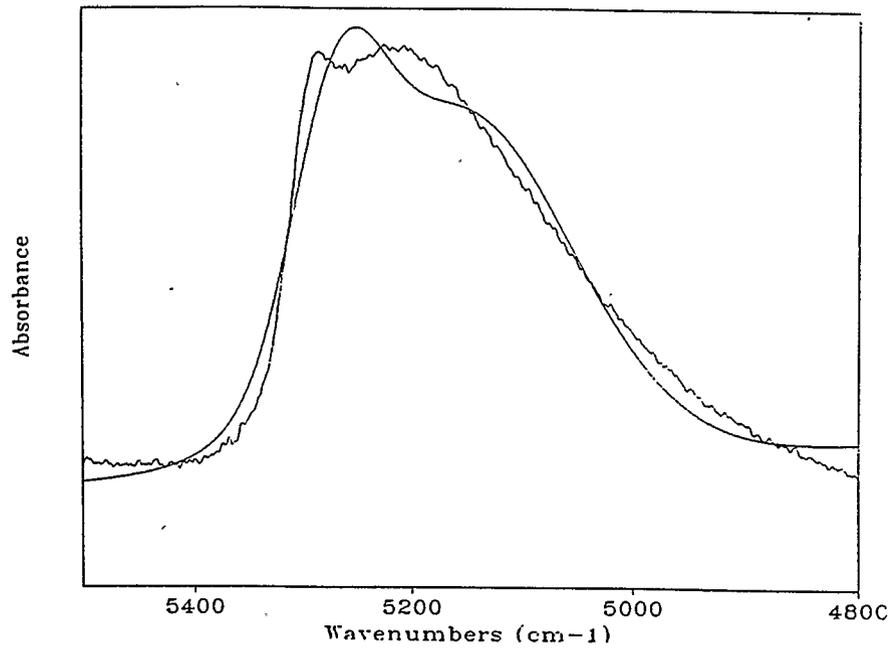


Figure IV.21

Nafion 1050 perfluorocarboxylate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

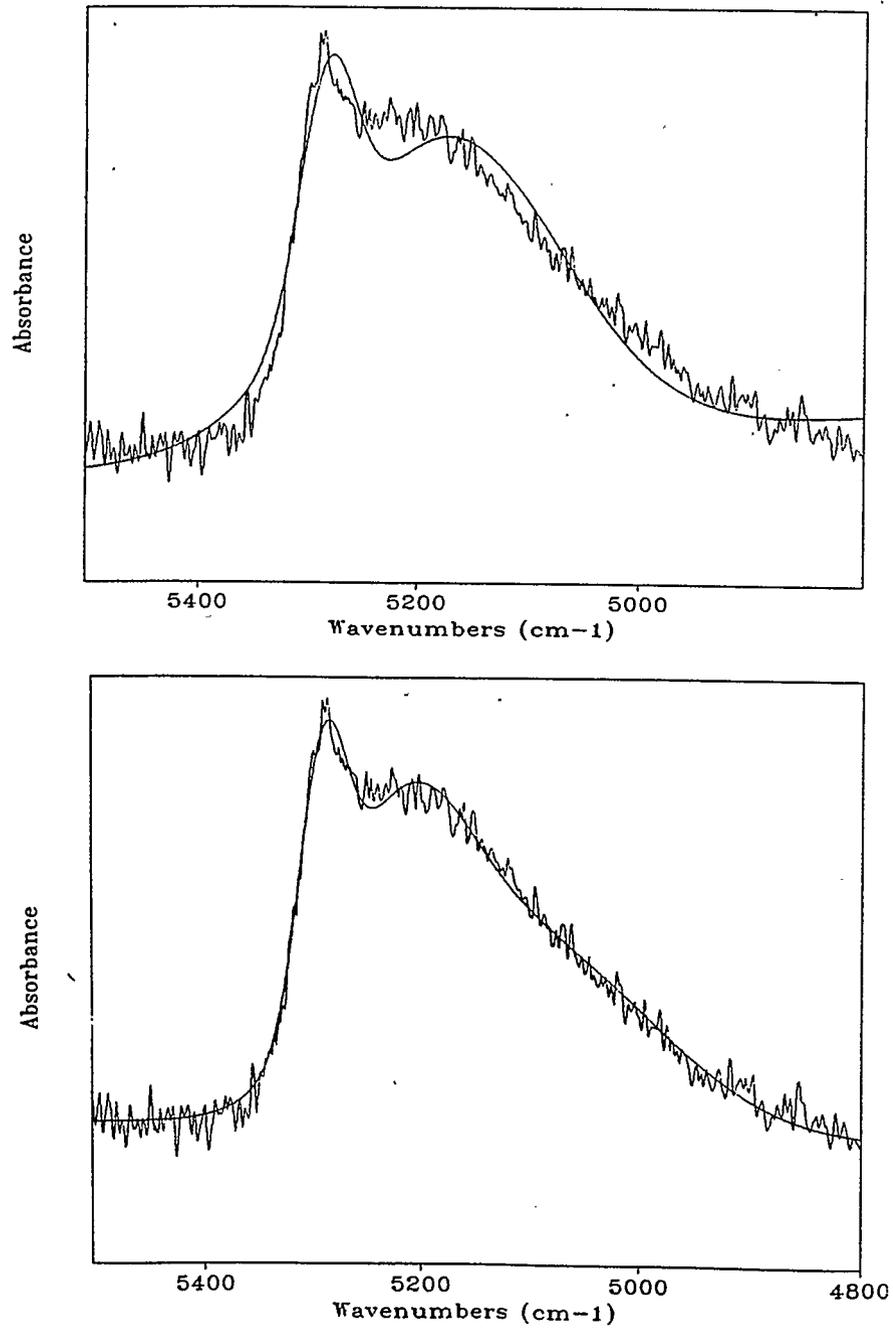


Figure IV.22

Nafion 1250 perfluorocarboxylate ionomer membrane in cesium ion form, near-infrared water stretch computer fit. Above, two component peak and below, three component peak.

frequencies for the spectra run at a relative humidity of 98% compared to that run at a relative humidity of 11%, showing a greater hydrogen bond strength at high water contents.

It is therefore necessary to distinguish the two forms of hydrogen bonding in the membranes when the water content is varied. Firstly at very low water content the hydrogen bonding is by ionic hydration with water molecules bound to the oxygen atom of the anion. As shown in Figure 23 (a) the cation polarizes the oxygen atom of the water of hydration. As a result the hydrogen bond strength of the hydrogen atom of these water molecules to exchange site oxygen is increased for cations with high charge density (51). The hydrogen bond strength can exceed that of water-water hydrogen bonding for high charge density polyvalent cations, not for univalent cations (51). The hydrogen bond strength due to clustering of water molecules can be discussed in terms of the angle dependence of hydrogen bonds. In linear hydrogen bonds the bond angle between the axes of OH and the lone pair electron orbital is 0° . The strength of the linear hydrogen bonds (type III) correlate with the bond angle, the larger the bond angle the weaker the hydrogen bond. The bond angle between the OH and the lone pair electron orbital for the type II hydrogen bond is about 110° , according to Luck (53).

In discussing the results of the present study, one can assume that the absorbance due to the water of hydration would be located in the type II hydrogen bonded water at low water contents. This is because at very low water contents; the ratio of water to sulfonate site is 1.2 or less, Barnes found only the higher two component bands. The contribution of hydrogen bonding as a result of water-water interaction is increased as the water content increases, in assigning both types II and III hydrogen bonded water. This is because the hydrogen bond strength of this type of interaction is higher than that due to polarization (52).

For now we will concentrate on Table IV.8. The 680 EW sulfonate Dow

polymer is distinctly different from the other Dow polymers. The strength of hydrogen bonding relative to that in liquid water is higher than in the other Dow PFSI'S. This is due to the fact that the polymer is highly swollen. It contains 53 moles of water per mole of exchange site. Since it contains relatively large amounts of exchange sites and side chains it swells extensively, and also the side chains disrupt crystallinity of the backbone to a larger extent compared to the other equivalent weights. As a result the cluster size deduced from Table I.1 is relatively large compared to those of the other Dow PFSI'S. Since it contains a relatively large amount of water, the hydrogen bonding due to the water of hydration will be relatively small compared to the hydrogen bonding due to the water-water interaction. As a consequence the strength of hydrogen bonding as deduced from the peak center for the types II and III water are relatively high compared to the other Dow PFSI'S and Nafion polymers except the carboxylates. The hydrogen bond strength of water in the 680 EW Dow polymer is weaker than in pure water. This suggests that even for this highly swollen membrane, there is significant disruption of clustered water, so that the average frequency is high.

The contribution of hydrogen bonding due to clustering of water molecules in types II and III water decreases as the water content of the membrane decreases. Since the hydrogen bonding of the hydration water molecules is weaker than that of clustered water molecules, the overall hydrogen bond strength of the membrane, deduced from the types II and III water will decrease as the equivalent weight is increased. The high values of the wave numbers for the type III water suggests a greater disruption of clustered water molecules compared to that of the 680 EW Dow sulfonate polymer.

An interesting aspect of these results is that the peak centers of the types II and III water for the carboxylates are at relatively low wave numbers compared to the Dow PFSI'S and the Nafion sulfonate. This can be attributed to a greater micro-phase

separation for the carboxylates. Evidence for this is supported by diffusion studies done by Yeager and coworkers (25). The ratio of Na^+ to Cs^+ ion diffusion coefficients in dilute solution is 0.65. The ratios adapted from previous studies are 1.65 and 5.55 for 1050 Nafion carboxylate and 1200 EW Nafion sulfonate polymers respectively. This shows that the mechanism of diffusion in the 1050 EW carboxylate membrane and in water are about the same, and that diffusion of sodium and cesium ions in the membrane are aqueous-like whereas they are not for the 1200 EW sulfonate polymer. Thus the fact that the hydrogen bond strength in the carboxylates is higher compared to the other membranes suggests the aqueous-like nature of the water molecules in the clusters for the 1050 carboxylate polymer.

Also interesting is the results of the near infrared study of water in the membranes in the cesium ion form. Firstly the peak centers for both the type II and III water are shifted to smaller wave numbers compared to the peak centers for the membranes in sodium ion form. Secondly the relative amount of type I water for the membranes in the cesium ion form is relatively low compared to that for the sodium ion form. With reference to the three state model of Quezado, Kwak, and Falk, they concluded that for Nafion sulfonate membranes with low water contents the mode of attachment as shown in Figure 23 (a) is preferred for cesium ion while that of Figure 23 (b) and 23 (c) is preferred for sodium ion (24). Whether a counter-ion preferred one mode or another was found to be related to the match of Lewis acidity of the cation and basicity of the ion exchange site. Thus, for either small cations of high charge or large cations of low charge (like Cs^+) the mismatch generates insertion of water molecules between the cation and the exchange site. Sodium ion was found to favor water attachment to the outside of the ion pairs in the membrane. Thus, there was found to be a greater percentage of non-hydrogen bonded OH groups for sodium ion than for cesium ion in these dried membranes.

Also interesting in Tables IV.8 and IV.9 are the proportion of non-hydrogen bonded water of the membranes in the sodium and cesium ion forms. The proportion of non-hydrogen bonded water of the membranes in the cesium ion form is distinctly less as compared to those in sodium ion form. However, the interpretation must be different from that of Falk's due to the much higher water contents here. Ion pairs of any type are not expected in these cases, as has been confirmed by nmr and infrared spectroscopic studies of fully hydrated Nafion sulfonate membranes (54). Thus the difference between the proportion of non-hydrogen bonded water found for the cesium ion forms and sodium ion forms should be assigned to a different cause. In the near infrared study of different cationic forms of Nafion 1100 EW perfluorosulfonate membrane, Barnes found that the relative proportion of non-hydrogen bonded water to hydrogen bonded water decreased as the cationic size is increased (26). His results are listed in Table IV.11. His results cannot be directly compared with the results of the present study due to the fact that membrane pretreatments in the two studies are different; however an indirect comparison can be made. In Barnes work membranes were heated at 120°C in vacuum for 70 hours, a procedure which reduces the amount of hydrogen bonded water in the clusters and therefore increases the amount of non-hydrogen bonded water in the membrane (24). Thus the fact that the percentage peak area for the non-hydrogen bonded water is larger in Barnes work as compared to this study is due to the different pretreatment procedures used. Since Barnes heated the membranes at 120° C, the amount of hydrogen bonded water was reduced. As a consequence the amount of non-hydrogen bonded water was increased. Barnes explains why the proportion of type I water decreases as cationic size increases by using hydration energy arguments. Large hydrophobic cations interact with the interface, thus displacing the type I water from the interface. Cesium ion, with a relatively low hydration energy as compared to sodium ion will prefer to be at the interface, thus displacing the non-hydrogen bonded water from

the interface. As a result there is a reduction in the fraction of the non-hydrogen bonded OH groups for sorbed water molecules. That is, the lower fraction of non-hydrogen bonded OH groups may reflect an altered interfacial zone, because of the increased influence of the cation. While rather speculative, this does correlate with the lower diffusion coefficients seen for cesium ion compared to sodium ion with sulfonate membranes.

The average hydrogen bond strengths of types II and III water are higher for cesium ion forms compared to the sodium ion forms, as reflected in lower frequencies. This suggests that the identity of the cation can affect water structure in the ionic clusters. Such variables as the shape and size of the cluster, as well as the amount of fluorocarbon material which intrudes into the cluster interior, might be responsible for the differences seen. Interestingly, the extent of change of the character of water appears to be less influenced by the cation for the carboxylate membranes, which correlates with the observation that the cesium and sodium ion diffusion coefficients remain similar with these materials.

A very interesting aspect of these results is the amount of water present as type I in the sodium and cesium ion forms for the 1050 EW and 1250 EW perfluorocarboxylates. The amount of type I water is the same for both sodium and cesium ion forms in the 1250 EW carboxylate polymer. The implication is that cesium ion in this membrane is not located in the interface and may be present in the clusters within the limits of electrical neutrality, since its presence in the interface results in a decrease in the proportion of type I water (26). The proportion of type I water in the 1050 EW perfluorocarboxylate polymer in the cesium ion form is very close to the relative amount when the membrane is in the sodium ion form. This also implies that the proportion of cesium ions in the clusters is high for the carboxylates compared to the sulfonates. This inference is supported by the ratio of self diffusion coefficient of Na^+

Table IV.11

Near-Infrared Absorbance of Water in 1100 EW Sulfonate
Polymer of Different Cationic Forms

Cation	Area% Non H-Bonded	Area%H-bonded
Na ⁺	32	68
K ⁺	30	70
Rb ⁺	25	75
Cs ⁺	21	79

Adapted from reference 26

to Cs^+ in the 1050 EW carboxylate and 1200 EW sulfonate membranes. The ratio in water is 0.65 whereas it is 1.65 in the carboxylate and 5.55 in the sulfonate. The ratio is therefore aqueous-like for the carboxylate, and that in the carboxylate, cesium ion might be somehow diffusing through the clusters as compared to the sulfonates where cesium ion mainly diffuses along the interface. The difference is due to the high phase separation in the carboxylates.

CHAPTER V

Conclusions

The results obtained in this study indicate that perfluorinated ionomer membranes obey the Donnan equilibrium. An exception was the iodide ion which showed sorption characteristics which are not Donnan-like. It is believed that the iodide ion interacts with the polymer in a way to increase its molal concentration in the polymer phase as equivalent weight is increased. This may have an implication for the diffusional trend of iodide ion in the polymer.

The diffusion trends of ions in perfluorinated ionomers are quite different from that of conventional ion exchange polymers. Whereas in cation exchange polymers, anions have larger diffusion coefficients than cations with activation energies that are solution-like, the reverse is found for diffusion in perfluorinated ionomer membranes. Sodium ion has a larger diffusion coefficient with an activation energy that is solution-like. The diffusion coefficients of iodide and chloride ions are smaller than that of sodium ion. Their activation energies of diffusion are also higher. These trends have been explained with a three region diffusional model that is consistent with all the spectroscopic results reported so far.

For the Dow PFSI'S a similar trend to Nafion was observed for the 960 EW and 1290 EW sulfonate polymers. The spread of diffusion coefficients among the ions increases with increasing equivalent weight. Permselectivity seems to be lost for the lower equivalent weights i.e. 680 and 760. The diffusion coefficient of sodium ion is greater in the Dow PFSI'S than in both 1150 sulfonate and 1050 carboxylate Nafion. This is supported by values of the efficiency parameters for the 1200 EW Nafion sulfonate and the 960 EW Dow sulfonate polymers. Although both polymers have about the same volume fraction of water, the efficiency parameter of the 960 EW Dow polymer is about twice as large as that for the 1290 EW Nafion sulfonate. The Dow

PFSI'S, however, leak chloride ions, but the overall permselectivity in terms of the ratio of Na^+ to Cl^- diffusion coefficients is better in the 960 EW and 1290 EW Dow PFSI'S than in 1150 EW Nafion sulfonate polymer but worse compared to the 1050 EW Nafion carboxylate. This comparison was made on the basis of the same ratio of TFE units to functional monomer. The Dow ionomers are therefore between the sulfonate and the carboxylate versions of Nafion in regard to being superselective.

The efficiency parameter for the 960 EW Dow polymer in cesium ion form is about twice as large as that for the 1200 EW Nafion polymer, although both polymers have about the same volume fraction of water. This implies that the extent of phase separation for the Dow polymer is relatively high. Also, the ratio of self diffusion coefficients of Na^+ to Cs^+ ions indicates that phase separation in the Dow PFSI'S may be a little better than in 1200 EW Nafion sulfonate. This comparison is made on the basis of the same TFE/functional monomer. The ratios for the 960 EW and 1290 EW sulfonate polymers are closer to the solution value than for the 1200 Nafion sulfonate polymer. The ratio for the 1050 EW Nafion carboxylate is closer to the solution value compared to all the other membranes mentioned above. Thus in this respect the Dow PFSI'S are between the sulfonate and the carboxylate versions of Nafion.

Although chloride ion and the iodide ion diffuses mainly through the interface which is the region between the ionic clusters and the fluorocarbon backbone, their diffusion trends may be different in the Dow PFSI'S. Depending on the water content of the membrane, the ionic size and the hydration energy of the anion, the anion will partition between the ionic cluster and the interface. Iodide ion with a larger size and a more polarizable nature will interact with the interface to a greater extent than chloride ion. This claim is supported by the sorption characteristics of iodide ion on the Dow PFSI'S and the large ratios of Cl^- to I^- diffusion coefficients in the 1290 EW, 960 EW Dow sulfonate polymers and 1050 EW Nafion carboxylate polymer. Thus there is

the need to look at the local environments of the perfluorinated ionomer membranes on the molecular scale by using fluorescence studies. Large hydrophobic ions could be used as fluorescence probes in furthering our understanding of the transport of ions in the perfluorinated ionomer membranes.

Near infrared studies revealed that the proportion of non-hydrogen bonded to hydrogen bonded water in the membranes are different for the membrane in sodium and cesium ion forms. Also, the average hydrogen bond strength of the types II and III are higher for cesium ion forms compared to sodium ion forms. Interestingly, the hydrogen bond strength of the types II and III water are about the same for the carboxylates in both cesium and sodium ion forms which correlates with the observation that sodium and cesium ion diffusion coefficients are similar with the carboxylates. The proportion of non-hydrogen bonded water is lower in the cesium ion form, which implies that cesium ion might be displacing the non-hydrogen bonded water from the interface (26). This supports the argument that the diffusion of cesium ion in less phase separated perfluorinated ionomer membranes is through the interface.

The ratio of non-hydrogen bonded water to the hydrogen bonded water in the 1250 carboxylate is the same in both sodium and cesium ion forms. This implies that cesium ion may diffuse through the same path as sodium ion in the 1250 carboxylate membrane. Further the ratio was nearly the same for the 1050 carboxylate membrane. The ratio of self diffusion coefficient of Na^+ to Cs^+ is solution-like. The values in solution and in the membranes are 0.65 and 1.65 respectively. The corresponding value in the sulfonate membrane is 5.55. This shows that the carboxylate is more phase separated than the sulfonates. Also the ratios for the 1290 EW and 960 EW are between the sulfonate and the carboxylate versions of Nafion.

To conclude, the Dow PFSI'S are between the carboxylates and the sulfonate versions of Nafion in terms of permselectivity, being slightly better than the sulfonate

version of Nafion.

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