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Thesis

# Nitric Acid Dehydration Using Perfluoro Carboxylate and Mixed Sulfonate/Carboxylate Membranes

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Richard L. Ames

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# NITRIC ACID DEHYDRATION USING PERFLUORO CARBOXYLATE AND MIXED SULFONATE/CARBOXYLATE MEMBRANES

by
Richard L. Ames

# STATEMENT OF WORK COMPLETION

TO: Graduate School

By affixing signatures below, the advisor(s) and thesis committee members affirm that Richard Louis Ames has successfully completed all of the requirements for the degree Doctor of Philosophy
Chemical Engineering including:
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1. Completion of all courses listed on the Admission to Candidacy form dated 9-16-03 with a cumulative grade point average of 3.73 .

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Committee Member/Date

9/16/04
Committee Member/Date

Committee Member/Date

Reviewed by:
Department Head/Division Director
9/20/04
Date

A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirement for the degree of Doctor of Philosophy (Chemical Engineering).

Golden, Colorado

Date_______________

Signed:_________________________
Richard L. Ames

Approved:______________________
Dr. J. Douglas Way
Thesis Advisor

Golden, Colorado

Date_______________

_________________________
Dr. James F. Ely
Professor and Head
Department of Chemical Engineering
And Petroleum Refining

# ABSTRACT

Perfluoro ionomer membranes are tetrafluoro ethylene-based materials with micro-heterogeneous structures consisting of a hydrophobic polymer backbone and a hydrophilic side-chain cluster region. Due to the ionomer cluster morphology, these films exhibit unique transport properties. Recent investigations with perfluoro sulfonate and perfluoro sulfonate/carboxylate composite polymers have demonstrated their value in the dehydration of nitric acid and they show potential as an alternative to conventional, energy intensive unit operations in the concentration of acid feeds.[1,2,3] As a result, investigations were conducted to determine the feasibility of using pure perfluoro carboxylate and mixed perfluoro sulfonate/carboxylate films for the dehydration of nitric acid because of the speculation of improved water selectivity of the carboxylate pendant chain.

During the first phase of these investigations the effort was focused on generating a thin, solution cast perfluoro carboxylate ionomer film, to evaluate the general, chemical and physical characteristics of the polymer, and to assess the material's aqueous transport performance (flux and nitrate separation efficiencies) in pervaporation and high-pressure environments. Results demonstrated that generating robust solution-cast films was difficult yet a number of membranes survived high trans-membrane pressures up to 700 psig. General characterization of the solution cast product showed reduced ion exchange capacities when compared with thicker, "as received" perfluoro carboxylate and similar sulfonate films. Small angle x-ray scattering analysis results suggested that the solution cast carboxylate films contained a small fraction of sulfonate terminated side-chains. Aqueous transport experimentation showed that permeate fluxes for both pure water and nitric acid were approximately two orders of magnitude smaller for the carboxylate solution cast membranes when compared to their sulfonate counterparts of similar thickness (Nafion$^{TM}$ 111). Additionally, nitric acid separation efficiencies ($\alpha$) were approximately one order of magnitude higher for the carboxylate solution cast films when compared to Nafion$^{TM}$ 111.

The second phase of our work included the generation of thin carboxylate films made by the chemical synthesis perfluoro sulfonate and mixed sulfonate/carboxylate polymers from a perfluoro sulfonyl fluoride precursor, the characterization of the newly generated material, and a study of the transport characteristics of these membranes. Transport studies consisted of the dehydration of nitric acid feeds by pervaportation. In addition, the initial hypothesis was expanded to include demonstration that trans-membrane flux and separation efficiencies are a function of the ratio between sulfonate and carboxylate terminated side chains of the perfluoro ionomer. Investigations demonstrated the ability to generate in-house films with varying sulfonate/carboxylate concentrations from commercially available perfluoro sulfonyl fluoride material, and showed that the converted films could be characterized using Fourier transform infrared (FTIR) and x-ray fluorescence (XRF) spectroscopy. Finally, the mixed films where subjected to nitric acid dehydration transport tests and a relationship was found to exist between sulfonate/carboxylate pendant chain ratio and both flux and water separation capability. In summary, experimental results confirmed that, when compared to Nafion 111™, the mixed film’s bulk fluxes decrease by approximately three orders of magnitude and the water separation factor increases by as much as two orders of magnitude as the carboxylate side-chain content was increased from 0 (pure sulfonate film) to 53 mole%, supporting the hypothesis given for this effort.

It was observed that the water selectivity improved for both the solution cast perfluoro carboxylate and mixed perfluoro sulfonate/carboxylate films when judged against similar perfluoro sulfonate materials. Of great benefit was that during the investigation a number of research tools were utilized including, but in no way limited to, basic chemical operations, procedure development and refinement, the use of a number of analytical systems (FTIR, XRF, thermal gravimetric analysis, nuclear magnetic resonance, etc.), data interpretation and analysis, and presentation and debate (defense) of results.

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# ACKNOWLEDGEMENTS

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# 1.0 INTRODUCTION

At the center of our investigation is the use of perfluoro carboxylate and mixed perfluoro carboxylate/sulfonate ionomer films to dehydrate nitric acid solutions. Previous investigations suggest the use of the carboxylate material for the dehydration of nitric acid and preliminary research demonstrated that the membranes offer high nitrate (or generally ionic) exclusion capabilities in aqueous environments.[1,2,3] The fundamental hypothesis for this effort was that water separation efficiencies for the carboxylate membranes are large in comparison to those for similar pure perfluoro sulfonate polymers. Early research also showed that mixed perfluoro carboxylate/sulfonate polymers could be generated from a sulfonyl fluoride precursor.[4] Our experimental effort successfully reproduced the polymer synthesis procedure, as well as a procedure used to solution cast pure carboxylate ionomer membranes, and made obvious that trans-membrane flux and water separation efficiencies were a function of the ratio between ionomer sulfonate and carboxylate terminated side chains.

Interest in perfluoro carboxylate ionomer membranes at the Los Alamos National Laboratory (LANL) is predominantly in the area of nitric acid dehydration and low level waste solution processing. Actinide processing at LANL is conducted in an aqueous system predominantly divided between nitric acid and hydrochloric acid based unit operations. As a result of the ever increasing cost of waste disposal, LANL facilities use reprocessed or recycled nitric acid in many of the systems not requiring acid of high purity. The nitric acid recycle system (NARS) has been designed around an energy intensive distillation column where bottoms from the column are recycled to the plant facilities and overheads are discarded as dilute aqueous waste. In addition to being an energy intensive process, the distillation column bottoms and overheads must meet stringent standards requiring solution reprocessing if these standards are not achieved. It has become apparent that the NARS is in need of a purification unit operation that would aid or eliminate reprocessing of distillation product streams. Previous investigations by Sportsman (1998 and 2002) postulated that perfluoro sulfonate ionomer membrane films could not only dehydrate acid feeds (distillation bottoms) and concentrate ionic contaminates (distillation overheads), but also require little energy and operate in a pressurized (high trans-membrane differential pressure) or pervaporation (permeate-side vacuum) environment.[1,2] Following this postulate, Sportsman conducted preliminary research on the use of perfluoro sulfonate/carboxylate composite membranes for the dehydration of nitric acid and hypothesized that the perfluoro carboxylate ionomer material alone might offer improved water separation capabilities when compared to the sulfonate or composite ionomer films.

The goal of investigations beyond the scope of this work is to develop a perfluoro carboxylate ionomer membrane system which will complement the LANL Nitric Acid Recycle System (NARS) distillation unit operation by purifying column product and/or waste streams. The incorporation of a membrane operation module into the NARS could benefit the Los Alamos aqueous processing infrastructure by relaxing distillation operating specifications and has the potential of replacing the distillation system entirely.

# 2.0 BACKGROUND AND PRIOR WORK

## *2.1 Perfluoro Carboxylate and Sulfonate Membranes*

Perfluoro carboxylate membranes were first created by E. I. Du Pont de Nemours and Company personnel in the 1960's from chemistry developed for the perfluoro sulfonate ionomer.[1] These ion-exchange (perfluoro sulfonate/carboxylate ionomer) membranes have been utilized in production of caustic soda and in the chlorine industry for decades, and more than 44 countries use some form of ionomer membrane system to generate approximately 25 % of the world's chloralkali product.[5] Recent applications utilizing the ionomers include as cell components in batteries, diffusion rate limiting barriers in time-release drug systems, proton exchange membranes in fuel cell development, and as ion separation membranes in the acid dehydration process.[6] In fact, fuel cell development using these ionomers has grown to such proportion that both corporate and federal research activities have received a great deal of national attention and the proton exchange membrane fuel cell system is believed to have potential to cause a revolution in energy production.[7] Acid dehydration systems are of recent interest in that both commercial (acetic acid production) and federal (nitric acid recycle and purification) entities are currently investigating this potential application of ionomer films.[8,1,2,3]

### *2.1.1 Ionomer Composition*

The perfluoro precursor used in the perfluoro ionomer manufacturing process is made by the copolymerization of tetrafluoroethylene (TFE) and a functionalized form of TFE which allows the introduction of an ionic side chain. Both the sulfonate and carboxylate (Nafion™) products are made from the resulting perfluoro sulfonyl fluoride precursor polymer film shown in Figure 2.1 where m is 0, 1 or 2, p is from 1 to 10, q is from 3 to 15, and M is usually a halogen (F in this instance) or hydrogen. [4,9] For example, with the precursor shown in Figure 2.1 having the side chain

$$—O—(CF_2)_2—SO_2F \qquad 2.1$$

in combination with an oxidizing agent will convert the side chain to

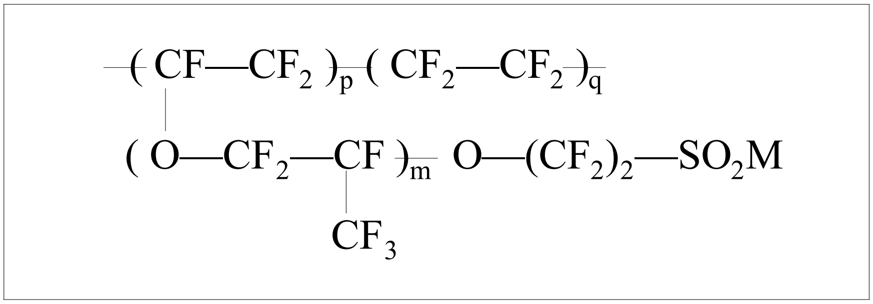
$$—O—CF_2—COOH \qquad 2.2$$

This reaction is conducted at an elevated temperature (50 to 60°C) or in the presence of a metal catalyst (salts of iron, vanadium or copper) at room temperature. Conversion to the sulfonic acid or sulfonate form (Nafion™) membrane pendant side chain

$$—O—(CF_2)_2—SO_3H \qquad 2.3$$

is achieved by hydrolysis of the precursor. Materials with a mixture of both carboxylate and sulfonate pendent chains (Equations 2.2 and 2.3) can be generated by controlled exposure of the precursor to oxidizing and reducing reagents. For example, a film of the precursor material is hydrolyzed to a known depth to convert a layer to the sulfonic form, and exposure of the remainder of the polymer to an oxidizing agent will convert the remaining sulfinic groups to the carboxylic form.

Figure 2.1 – Nafion™ precursor.



$$\mathrm{-(\underset{|}{CF}-CF_2)_p\,(CF_2-CF_2)_q-}$$
$$\mathrm{(O-CF_2-\underset{\underset{\displaystyle CF_3}{|}}{CF})_m\,O-(CF_2)_2-SO_2M}$$

Figure 2.2 shows a scanning electron microscopic (SEM) photo of the perfluoro sulfonate/carboxylate composite membrane Nafion™ 90209. The dark band at the top edge of the material is the carboxylate layer (~40 µm in width), the center section a sulfonate layer (~140 µm), and the bottom a sulfonate layer with and imbedded PTFE mesh support (total layer width ~40 µm).

Mixed ionomer membranes have been synthesized from the sulfonyl fluoride precursor using procedures comprised of both reduction and oxidation steps (for example, hydroxide and hydrazine in water) with the resulting materials having from 5 to 95% carboxylate terminated side chains.[4,10] Boyle et al. (1984) describe using x-ray fluorescence (XRF) microbe analysis to characterize chemically synthesized perfluoro carboxylate films and concluded that the polymers contain a small fraction of the sulfonic terminated side-chains.[11]

Perfluoro carboxylate and sulfonate films are available with slight chemical differences as compared to films manufactured by E. I. Du Pont de Nemours and Company. For example, Asahi Glass Corporation has developed a perfluoro carboxylate film (Flemion™) with the short pendent chain shown in Figure 2.3 where q is from 3 to 15 and M is either $CH_3$, F, a metal salt or H.[12,13]

### *2.1.2 Ionomer Ion-exchange Capacity*

The perfluoro ionomers described above containing anion terminated pendent side-chains have associated counter-ions (M in Figures 2.1 and 2.3) that can be exchanged as

Figure 2.2 - Nafion™ perfluoro sulfonate/carboxylate composite film.

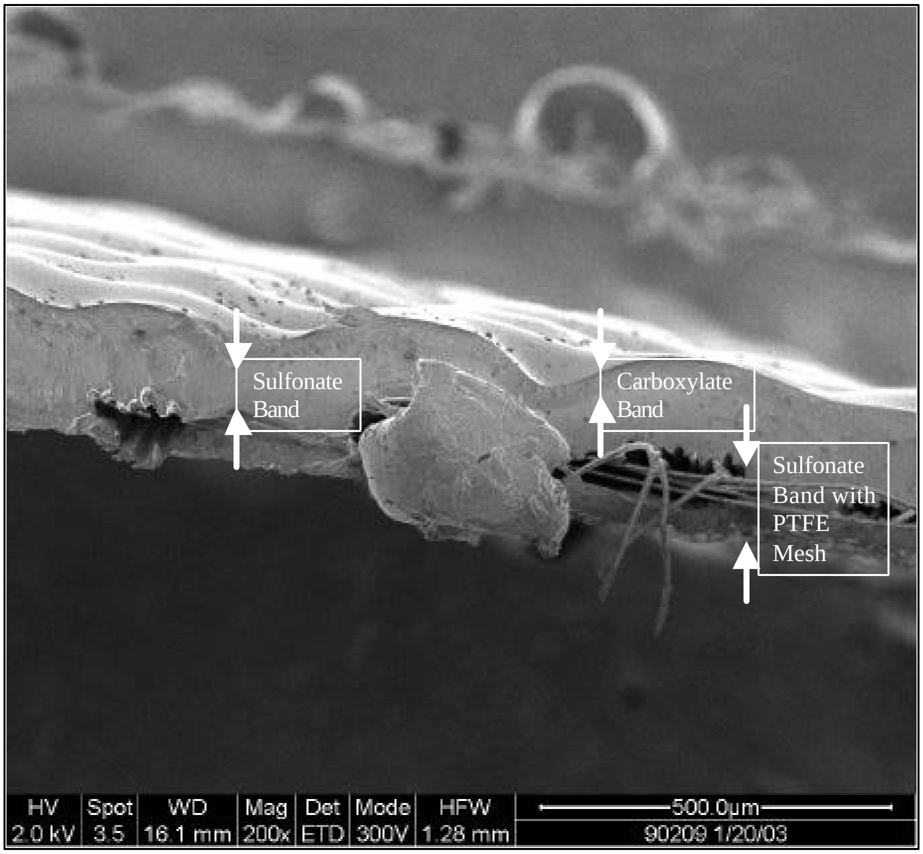
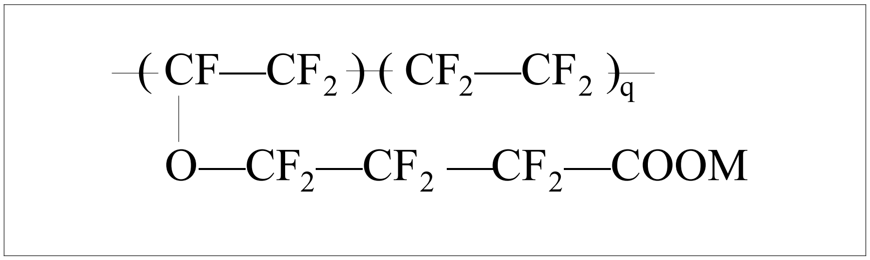


Figure 2.3 – Flemion™ ionomer film composition
(Asahi Glass perfluoro carboxylate polymer).

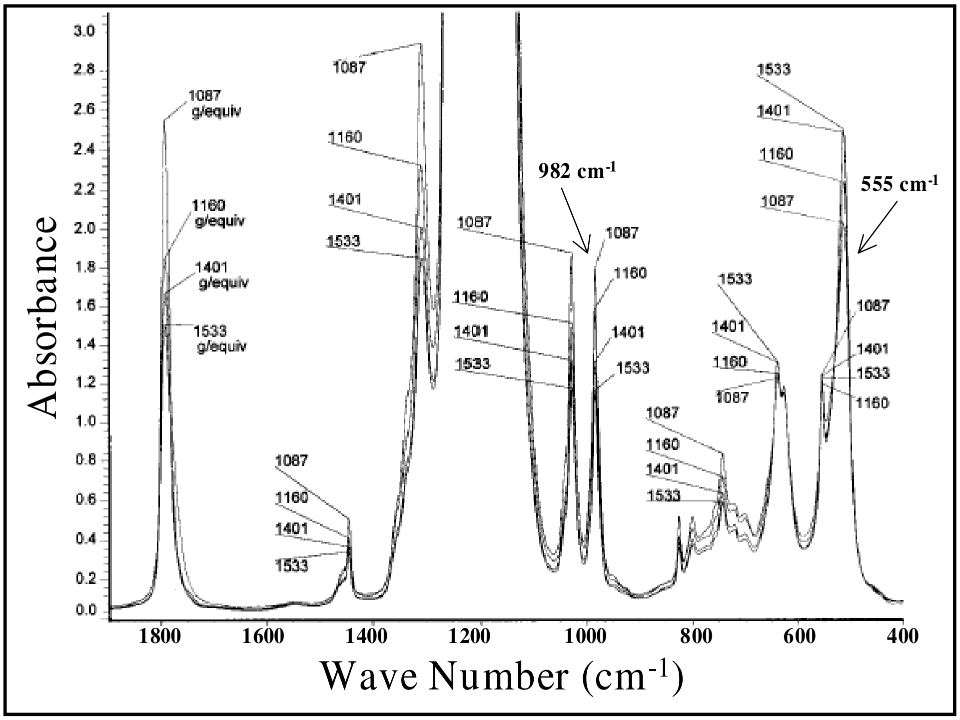


$$\begin{array}{l} -(\mathrm{CF}-\mathrm{CF_2})(\mathrm{CF_2}-\mathrm{CF_2})_q- \\ \quad | \\ \quad \mathrm{O}-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{COOM} \end{array}$$

desired. Measurement of the ion-exchange capacity of the ionic side chain is described by the equivalent weight (EW) which is defined as the number of ionic sites per dry gram of polymer or mmoles exchange groups per gram of dry membrane material (meq. $g^{-1}$). Perfluoro sulfonic and carboxylate ionomer EW is dependant on the ratio of pendent side chain to TFE monomer, however, most films have an EW near 1000 meq. $g^{-1}$.[14,15] Perfluoro sulfonate films are manufactured and distributed with a variety of equivalent weights and in a number of thicknesses. For example, Du Pont markets the Nafion™ series of membranes, Nafion™ 111 through 117. The Du Pont numbering convention for these ionomer films is defined by the first two digits being the EW ($100\times g\ eq^{-1}$) and the third digit the membrane's thickness ($1\times0.001$ inches).

Equivalent weight can be determined by a number of methods including titration of the acid form of the ionomer or by Fourier transform infrared spectroscopy. [13] Figure 2.4 shows the FTIR spectrum for Nafion™ in the (perfluoro carboxylate) ester form. In order to determine an estimate of the EW, absorbance band peak intensities at 555 $cm^{-1}$ ($CF_2$ band) and at 982 $cm^{-1}$ (C-O-C, ether band) for materials with unknown EWs are compared to the same band peak intensity information from films with know EWs. The EW of the films shown in the figure were found to range from 0.652 to 0.919 meq. per gram of polymer (1533 to 1087 g $eq^{-1}$).

Figure 2.4 – FTIR spectra for Nafion™ perfluoro carboxylate ionomer (Adapted from Perusich 2000).



### *2.1.3 Distinguishing Between Sulfonate and Carboxylate Forms*

Fourier transform infrared spectroscopy (FTIR) can be used to distinguish between perfluoro polymer films, or to determine if material contains a mixture of the sulfonate and carboxylic pendent side-chains.[13] Table 2.1 lists infrared active bands and assignments for both perfluoro sulfonate and carboxylate films. With this information, and by changing the form of a given film (acid, potassium, methyl ester, etc.), peak positions in the spectrum can be used to distinguish between perfluoro sulfonate and carboxylate forms or to determine if a mixture of sulfonate and carboxylate side-chains are present. Similar FTIR peak positions are observed for both the Asahi Glass short side-chain and the Du Pont long side-chain materials for perfluoro carboxylate forms. In addition, when comparing spectra for perfluoro sulfonate materials manufactured by the two companies, comparable peak positions are also observed for the sulfonate terminated chain regardless of chain length.

Table 2.1 – Infrared active bands and assignments.[2,13]

| Perfluoro Film Form | Peak Position (wave number, $cm^{-1}$) | Bond Assignment |
|---|---|---|
| Carboxylate | 1468 | -C-O-H, in $-CO_2H$ |
| Carboxylate | 1444 | $-C-O-CH_3$ in $-CO_2CH_3$ |
| Carboxylate | 1444 | $-CO_2H$ |
| Carboxylate | 1408 | $-CO_2K$ |
| Carboxylate | 1790 | C=O, in $-CO_2-$ |
| Carboxylate | 2908 | C-H in $-CO_2CH_3$ |
| Sulfonate | 2850 | S=O, in $-SO_3H$ |
| Sulfonate | 1425 | S=O, in $-SO_3H$ |
| Sulfonate | 1350-1200, 1060 | $-SO_3^-$ |
| Sulfonate | 920 | S-O, in $-SO_3H$ |
| Sulfonate | 655 | S-O, in $-SO_3H$ |

### *2.1.4 Ionomer Thermal Properties*

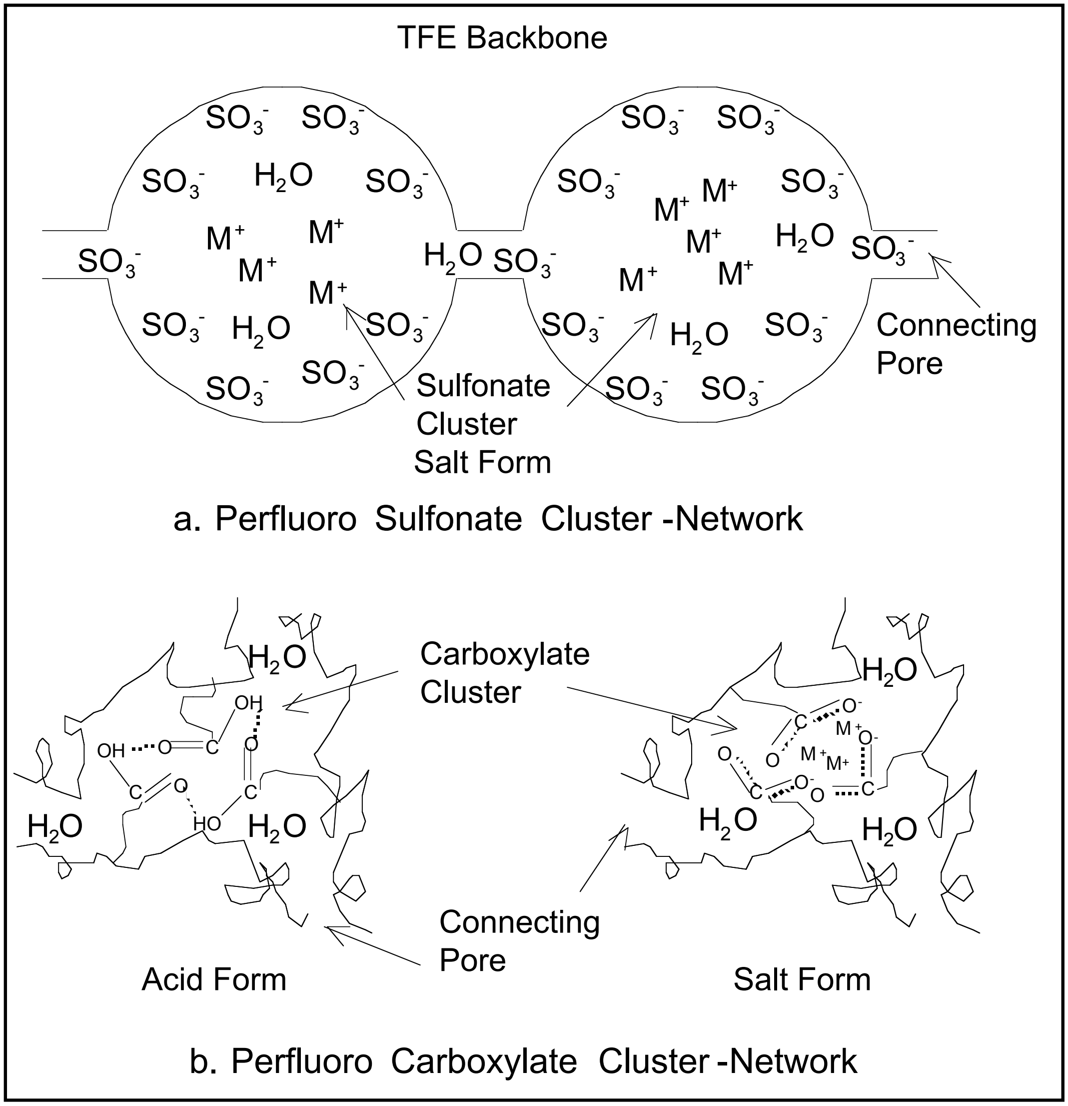
Thermal properties of perfluoro sulfonate and carboxylate membranes are typically determined experimentally by destructive processes such as thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and dynamic mechanical thermal analysis (DMTA).[16,17,18] Depending on the counter cation present in the ionomer, the glass transition temperatures ($T_g$) for the polymer material can vary widely. Two distinct glass transition temperatures are present for salt forms of the ionomer ($Na^+$ or $K^+$): The lower transition temperature is characteristic of the polymer material and the higher representative of the ionic side-chain cluster. For the sulfonate salt forms, the polymer glass transition temperatures range from 122 to 150 °C and the clustered ionic side-chain glass transition temperatures range from 237 to 250 °C.[15] For perfluoro carboxylate $Na^+$ or $K^+$ salt forms of the polymer film, dielectric relaxation and DMTA results indicate polymer glass transition temperatures range from 165 to 205 °C and from 207 to 245 °C for the $T_g$ of the clustered ionic side chains.[11,18] It is hypothesized that the reason for the similarities between the sulfonate and carboxylate glass transition temperatures is that in most cases the carboxylate form of the ionomer contains a sulfonate termination in a significant fraction of the pendent side chain groups (40 to 50 % as indicated by Boyle et al., 1984, and Nakano et al., 1984) as previously mentioned.[11,18] Nakano et al. (1984) speculate that, unlike the metal salt forms of the ionomer, the ether and acid forms of the carboxylate ionomer are believed to be in a single-phase when dry and the acid form is believed to be in an ionic cluster phase when hydrated.

### *2.1.5 Morphology*

A number of theories exist which describe the internal structure of the perfluoro sulfonate and carboxylate ionomer films. [14,19,20,21] Presently accepted theories propose that both the perfluoro sulfonate and carboxylate materials have microheterogeneous structures that consist of a hydrophobic TFE polymer region and a hydrophilic side chain region, or cluster. The two predominant models include the two-phase model and the core-shell model. [10,17,20,22] The most widely accepted model for the sulfonic polymer is detailed by Hsu and Gierke (1982), which evolved from early two-phase models and is based on previous theories and analytical data from small angle x-ray scattering (SAXS).[20,21] Figure 2.5.a illustrates the two-phase cluster-network model proposed by Hsu and Gierke. The model shows the sulfonic cluster region that has a cross-sectional diameter (and sulfonate density) believed to increase with increasing hydration, with pores connecting the spherical cluster structures. The hydrophilic clusters and pores are surrounded by the hydrophilic tetrafluoroethylene (TFE) backbone support structure. The most current theories on the physical configuration of the perfluoro carboxylate structure are also based on the model proposed by Hsu and Gierke.[10,12,17,18,23]

Figure 2.5.b illustrates the cluster model for perfluoro carboxylate film in both the acid and salt form. Electronic paramagnetic resonance (EPR) studies support the Hsu and Gierke model in the carboxylate films showing ion clustering in Flemion™ films with

Figure 2.5 – Cluster model for hydrated perfluoro ionomers.



copper, iron or europium counter-ions.[12] In addition, DMTA investigations support the two-phase model with a separate polar phase in the presence of water.[18] Figure 2.6 shows DMTA relaxation data for the dried alkali metal forms of the carboxylate film for which the regions of $T_g$ for the polymer matrix ($\beta$) and cluster ($\alpha$) can be identified. The relaxation assignment given to peaks at lower temperatures are due to the local motions of fluorocarbon groups in the polymer backbone ($\delta$) and to local motions of the polar portion of the side chains ($\delta$'), neither of which are theorized to be phase separated.

Another important tool used for ionomer morphological examination is small angle x-ray scattering. Figure 2.7 illustrates typical SAXS data for two perfluoro carboxylate and three perfluoro sulfonate ionomer membranes.[18] Two different scattering maxima can be observed (at $q \cong 0.007$ and $0.3\ nm^{-1}$) for the acid and amide forms of the sulfonate ionomer, where q is the angular variable (also represented as *s*, where $s = q/2p$)), $\lambda$ (0.154 nm) is the wavelength of the x-ray beam, and $2\theta$ is the x-ray beam angle of scatter. The first peak represents the polymer crystalline structure and the second peak represent the ionic cluster morphology, when present. However, only one peak can be seen for both of the carboxylate ionomers and for the sodium salt form of the sulfonate ionomer film. It has been proposed that the absence of the second peak in the carboxylate and the sodium salt form of the sulfonate films is not due to the absence of the cluster structure, but instead, the peak is not present due to similarities in the electron density of the polymer and cluster structures under the given conditions.[23,24,25]

Figure 2.6 – DMTA data for dried alkali salt forms of a perfluoro carboxylate ionomer (Adapted from Nakano et al. 1984).

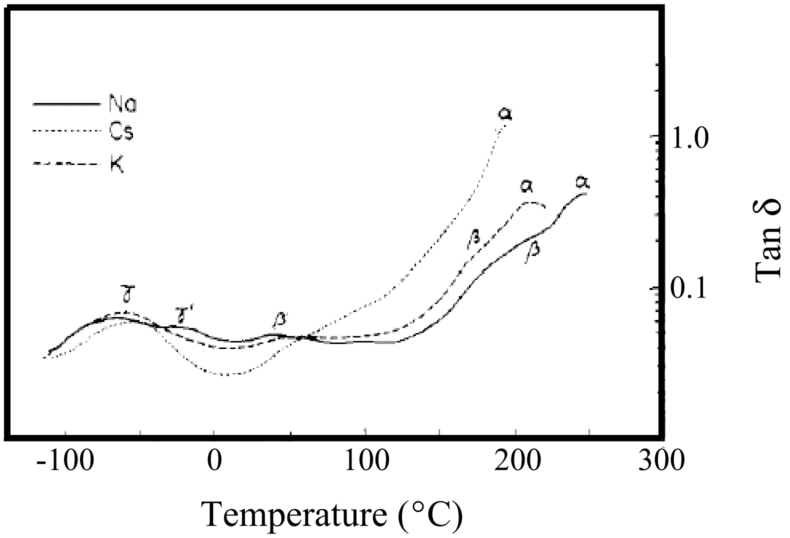
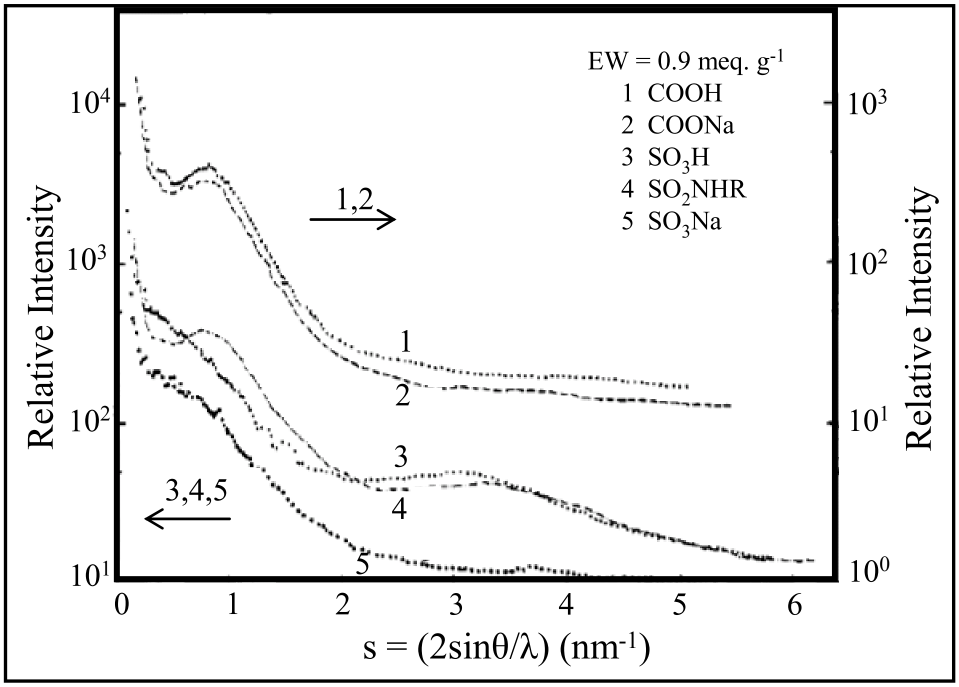


Figure 2.7 SAXS curves for perfluoro carboxylate and sulfonate ionomer films (Adapted from Fujimura et al. 1981).



From the position of the second peak in curves 3 and 4 in Figure 2.7, the magnitude of the distance between centers of the cluster features can be estimated based on the Bragg diameter (Equation 2.4).

$$d_{Bragg} = \frac{1}{s} = \frac{2p}{q} \qquad 2.4$$

Assuming the second feature maximum is at approximately s = 0.3 nm$^{-1}$, the d$_{\mathrm{Bragg}}$ is approximately 3.3 nm. Sportsman (2000) determined the Bragg distance for the cluster feature to be between 1.2 and 1.9 nm (cluster diameter between 2.3 and 3.6 nm). Using the cluster theory presented above, the number, volume and radius of the theorized cluster can be estimated from the relationships shown in equations 2.5 through 2.7.[1,26]

$$N = \frac{N_A r_d}{EW(1+f_w)} d^3_{Bragg} \qquad 2.5$$

$$V_c = \frac{f_w}{1+f_w} d^3_{Bragg} + NV_p \qquad 2.6$$

$$R = \left[\frac{3V_c}{4p}\right]^{\frac{1}{3}} \qquad 2.7$$

For these relationships $N$ is defined as the number of ionic groups per ionomer cluster, $N_A$ is Avogadro’s number, $f_w$ is the fractional volume change of the membrane, and $r_d$ is the density of the dry membrane. Additionally, $EW$ is the ionic equivalent weight, $V_p$ is the volume of an ionomer exchange site, $d_{Bragg}$ is the value of the Bragg diameter at the peak of the ionomer or cluster feature, $R$ is the cluster radius, and $V_c$ is the ionomer cluster volume.

### *2.1.6 Solution Casting*

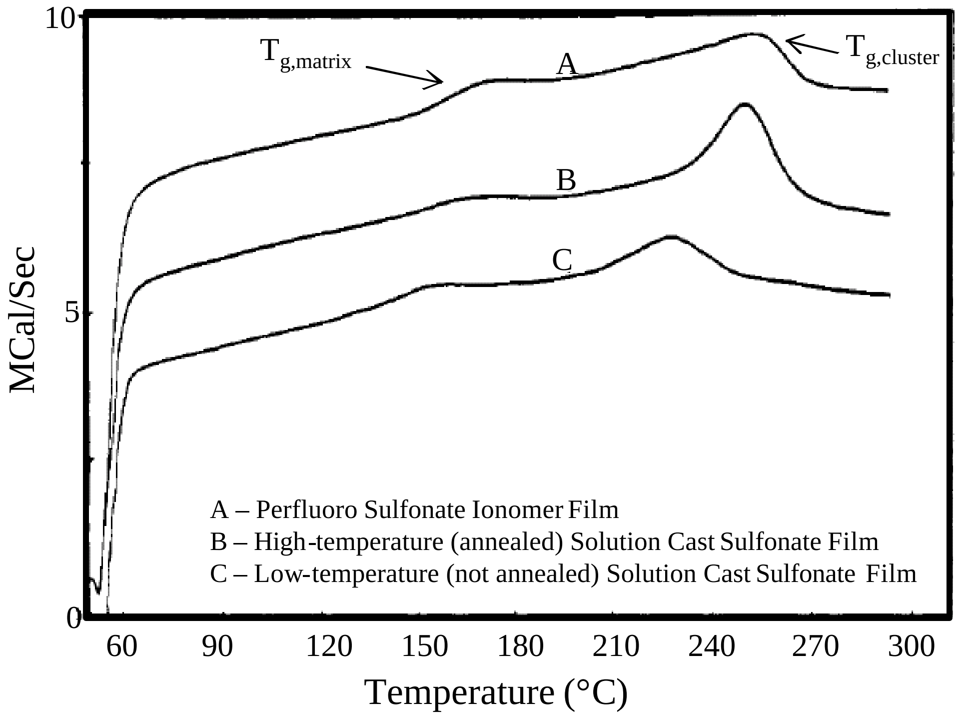
Manufacturers of perfluoro sulfonate, carboxylate and composite membranes have developed product manufacturing processes designed for the generation of large quantities of material and, as a result, the films are available for sale in a limited variety of thicknesses, with a limited range of equivalent weights, and with few composite combinations. Because of the small selection of commercial film characteristics, investigations were conducted and procedures were developed where the perfluoro sulfonate films could be dissolved and recast from solution.[27,28,29] By dissolving and recasting the films, researchers are able to vary the thickness of the film and able to precipitate the material on a variety of surfaces (surface modification). In fact, perfluoro sulfonate solutions are now available for purchase through most chemical supply warehouses. Unfortunately, a solution casting procedure that can generate a high quality film from perfluoro carboxylate ionomer solution has not been documented, thus information on the generation of carboxylate and mixed sulfonate/carboxylate films cast from solution is not available.

Martin et al. (1982) identified two binary solvent systems that were successful in dissolving the sulfonate ionomer: 50:50 propanol-water and 50:50 ethanol-water, both at high pressure in a sealed autoclave reactor near the glass transition temperature for PTFE (250°C). The binary solvent systems were chosen because the polymers exhibit unique solubility characteristics when compared to other binary mixtures or pure solvent techniques. Results verified that essentially all of the feed perfluoro sulfonate ionomer material was dissolved with little or no degradation. It was also determined that solution concentrations can be varied, however, solutions for purchase are generally less than 5% dissolved ionomer by weight.

Reconstituted ionomer films are cast from the perfluoro sulfonate solutions by slowly evaporating the solvents (at or near solvent boiling temperatures) on leveled surfaces in a vacuum oven or in an oil bath. The "solution cast" films resulting from the evaporation of dissolution solvents were found to have much different morphology than those of the feed material.[28] However, when an equal volume of a high boiling point solvent (dimethyl sulfoxide or N, N'-dimethylformamide) was added immediately following the dissolution process and evaporated, the solution cast films were generated with the morphology, chemical characteristics and pliable physical characteristics of the feed or manufactured ionomer film.[29] The procedure required that the alcohol-water solvents were evaporated in two stages, at low temperature to remove the dissolution solvent mixture, then at a temperature slightly above the boiling point for the solvent added after the dissolution process. It was discovered that cluster morphology was maintained when forming the solution cast films at lower temperature, but that the TFE crystalline polymer matrix backbone structure was not present. Higher temperature solution casting (greater than the glass transition temperature of the TFE matrix, 150 °C) was needed in order to create the molecular mobility in the TFE molecular chains required to reform the crystalline structure of the polymer matrix. Another way to create the same result was by annealing films (at greater than the $T_g$ of the TFE matrix) that were solution cast from lower boiling point solvents. These results were verified in that SAXS analysis of the feed material and high temperature solution cast films were virtually identical showing both polymer matrix and cluster features, whereas low temperature solution cast films lacked the polymer matrix feature. In addition, differential scanning calorimetry (DSC) reported by Moore et al. (1988) indicates that thermogram scan features for the feed material (commercially available membranes) and high temperature solution cast films were located in the same temperature range, yet both the polymer matrix and cluster thermogram features for the low temperature solution cast polymers were low by approximately 30 °C. Figure 2.8 shows the DSC thermograms for feed perfluoro sulfonate (A) high-temperature solution cast (B), and low-temperature solution cast (C) ionomer films. The films shown in Figure 2.8 were determined to have an EW of 0.909 meq. $g^{-1}$ (1100 g per mole equivalent).

Moore et al. (1986) reported that the ion-exchange capacity of the solution cast film can be reduced by as much as 30 % when compared to the feed material. Results from the same studies identified three critical attributes that were maintained through the dissolution and precipitation process: The polymers were again water insoluble, the pendent side-chains retained the majority of feed ion-exchange capabilities, and the cast film retained the two-phase hydrophobic-polymer and hydrophilic-ionomer cluster morphology.

Figure 2.8 – Differential scanning calorimetry (DSC) of perfluoro sulfonate films (Adapted from Moore et al. 1988).



### *2.1.7 In-Situ Film Conversion*

Conversion of Nafion perfluoro ionomer films to sulfonate, carboxylate and mixed sulfonate/carboxylate films has been accomplished. Du Pont research and development personnel established the baseline for conversion of the sulfonyl fluoride form of the polymer to the fluorinated ionomer with either or both the carboxylate and the sulfonate pendant side-chain.[4,24] Fujimura et al. (1981) describe a technique used to produce perfluoro carboxylate films from Nafion™ perfluoro sulfonate films. This procedure calls for the conversion of the acid form of the sulfonate film to the perfluoro carboxylate through a series of reactions with ammonium hydroxide, a mixture of $PCl_5$ and $POCl_3$, and finally HI solution. This procedure was demonstrated successfully during our research but it was difficult and time consuming when compared to the procedure developed by Grot et al. (1985) described below. The procedure developed by Fujimura et al. (1981) is detailed in Appendix A.5.

Grot et al. (1985) demonstrated multiple procedures for converting the Nafion™ sulfonyl fluoride precursor to the carboxylate form by first reducing the side-chain terminal group to the sulfinic acid then oxidizing it to the carboxylate form. In addition, it was demonstrated that a mixed ionomer film of the carboxylate and sulfonate form could be made first by an incomplete reduction of the sulfonyl fluoride followed by hydrolysis of the remaining sulfonyl fluoride, followed by the oxidation of the sulfinic acid groups to the carboxylate pendant side-chain. This procedure was used as the baseline conversion process during our effort for producing perfluoro sulfonate and mixed ionomer membranes (Section 4.0), is referred to throughout this document as the Grot conversion procedure, and is detailed in Appendix A.6.

### *2.2 Aqueous Mass Transport*

At the center of this effort was the desire to develop a material that has the ability to remove water from a nitric acid solution. Of most importance is the water sorption, and water and nitrate transport characteristics of the ionomer films of interest. The information that follows describes previous work concerned with the water, acid and ion transport characteristics of the perfluoro ionomer polymers.

### *2.2.1 Water Sorption*

A number of investigations have studied and reported water sorption characteristics for perfluoro ionomer materials.[18,19,30,31,32] Yeager et al. (1982) provide a summary of ion exchange capacity (EW) and water sorption data for both perfluoro carboxylate and perfluoro sulfonate films which are summarized in Table 2.2. Data are given for both as-received membranes and water saturated films (membranes soaked in boiling water for 3 hours). In general, the carboxylate film sorbs approximately 22 % less water per exchange site than the sulfonate form.

Table 2.2 – Water sorption for E. I. DuPont perfluoro carboxylate and sulfonate ionomers.[31]

| | Polymer | $Na^+$ Form (as Received) | $Na^+$ Form (water saturated) | $Cs^+$ Form (as Received) | $Cs^+$ Form (water saturated) |
|---|---|---|---|---|---|
| Ion Exchange Capacity (mole $L^{-1}$) | Carboxylate | 1.30 | 1.22 | 1.37 | 1.24 |
| | Sulfonate | 1.20 | 1.11 | 1.35 | 1.32 |
| Ratio $H_2O$: Exchange Site (mole $mole^{-1}$)* | Carboxylate | 9.5 (11) | 13.9 (16) | 5.0 (6) | 9.1 (10) |
| | Sulfonate | 11.9 (13) | 18.4 (19) | 6.6 (8) | 11.3 (14) |

*wt% water shown in parenthesis.

Table 2.3 shows the water uptake for a perfluoro carboxylate ionomer film (EW=1.25 meq. $g^{-1}$) for a variety of counter ion forms as reported by Nakano et al. (1984). Results show that the alkali salt forms ($Na^+$ or $K^+$) of the carboxylate ionomer have a larger capacity for water uptake than most other forms of the ionomer. Results from tests with a perfluoro carboxylate film with a higher EW (1.8 meq. $g^{-1}$) mirror the results shown in Table 2.3 in that $Na^+$ and $K^+$ forms of the ionomer show the largest absorption with 101 and 68 wt% water uptake, respectively. However, more recent studies with Asahi Glass Corporation material again verify that, when compared to similar sulfonate ionomer materials in the same counter-ionic form (Cu, Fe and Eu), the perfluoro carboxylate ionomers were found to have significantly lower water sorption capacities. For example, a 1.25 meq. $g^{-1}$ carboxylate membranes was shown to have approximately 25 % the water uptake of a sulfonated film having an EW of 0.8 meq. $g^{-1}$.[12]

Table 2.3 – Water sorption Asahi Glass carboxylate films (EW = 1.25 meq. $g^{-1}$).[18]

| Perfluoro Carboxylate Film Form | Water uptake (w %) – 4day soak in solution | Water uptake (wt%) – Boiled in water for 1 hour |
|---|---|---|
| H | - | 7.6 |
| Na | 36 | 41 |
| K | 8.6 | 19 |
| Cs | 8.5 | 13 |
| Ag | 5 | 5 |
| $N(C_4H_9)_4$ | 12 | - |
| Mg | 12 | 15 |
| Ba | 6.5 | 7.3 |
| Zn | 11 | 11 |

### *2.2.2 Ionic and Proton Diffusion*

As an example for comparison of ionic diffusion through both perfluoro sulfonate and carboxylate ionomer films, Twardiwski et al. (1982) provides self-diffusion rates for $Na^+$ in both the carboxylate and the sulfonate forms (Equations 2.1 and 2.2) which are summarized in Table 2.4.[32] Results show that diffusion coefficients for the two types of polymers are of the same order of magnitude for identical conditions, although the sulfonate form of the perfluoro ionomer does have significantly larger diffusion coefficients. For these data, the perfluoro carboxylate EW was determined to be 0.952 meq. $g^{-1}$ (1050 g $eg.^{-1}$), whereas the sulfonate form tested had a smaller EW of 0.869 meq. $g^{-1}$ of polymer (1150 g $eg.^{-1}$). Twardiwski et al. (1982) offer a partial explanation for the higher diffusion rates of $Na^+$ in the sulfonate film by noting that the films are shown to have significantly higher water content when compared to the carboxylate ionomer material. Boyle et al. (1982, 1983) provides information which supports the correlation between membrane water content and diffusivity. Additionally, more recent information has surfaced showing that carboxylate films have much lower ionic and water conductivity than do the sulfonate ionomer materials.[12,33] However, data exists that contradicts this conclusion: Initial studies by Yeager et al. (1982) provide data showing that the self-diffusion of water, $Na^+$ and $Cs^+$ was higher in perfluoro carboxylate films than in sulfonate films under the given test conditions.[31] In general, more recent studies show that carboxylate films have higher water permselectivities (water selectivity when compared to diffusing cations) and lower water diffusion rates than do similar sulfonate films.

Table 2.4 – Sodium diffusion coefficients in aqueous solutions (70°C) for E. I. DuPont perfluoro carboxylate and sulfonate ionomers.[32]

| Polymer* | Solution | Diffusing Species | Concentration (M) | Diffusion Coefficient (D) × $10^7$ ($cm^2\ sec^{-1}$) @ 25°C |
|---|---|---|---|---|
| Carboxylate | NaCl | $Na^+$ | 4.0 | 8.33 |
| Sulfonate | NaCl | $Na^+$ | 4.0 | 17.7 |
| Carboxylate | NaCl | $Na^+$ | 5.0 | 3.8 |
| Sulfonate | NaCl | $Na^+$ | 5.0 | 13.2 |
| Carboxylate | NaOH | $Na^+$ | 9.5 | 0.11 |
| Sulfonate | NaOH | $Na^+$ | 9.5 | 3.15 |

* Carboxylate and sulfonate film thicknesses tested were 200μm and 250μm, respectively.

Proton diffusion through these materials is of interest in that higher diffusivities make the film more attractive as proton exchange membranes in fuel cell applications. Unfortunately, detailed studies of electrical conductivity or proton diffusion has not been published for perfluoro carboxylate or composite ionomer films.[34,35] However, Edmondson et al. (2001, 2002) has investigated diffusivities in Nafion™ 117, as well as sulfonated styrene/ethylene-butylene/styrene (S-SEBS) films. Edmondson experimentally determined the proton diffusion coefficient through Nafion™ 117 and S-SEBS from conductivity data ($D_s$) using the Nerst-Einstein equation and from $^1$H pulse field gradient spin-echo NMR. Results for Nafion™ 117 indicate that the diffusion stops altogether (diffusion threshold value) at 4 wt% water and has an estimated value of $4.8\times10^{-6}$ cm$^2$ s$^{-1}$ for the saturated film (approximately 20 wt% water) as determined by NMR.[34] These data are illustrated in Figure 2.9. This information will be used for comparison with diffusion coefficients for saturated perfluoro sulfonate, carboxylate, and mixed ionomer films, also determined by NMR, later in this document.

### *2.2.3 Pressure Mass Transport*

In membrane (separation) processes a chemical potential gradient describes the thermodynamic driving force necessary for separation of a component in a multi-component solution system. Pressure, concentration, or temperature differences, or a combination thereof, promote solvent and solute diffusion across the membrane. The transport of pure water through perfluoro sulfonate and carboxylate films and the relationship between water transport and pressure differential is of initial interest. Pressure applications for membranes can be grouped into five categories which include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and piezodialysis.

Figure 2.9 – Proton diffusion through sulfonate films (Adapted form Edmondson et al. 2001).

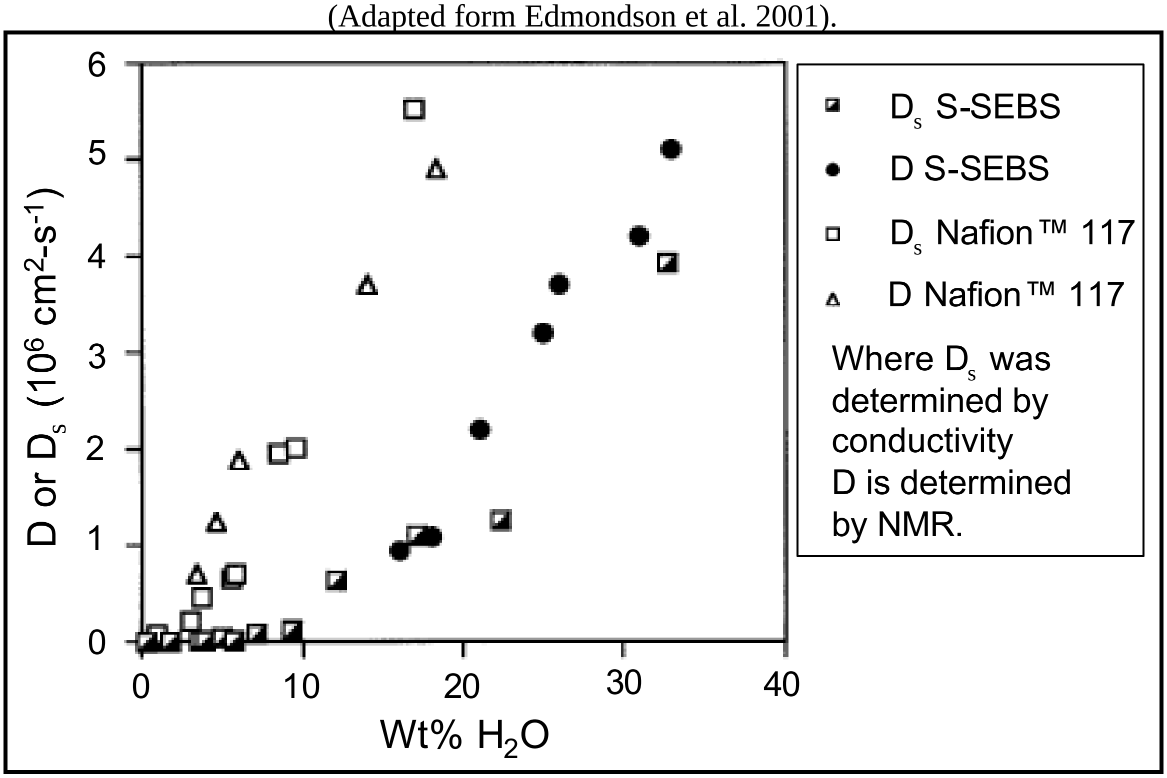


Table 2.5 lists the classifications of pressure membrane processes, general specifications, and examples of applications for each of the membrane processes.[36]

In the analysis of pure water permeation, due to diffusion and solubility, in perfluoro sulfonate and carboxylate polymer, the process can be theoretically described as a nanofiltration process due to characterization in terms of mass flux, trans-membrane pressure differential and effective pore radius in the membrane. Investigations conducted during the past decade have determined that Nafion™ membranes have "effective pore size" distributions from 1 to 10 nm.[1,37,38] Figure 2.10 shows water flux as a function of trans-membrane pressure through Nafion™ 112 film (acid form) at ambient temperature.[1] Permeabilities and diffusion coefficients for the trend line in Figure 2.10 are listed in Table 2.6.

Table 2.5 – Summary of pressure membrane process categories.

| Membrane Process | Membranes | Membrane Thickness (μm) | Pore Size (μm) | Pressure Differential (psi) | Separation Principle | Applications |
|---|---|---|---|---|---|---|
| Microfiltration | Porous | 10-150 | .05-10 | <30 | Sieving | Analytical, food, water purification |
| Ultrafiltration | Porous | 150 | 1-100 | 10-150 | Sieving | Textile, food, automotive |
| Nanofiltration | Composite | 1 (filtration layer) on substrate | <2 nm | 100-500 | Solution-diffusion | Desalination, water treatment, textile |
| Reverse Osmosis | Composite/ asymmetric | 1 (filtration layer) on substrate | <2 nm | 200-1200 | Solution-diffusion | Ultra-pure water, food, desalination |
| Piezodialysis | Composite/ asymmetric | 1 (filtration layer) on substrate | <2 nm | Osmotic pressure | Solute-diffusion | Energy production |

Figure 2.10 Pure water flux through acid form Nafion™ 112
(Adapted from Sportsman 2002).

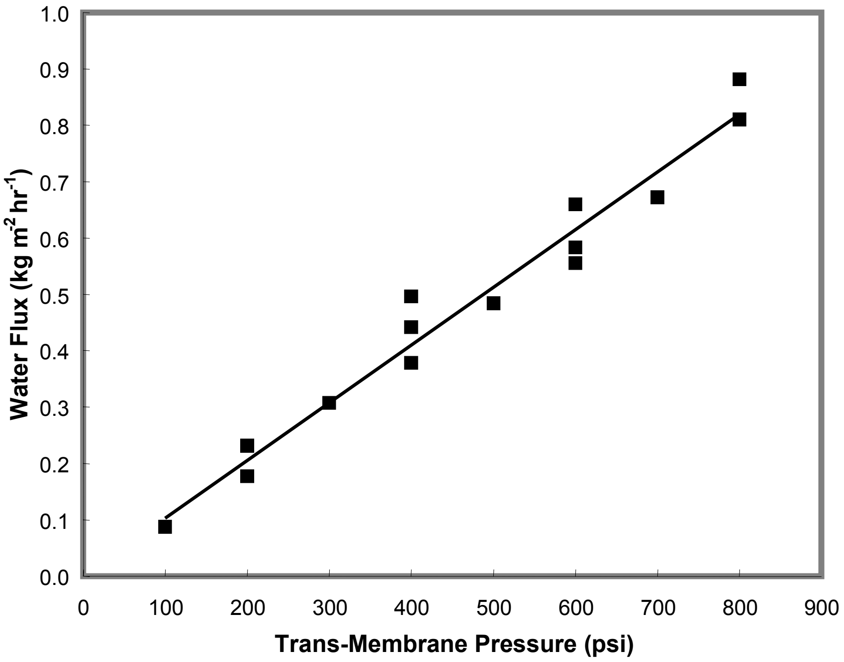


Table 2.6 – Permeability and diffusion coefficient summary.

| Trans-Membrane Pressure (psi) | P Nafion™ 112 ($cm^3$ cm $cm^{-2}$ $s^{-1}$ $Pa^{-1}$ × $10^{18}$)* | D Nafion™ 112 ($cm^2$ $s^{-1}$ × $10^7$) [a] |
|---|---|---|
| 100 | 1.27 | 0.878 |
| 200 | 1.48 | 2.04 |
| 300 | 1.54 | 3.19 |
| 400 | 1.59 | 4.35 |
| 500 | 1.60 | 5.51 |
| 600 | 1.61 | 6.67 |
| 700 | 1.62 | 7.83 |
| 800 | 1.63 | 8.98 |

* Permeability and diffusion coefficient calculated based on 10% water content.

For pressure driven ionomer systems it is widely accepted that ion transport is a function of chemical potential which consists of three driving forces; Fickian diffusion (concentration), ionic conductance (electrical) and bulk flow (convection). The Extended Nerst-Planck equation (Equation 2.8) provides a relationship between the trans-membrane flux, and the concentration, electrical and convection driving forces.

$$J_i = -D_i \frac{dc_i}{dx} + \frac{z_i F c_i D_i}{RT} \frac{dE}{dx} + c_i K_i V \qquad 2.8$$

In equation 2.8, $D_i$ is defined as the component hindered diffusion coefficient, $c_i$ is the component concentration, $x$ is the trans-membrane length, $z_i$ the component ion valance, and $F$ is Faraday's constant. Additionally, $R$ is the ideal gas constant, $T$ the temperature, $E$ the axial electrical potential, $K_i$ the component convection hindrance coefficient, and $V$ the solute velocity.[36,39,40,41]

In both reverse osmosis (RO) and nanofiltration (NF) solutions of different solute concentrations are separated by a permeable membrane barrier. As a result of the chemical concentration difference between the two solutions, a potential exists where the solvent will flow from the solution of lower solute concentration. This chemical potential creates a hydrodynamic pressure difference called the osmotic pressure ($Dp$). Reverse osmosis and NF processes operate such that a pressure (greater than the osmotic pressure) is applied to the more concentrated solution forcing the dilute phase solvent to permeate through the barrier to the less concentrated solution. These processes are considered to bridge the gap between porous membrane and non-porous membrane processes and the guiding principles for both RO and NF are identical with the only difference being the characterization of trans-membrane pressures and effective pore radius (Table 2.5).

The pressure driven processes investigated within our studies are considered to be NF and use of the Expanded Nerst-Planck model (Equation 2.8) where the model neglects the electrical potential as being small in comparison to the concentration and convection potentials (Equation 2.9).

$$J_i = -D_i \frac{dc_i}{dx} + c_i K_i V \qquad 2.9$$

In dilute solutions, the concentration potentials are very small when compared to the convection for bulk flow. So for the solvent (water), the bulk flux can be described as

$$J_v = P_w\left(\frac{dp}{dx} - s\,\frac{dp}{dx}\right) \qquad 2.10$$

where $J_v$ is the bulk flux, $P_w$ is the water permeability, *dp/dx* is the trans-membrane pressure, *dp/dx* is the trans-membrane osmotic pressure, and *s* is the reflection coefficient described by Equation 2.11.

$$s = (\frac{\Delta p}{\Delta p})_{J=0} \qquad 2.11$$

In addition $P_w$ is described as

$$P_w = \frac{D_w c}{RT} \qquad 2.12$$

where $D_w$ is the water diffusivity in the membrane, and *c* is the concentration of water in the membrane. Finally, the bulk water flux can be simplified as

$$J_v = \frac{P_w}{l}(\Delta p - \Delta p) \qquad 2.13$$

when it is assumed that *dp* can be estimated by *Dp*, *dx* can be estimated as *Dx* (or the thickness of the film, *l*), and σ as unity for an ideal, semi-permeable membrane.

For the dilute solute in solution, both convection and concentration terms of the Expanded Nerst-Planck equation must be considered as shown by Equation 2.14

$$J_s = -P_s \frac{dc_s}{dx} + (1 - s)c_s J_v \qquad 2.14$$

where $P_s$ is the solute permeability. The permeability of the solute is described by Equation 2.15

$$P_s = D_s K_s \qquad 2.15$$

where $D_s$ is the solvent diffusion coefficient and $K_s$ is the solute convection hindrance coefficient. Similarly, the solute flux equation can be simplified for an ideal, semi-permeable membrane as being that shown in Equation 2.16.

$$J_s = -\frac{P_s \Delta c}{l} \tag{2.16}$$

When choosing membrane materials, an empirical mass transport comparison between candidate films is usually pertinent and is conducted by measuring trans-membrane flux for a given pressure driving force for the solvent (or concentration driving force for the solute) or by calculating the permeability from flux and driving force information.

### *2.2.4 Pervaporation*

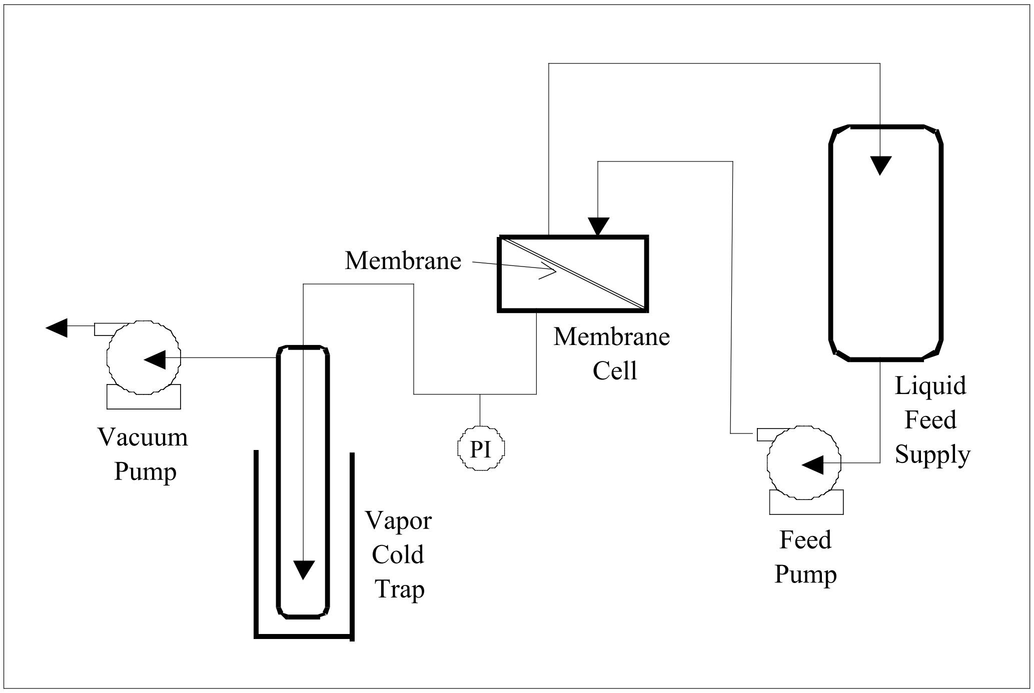
The pervaporation of a single-component liquid permeate through a membrane can be described by a simple three step mechanism. First, the liquid absorbs into the membrane, followed by diffusion of the liquid through the membrane, and finally, evaporation of the liquid phase penetrant as it exits the permeate side of the membrane. The driving force for the process is the difference between the vapor pressure of the pure water feed and pressure (vacuum) on the permeate side of the membrane. Figure 2.11 provides an illustration of an experimental membrane pervaporation test apparatus.

In analyzing the performance of a fluid-membrane system, the trans-membrane flux is of primary interest. The rate of flux ($J$) across the membrane is generally limited by diffusion of the liquid through the membrane that can be described by Fick's law,

$$J = -D\frac{dc}{dx} \tag{2.17}$$

where $D$ is the diffusivity (or diffusion coefficient), $c$ is the penetrant concentration in the membrane, $x$ is the membrane thickness, and $dc/dx$ is the concentration gradient across

Figure 2.11 – Membrane pervaporation transport test apparatus.



the membrane. The diffusion coefficient can be represented as a function of the infinite dilution diffusion coefficient ($D_0$), the plasticizing coefficient ($\tau$), and the concentration of the penetrant in the membrane or

$$D = D_0 e^{(t\,c)} \qquad 2.18$$

Substituting Equation 2.18. into Equation 2.17, separating and integrating across the membrane (thickness *l*) gives Equation 2.19,

$$J = \frac{D_0}{t\,l}\left(e^{(t\,c_s)} - e^{(t\,c_l)}\right) = \frac{D_0}{t\,l}\left(e^{(t\,c_s)} - 1\right) \qquad 2.19$$

or,

$$\frac{Jl}{D_0 c_s} = 1 + \frac{t\,c_s}{2} \qquad 2.20$$

where *l* is the membrane thickness, $c_s$ is the saturated liquid concentration of the feed side of the membrane, and $c_l$ is the concentration at the permeate side of the membrane (assumed to be zero at vacuum). In Equation 2.20 the flux relationship is simplified by expansion of the exponential term and neglecting the fourth term and higher. Given empirical flux and concentration data for the system, Equation 2.20 can be used to obtain $D_0$ and $\tau$ from a linear plot of $Jl(D_0Cs)^{-1}$ vs. $C_s$.[42,43,44]

Additionally, a relationship can be developed which gives the flux as a function of the trans-membrane pressure drop as shown by Equation 2.21

$$J = \frac{P(\Delta \mathrm{P})}{l} = \frac{DS(\Delta \mathrm{P})}{l}$$

2.21where $\Delta$P is the trans-membrane pressure differential (or feed vapor pressure less the permeate pressure), $P$ is the permeability, and $S$ is the solubility of the penetrant in the membrane. Equation 2.21 is developed from Fick's law (Equation 2.17) by equating the chemical potentials in the membrane at the feed and permeate interfaces.

Pure water perfluoro sulfonate pervaporation flux information is not available but can be extrapolated from aqueous flux data for two component (acetic acid and water) systems.[8] Kusumocahyo et al. (1999) gathered data for the dehydration of acetic acid through Nafion™ 117 ionomer film in the acid form. Their results showed that water flux through a perfluoro sulfonate film was approximately 2.5 kg $m^{-2}$ $h^{-1}$ at a downstream pressure of 0.5 torr for membranes with a water content of 20 %. The pure water diffusion and plasticizing coefficient for the acidified membrane were estimated to be $7\times10^{-5}$ $cm^2$ $s^{-1}$ and $3.14\times10^{-3}$ $cm^2$ $g^{-1}$, respectively. Pure water pervaporation data was not available for perfluoro carboxylate ionomer films.

### *2.2.5 Water Flux in Perfluoro Carboxylate and Sulfonate Polymers*

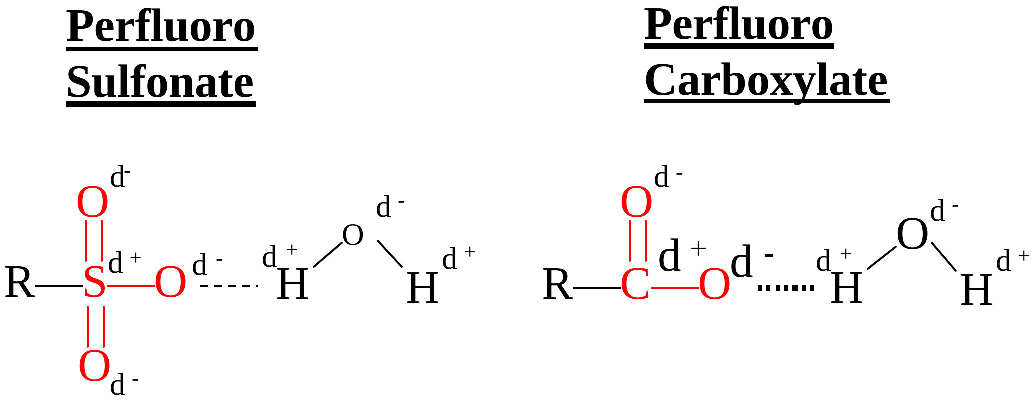
When perfluoro ionomer materials first caught the interest of membrane experimentalists, a number of studies were conducted in an attempt to explain why the observed water flux in pure perfluoro carboxylate and mixed carboxylate/sulfonate membranes was much lower than in similar pure perfluoro sulfonate polymers. To clarify, Boyle et al. (1982, 1983) determined that water diffusivities in pure perfluoro carboxylate and mixed carboxylate/sulfonate material were comparable to those in pure sulfonated Nafion™ product at similar membrane water content. The problem is that the hydration limit for the pure perfluoro carboxylate ionomer are approximately 50 % that of the content for similar sulfonate films, and with lower water solubility (or lower permeability), the water flux is expected to be lower. More specifically, the hydration of exchange sites (mole water per mole exchange site) for similar carboxylate and sulfonate terminated pendant chains was approximately 22 % lower for the carboxylate which is believed to be the predominant reason for the lower water saturation limits and permeabilities (Yeager et al., 1982). Blatt et al. (1988) attributed, at least in part, the reduction in total polymer hydration to an increased hydrophobicity in the ionomer perfluoro ethylene backbone phase of the carboxylate material when compared to the sulfonated polymer backbone. Yeager attributed the reduction in hydration in the carboxylate films to the increased hydrogen bond strength between the carboxylate hydroxyl oxygen and water hydrogen. Experimental results showed that the hydrogen-oxygen bond strength for the sulfonate ionomer (sulfonate hydroxyl) was 62 % of the pure water the hydrogen-oxygen bond strength, whereas the carboxylate film oxygen-hydrogen bond strength was determined to be approximately 92 % of that determined for pure water. One possible explanation is that in the difference in the hydrogen-oxygen bonding strengths for these two polymers is the result of inductive effects. In other words, in the sulfonate product the two-double bond sulfonate oxygens draw electrons from the sulfur which, in turn, draws the electrons from the hydroxyl oxygen creating the net negative charge on the hydroxyl oxygen. In the case of the carboxylate ionomer, only one-double bond oxygen is present to compete with the carbon atom for electrons thus the net negative charge on the hydroxyl oxygen is larger in comparison to that of the hydroxyl oxygen in the sulfonate terminated pendant chain (see Figure 2.12).

The observation made by Yeager et al. (1982) is also seen when comparing water saturated forms of different carboxylic acid and sulfonate acid materials when assuming both acid forms have the same substituent, as is nearly the case with the perfluoro sulfonate and carboxylate films. This is evidenced by comparing the acid/base equilibrium constant, or pKa, for triflic acid (trifluoromethane sulfonic acid) with that for trifluoroacetic acid (trifluoromethane carboxylic acid). These two acids contain the same trifluoro methane substituent and have pKas of -0.25 and -13.6 for the carboxylic and sulfonic acids, respectively. Such a dramatic difference between these constant values demonstrates that the extent of proton dissociation is much higher and thus water hydrogen-hydroxyl oxygen bond strength is much lower, for the sulfonic acid.

### *2.2.6 Nitric Acid Dehydration*

Dehydration of acid solutions using perfluoro sulfonate and composite perfluoro sulfonate/carboxylate ionomer films has been investigated for a number of mixtures including acetic acid, methanol/water and nitric acid.[2,7,8,38,42,44] Interest in both pressure and pervaporation dehydration for nitric acid has been expressed for a variety of reasons including low energy separation for the replacement of distillation and generation of highly concentrated acid (dehydration in order to break the nitric acid/water azeotrope).[1,3]

Figure 2.12 – Relative hydrogen bond strength between the hydroxyl oxygen and water hydrogen for perfluoro polymers.



**Perfluoro Sulfonate**

**Perfluoro Carboxylate**

Net negative charge on the hydroxyl oxygen in carboxyl group is larger in comparison to that of the hydroxyl oxygen in the sulfonate terminated pendant chain resulting in relatively higher hydrogen bond energy between the hydroxyl carboxylate oxygen and water hydrogen.

For both single and multi-component systems, permeate flux and permeability are characteristics used to evaluate a membrane's performance, and development of the transport equations for multi-component pervaporation is very similar to that for a single component system as detailed in the previous section if ideality is assumed. In a non-ideal system, the flux of component *i* is not only dependant on the component *i* permeability ($P_i$), but is also a function of the interaction between the components (described by a drag factor, $Q$) and the flux of the other components. If the solution is dilute or if the interaction between the components is small, as is the case with the nitric acid, the system can be assumed to be ideal.

Additionally, in a multi-component system, performance is determined by component separation efficiency ($\alpha$). The calculation of a component separation efficiency for a binary solution is principally a ratio of component concentration (ratios) in the permeate to those in the feed,

$$a = \frac{\left[ {}^{c_i}\!/\!_{c_j} \right]_{Permeate}}{\left[ {}^{c_i}\!/\!_{c_j} \right]_{Feed}} = \frac{\left[ {}^{p_i}\!/\!_{p_j} \right]_{Permeate}}{\left[ {}^{c_i}\!/\!_{c_j} \right]_{Feed}} \qquad 2.22$$

where *i* and *j* are each of the two components in the solution.[45] In general, relatively large separation efficiencies and permeate fluxes are optimal for a membrane separation unit operation. The flux, and to a lesser extent, the separation efficiency can be adjusted as required through the manipulation of physical characteristics such as membrane thickness (resistance). However, a trade-off is usually realized as when permeabilities (flux) increases, the separation factors generally decrease.

Nitric acid dehydration studies using pervaporation through perfluoro sulfonate/carboxylate composite films (Nafion™ 90209) were conducted by Sportsman (2002). Figure 2.13 illustrates the separation efficiency ($a$) and permeability ($P_w$) of feed solutions ranging from 10 to 80 wt% nitric acid at permeate side pressure of 8torr. The physical features of the composite ionomer film tested are illustrated by the SEM photo in Figure 2.2 and the diagram in Figure 2.14. Under the given conditions, permeate flux (permeability) appears to reach a maximum at approximately 30 wt% nitric acid, whereas maximum separation is seen at approximately 50 wt% nitric acid. Sportsman also demonstrated that the permeate flux and separation efficiencies were directly dependent on the permeate pressure. However, results indicated that permeate transport was nonexistent at permeate pressures below 8 torr, as the author speculated that transport through the membrane stops as the water content of the ionomer film reaches a minimum level.

Nafion™ perfluoro sulfonate 112 (and to a lesser extent, Nafion™ 115 and 117) ionomer films were also the subject of an investigation by Sportsman (2002) for the purpose of dehydration of acid feeds (2 wt% to 68 wt%) in high trans-membrane differential pressure systems. The thinner Nafion™ 112 polymer was chosen as the membrane to be examined for Sportsman's study as the membrane's thin profile maximized the permeate accumulation rate and thus the rate at which separation data was

Figure 2.13 – Nitric acid dehydration in Nafion™ 90209 (K form) using pervaporation at permeate pressure of 8torr (Adapted from Sportsman 2002).

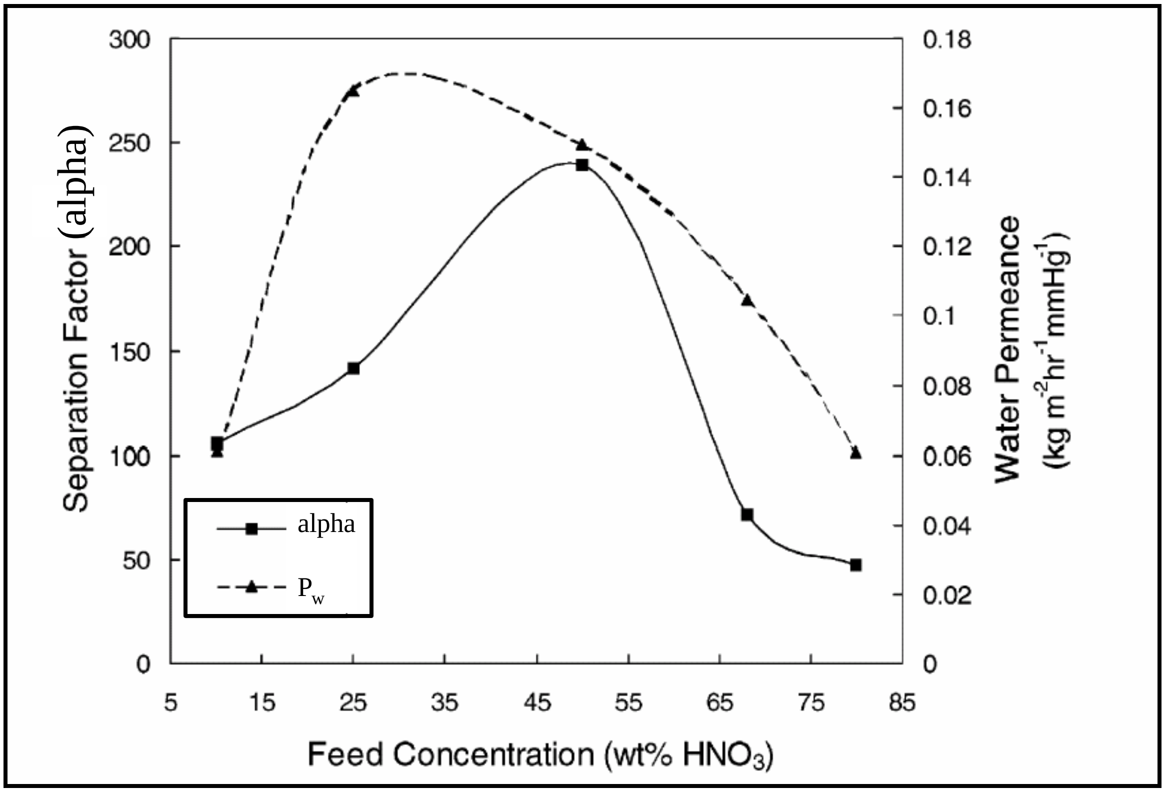
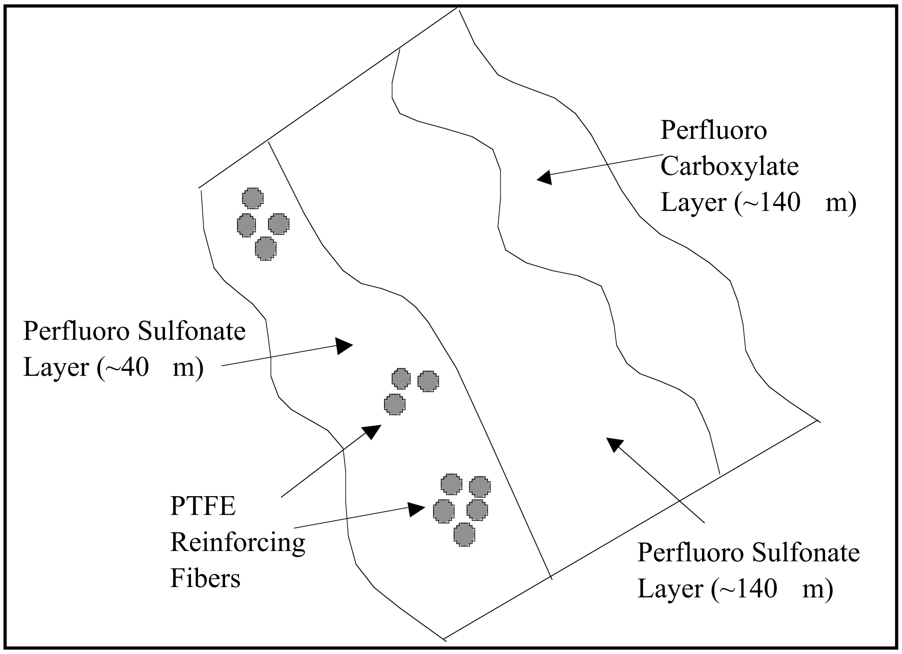
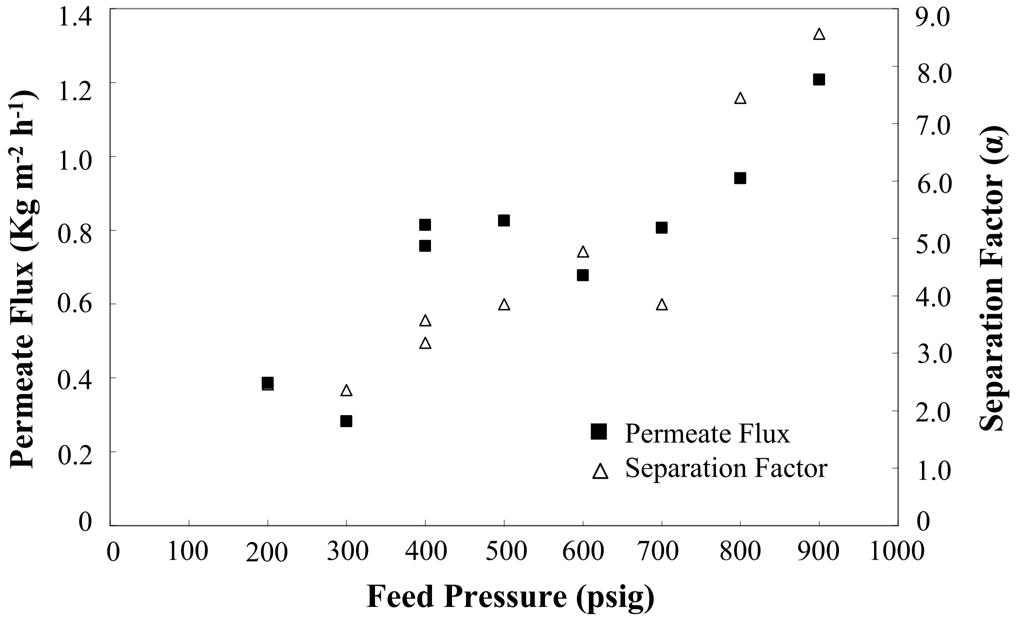


Figure 2.14 – Composite perfluoro sulfonate/carboxylate ionomer Nafion™ 90209.



obtained. Figure 2.15 shows both the permeate flux and separation factor for experiments conducted at various feed pressures. Permeate fluxes are lower but on the same order of magnitude as those for pure water feeds (Figure 2.10). Separation efficiencies $(a)$ increase in value from approximately 2.0 to 8.5 (Equation 2.22, where component $i$ is water and $j$ is nitric acid) when increasing the feed pressure from 200 to 900 psig, respectively.

Figure 2.15 Pressure dehydration of 2 % nitric acid in Nafion™ 112 (H form) at room temperature (Adapted from Sportsman 2002).



# 3.0 EXPERIMENTAL

## *3.1 Ionomer Film Generation*

Our primary objective for producing in-house perfluoro carboxylate films was to generate ionomer films that were much thinner than those available by either ionomer manufacturer (Du Pont or Asahi Glass) such that the films could be the subject of nitric acid dehydration studies. Preliminary pressure transport tests conducted with relatively thick, off-the-shelf Flemion™ (Asahi Glass) carboxylate ionomer membrane material ($K^+$ form, EW of 1.25 mmole eq.$^{-1}$, 162 μm thick) indicated that pure water permeation rates are too low to measure even at trans-membrane pressures up to 900 psig. Sportsman (1999) also discovered that permeate fluxes could not be measured through this film for pure water, 50 wt% or concentrated nitric acid feeds during pervaporation tests with permeate pressures of 8 torr.

### *3.1.1 Solution Cast (Solcast) Films*

Solution casting of perfluoro sulfonate films has been examined in detail and is well documented.[10,22,23] However, solution casting of perfluoro carboxylate films has not been demonstrated prior to this work. However, using reagents, equipment and procedures similar to those described by Moore et al. (1986), successful dissolution and casting of thin films from off-the-shelf Flemion™ carboxylate ionomer membrane material (K+ form, EW of 1.25 mmole/eq., 162 μm thick) was possible. The procedure consisted of dissolving the feed Flemion™ (Asahi Glass) in a 50:50 mixture of de-ionized (Milli-Q™ processed) water and propanol for 4 hours at 190 °C. The resulting solution was clear to slightly cloudy (colloidal) containing approximately 1 to 3 wt% ionomer. Dissolution was conducted at pressure in a Parr Instrument™ acid digestion bomb (model 4766) fitted with a custom made Teflon™ block liner. A cylindrical shaped void was machined from the Teflon™ block and the void was lined with a 60ml glass dissolution vessel. Dissolution operating parameters were based on Nafion™ studies conducted by Moore et al. (1986) yet dissolution temperatures, processing times, pressures, and dissolution solvent mixtures were varied prior to determining the optimal procedure (detailed in Appendix A).

Solution casting of perfluoro carboxylate films (solcast films) was conducted in a National Appliance Co. Model 5831, vacuum oven in three-3 hour stages (at temperatures of 100, 130 and 150 °C) at 1-2 in. Hg vacuum. The dissolved ionomer solution was mixed with a solvent having a boiling temperature above 130 °C (N,N$^1$-dimethylformamide, DMF), placed in a level, tempered glass, 7 cm diameter, flat-bottom casting vessel, and held at temperature and pressure until all of the solution was evaporated and the film appeared to be completely dry (stage three). Next, the casting vessel and film were removed from the furnace and the solcast film was hydrated and removed from the vessel by soaking in de-ionized water at 40 °C for 1 hour. The solcast films were then ion-exchanged to the desired form. Film thicknesses were easily varied by estimating the amount of material in solution needed and based on the density of the as received material.

### *3.1.2 Sulfonate and Mixed Film Fabrication (Chemical Conversion)*

Casting of perfluoro carboxylate ionomer films proved to be difficult and resulting films were of much lower quality, both physically and in terms of EW, when compared to those purchased from the manufacturer. Although all preliminary investigations were conducted with the solcast perfluoro carboxylate ionomer, a search was conducted for the purpose of finding an aqueous procedure that could be used to convert Nafion™ perfluoro sulfonate films to the carboxylate form of the ionomer. Based on information available in patent literature and mentioned in various journal articles, it was discovered that perfluoro carboxylate films are manufactured from the same perfluoro sulfonyl fluoride precursor as the sulfonate form (see section 2.1.1).[4,9,12,13,24] Given this information, we hypothesize that thin sulfonate and mixed sulfonate/carboxylate forms of the film could be made in house from the commercially available precursor films (Nafion™ R1100 films, 25 µm thickness) which are available from Du Pont. Early literature describes procedures that use severe fluorine gas environments to complete the oxidation from the precursor to the carboxylate but do not make any mention of aqueous techniques used to convert the perfluoro sulfonate film to the sulfinate form. However, to convert the perfluoro sulfonate film to the carboxylate form, Fujimura et al. published a procedure (Appendix A) using common aqueous reagents (HCl, $CCl_4$, HI, etc.).[10,24]

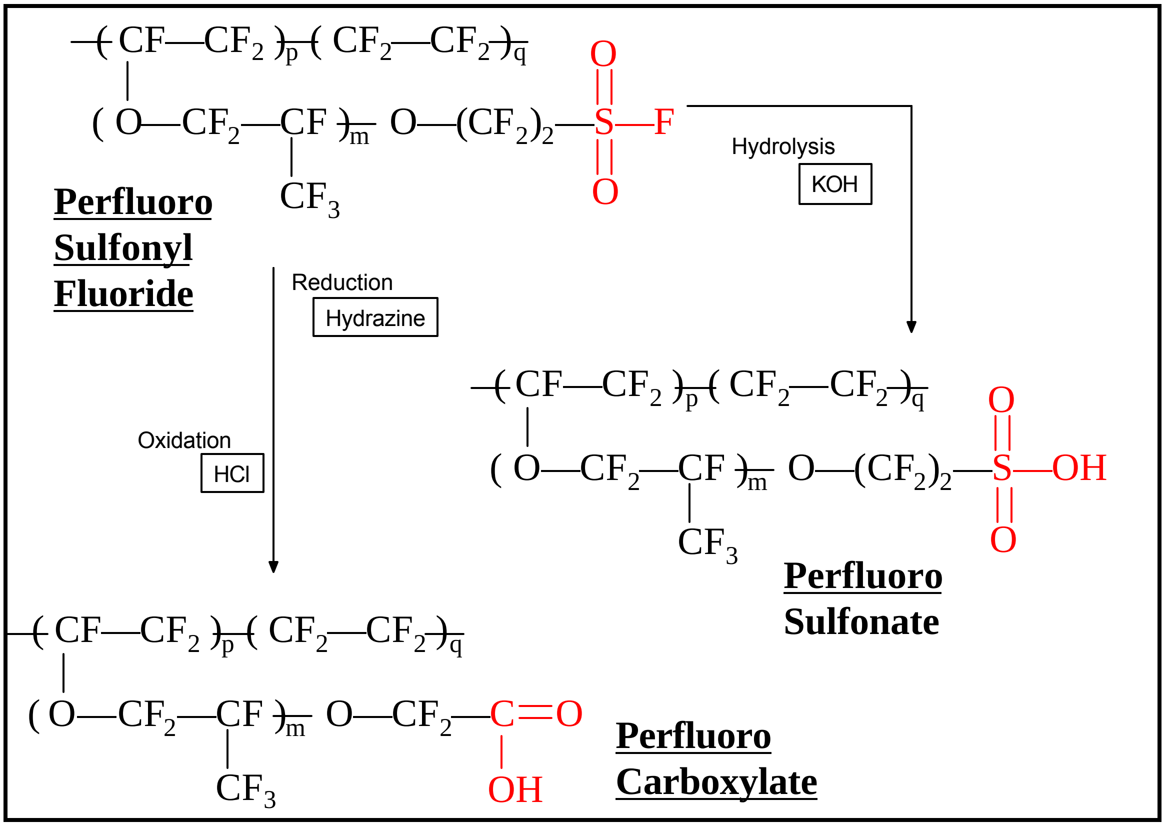
Subject matter experts agreed that the procedure was valid and, as a result, experimentation was initiated in order to determine if a quality, thin carboxylate ionomer film could be manufactured using this procedure. Our experimental success with the Fujimura procedure was limited resulting in partially converted mixed perfluoro sulfonate/carboxylate membranes; however, the procedure was very cumbersome so an alternative chemical conversion flow sheet was pursued.

The chemical conversion procedure used for second phase of the investigation was developed by Grot et al. (1985).[4] The procedure uses a two step conversion where the sulfonyl fluoride precursor is converted to the carboxylate form by first reducing the precursor pendant side-chain to the sulfinic acid then oxidizing it to the carboxylate terminated side-chain form. Additionally, the procedure specifies the production of a mixed film of the carboxylate and sulfonate form by first conducting an incomplete reduction of the sulfonyl fluoride, followed by hydrolysis of the remaining sulfonyl fluoride, and finally followed by the oxidation of the sulfinic acid groups to the carboxylate pendant side-chain. A brief illustration of the reaction mechanism is found in Figure 3.1 and details of the procedure are given in Appendix A.6.

## *3.2 Film Characterization*

Key to this study was the characterization of our materials prior to transport testing. Below is a description of characterization techniques used for both solution cast and mixed ionomer films.

Figure 3.1 – Chemical conversion flow (1985).[4]



### *3.2.1 Solution Cast (Solcast) Membrane Characterization*

A number of analytical techniques were used in the characterization of solution cast films. Analysis primarily included determining the ion exchange capacity (EW) using acid/base titration (Appendix A.2), morphology from small angle x-ray scattering (SAXS), and chemical makeup from Fourier transform infrared analysis (FTIR-ATR). Unless stated otherwise, analytical testing was conducted with hydrated solcast films in the hydrogen ($H^+$) form.

### *3.2.2 Mixed Ionomer Membrane Characterization*

Table 3.1 lists the fundamental analytical techniques that were used for chemical, morphological and general analysis of mixed ionomer films produced. As with the studies of the solcast membranes, a number of analytical techniques were used to determine characteristics of perfluoro sulfonate and carboxylate ionomer films. Primary analytical techniques used included acid/base titration (EW), nuclear magnetic resonance (NMR) (proton diffusivity), FTIR-ATR (chemistry), and SAXS (morphology).

Table 3.1 – Analytical techniques and information obtained.

| Analysis | Information to be obtained |
|---|---|
| Equivalent Weight (acid/base titration) | Ion-exchange capacity |
| Fourier Transform Infrared (FTIR-ATR) analysis | Chemical composition |
| Small Angle X-ray Scattering (SAXS) | Perfluoro backbone morphology |
| X-Ray Fluorescence (XRF) | Sulfonate to carboxylate ratio |
| Scanning Electron Microscopy (and SEM-EDS) | General physical characteristics and pendent chain morphology |
| Specific Ion Electrode – Nitrate/pH | Determination of nitrate flux and separation efficiencies. |

In addition, x-ray fluorescence (XRF) was utilized in the quantitative determination of the ratio between ionomer sulfonate and carboxylate pendent chains.

### *3.3 Pervaporation and Pressure Transport Experimentation*

Pure water and nitric acid transport testing was conducted in the pervaporation and pressure experimental systems described below.

#### *3.3.1 Pressure Transport*

The pressure transport apparatus used consisted of a syringe pump, a 1 inch diameter Millipore™ membrane cell with a needle valve down stream of the cell to control retentate flow, a ball valve upstream of the pump, two check valves to control directional flow and a permeate vessel for permeate collection. Components included Swagelok stainless steel valves and tubing, and an ISCO™ Model 500D syringe pump with an ISCO™ series D pump controller. The system is shown in detail in Figure 3.2. and operating procedures are described in Appendix A-4.1.

#### *3.3.2 Pervaporation Transport*

Pervaporation experimental runs were performed according to the procedures detailed in Appendix A.4.2. Figure 3.3 shows the pervaporation apparatus used to collect permeation data. The system consisted of a 316 stainless steel feed reservoir fitted with stainless steel or Teflon™ hardware, a Fluid Metering, Inc (FMI) feed pump and

Figure 3.2 – Pressure transport system flow.

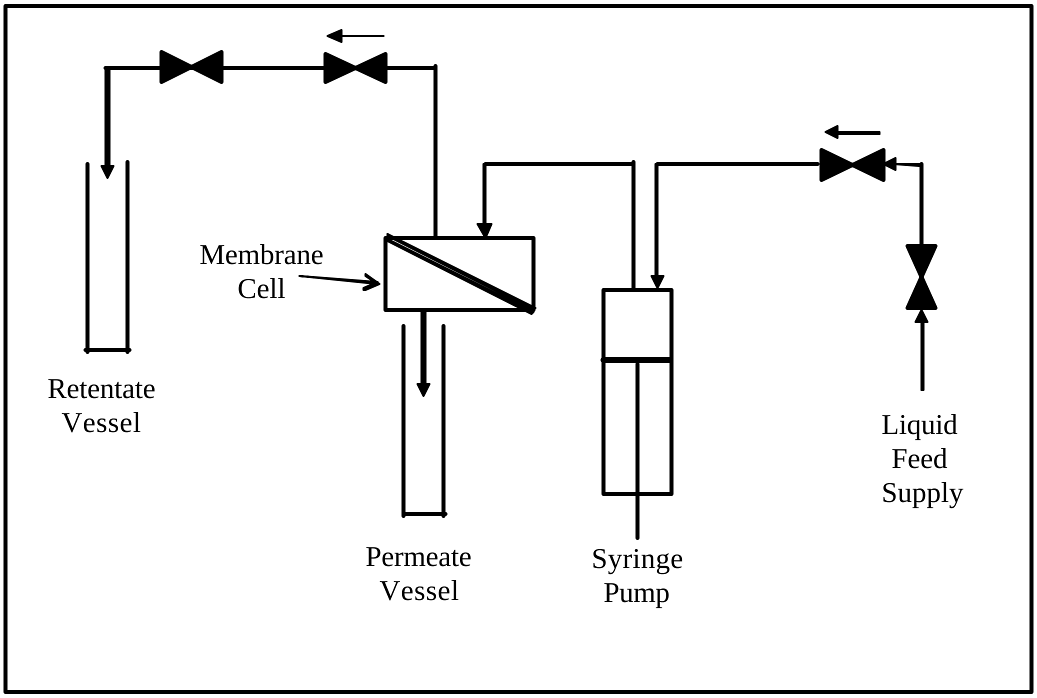
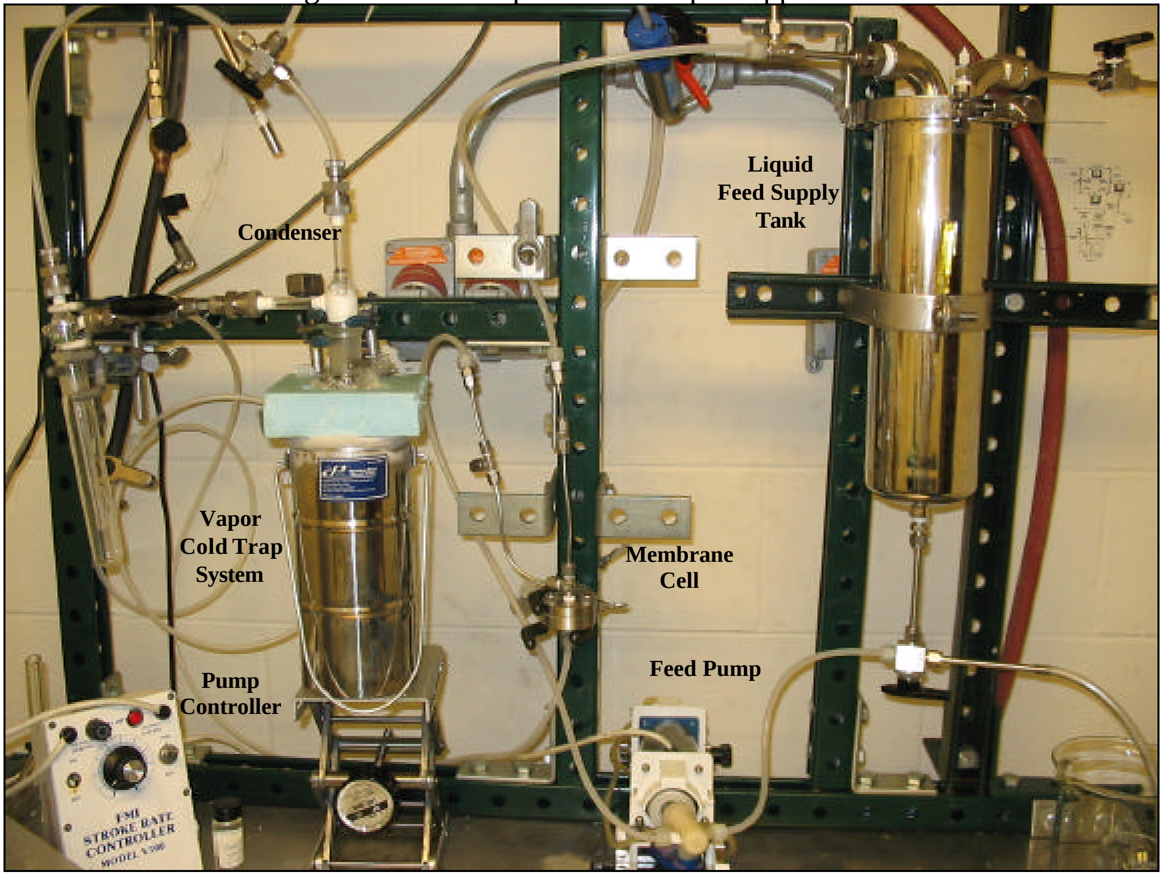


Figure 3.3 – Pervaporation transport apparatus.



controller, a 1 inch diameter Millipore™ membrane cell, a glass condenser cooled with liquid nitrogen, a Welch Duo Seal™ vacuum pump, and a permeate-side pressure transducer and Grandville-Phillips model 275 analog pressure gauge. Nitrate ion concentrations were determined using an Orion™ nitrate ion specific electrode system.

### *3.4 Analytical Equipment Utilized*

Fourier transform infrared spectroscopy in the attenuated total internal reflectance mode (FTIR-ATR) was used to collect spectra for the ionomer films. FTIR was immediately available and extremely useful in determining the extent of conversion, as well as specific pendant chain composition. Data were collected using a ThermoNicolet™ Nexus 670 system with a KBr beam splitter, a high sensitivity mercury cadmium telluride (MCT) detector, and KRS-5 (thallium bromide iodide) ATR crystal. Spectra were measured in the range of 650 to 4000 $cm^{-1}$ and liquid nitrogen was used to cool the detector to required operating temperatures.

Small angle x-ray scattering analysis was accomplished for the purpose of determining the polymer backbone cluster morphology of our films. The SAXS system consisted of a Kratky small angle instrument with a Rigaku rotating copper anode x-ray generator having $\lambda$ = 0.15418 nm. Perfluoro ionomer samples were hydrated and sealed in a polyethylene envelope (substrate) in order to maintain the film in the hydrated form. Perfluoro ionomer film scans were adjusted by removing the baseline scan of the polyethylene envelope material, accounting for the film thickness, and normalizing the absolute intensity of the beam with scans collected with and without the sample prior to and after a given SAXS run.

Scanning electron microscopy (SEM) was used to view the edge of film samples for the purpose of determining if the technique could be used to distinguish between perfluoro sulfonate and perfluoro carboxylate ionomer material. Valuable data were developed for the Nafion™ 90209 composite membrane but the technique was not useful in characterizing solution cast or in-situ conversion films.

Thermal gravimetric analysis was performed to assist in determining if a correlation existed between membrane type and water evaporation temperature for the perfluoro sulfonate and carboxylate films. The TGA system used for analysis consisted of a Seiko (serviced by Thermal Haake Inc.) model TG/DTA 220.

Nitrate ion concentrations were determined using an Orion™ nitrate ion specific electrode model 9307, and a model 9002 reference electrode in conjunction with a model 290A multi-purpose meter. Procedures for use of the nitrate ion specific system are found in Appendix A

X-ray fluorescence analytical determination of mixed ionomer membrane compositions was accomplished by Chemistry Division personnel at LANL facilities. The x-ray excitation and detection was performed using an EDAX Eagle II XLP micro-x-ray fluorescence system equipped with a Rh target excitation source and a SiLi detector (EDAX, Mahwah, NJ). The x-ray source was equipped with a polycapillary focusing optic (X-ray Optical Systems, Albany, NY).

# 4.0 SOLUTION CAST PERFLUORO IONOMER FILMS

## *4.1 Solution Cast Film Characterization*

The goal of the study of solution cast membranes was to determine the ability of solution cast perfluoro carboxylate ionomer membrane films to dehydrate nitric acid feed solutions. Characterization of materials was useful in attempting to explain film behavior and for comparison with results from previous investigations.

### *4.1.1 General Characterization*

Fundamental characteristics such as film thickness, counter ionic form, and equivalent weight are selected before choosing a particular perfluoro sulfonate membrane for a given application. The solution cast films generated during these studies were also inventoried using these basic properties and are summarized in Table 4.1. The equivalent weights were determined using a titration technique where materials were pretreated by boiling in 1.0M nitric acid for 4 hours, rinsed three times with de-ionized water, soaked in 0.01M NaOH (or KOH) for 24 hours at 40 °C, and finally, titration of the NaOH solution with $HNO_3$. The EW of the material could then be calculated based on the NaOH required to neutralize the acid form of the polymer. On average, solution cast film equivalent weights decreased, when compared to the as received feed material, from $1.25\pm0.03$ to $0.69\pm0.32$ meq. $g^{-1}$. One possible explanation for this result is that the alcohol solvent/ionomer side-chain reaction was not completely reversible using our procedures. Figure 4.1 provides evidence that an isopropyl ester form of the ionomer side chain exists as the FTIR spectra signature for C-H bond stretching is seen in peaks near 2960 and 2850 $cm^{-1}$.[13]

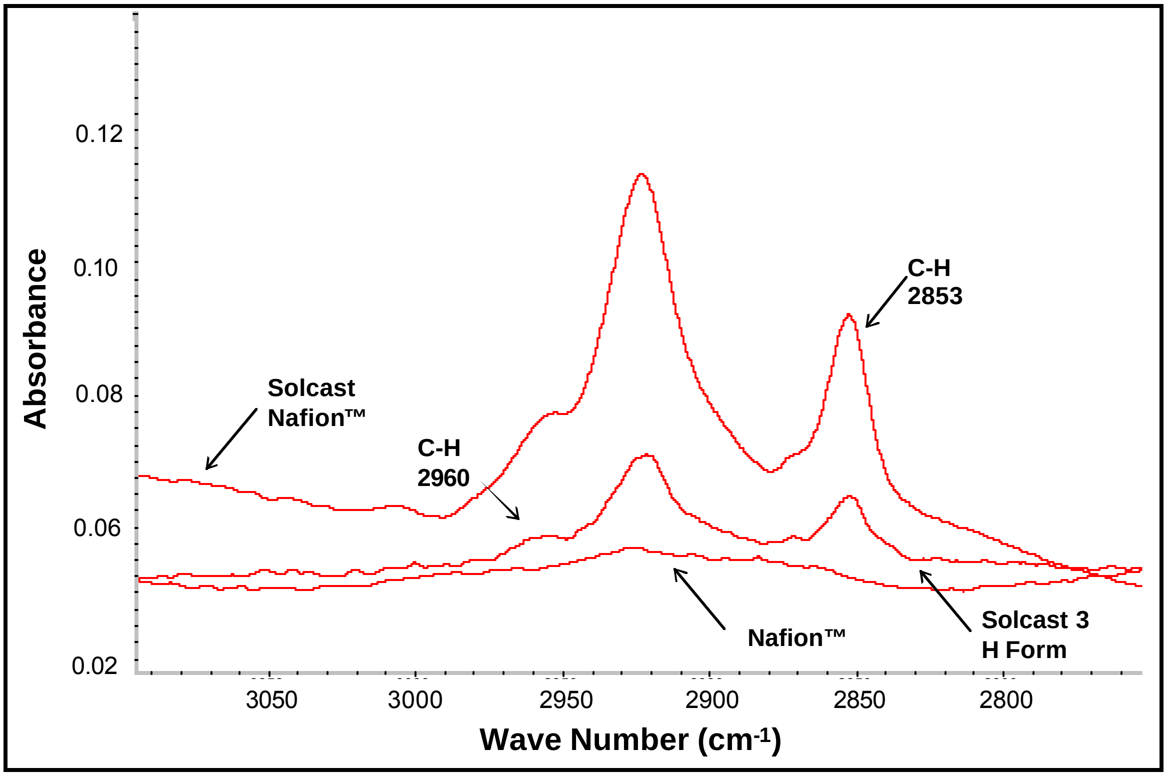
Water sorption measurements were determined as part of the procedure used to obtain the EW and results indicated that the average solcast polymer material water content (10.2 wt%) was slightly higher than that for the as received Flemion™ material (8.0 wt%).

Table 4.1 – Perfluoro carboxylate solcast ionomer film general characterization data.

| Sample | EW (meq $g^{-1}$) | Film Thickness (μm) | Water Sorbed in $H^+$ Form (wt%) |
|---|---|---|---|
| Virgin Flemion™ 1 | 1.25±0.03 | 162 | 8.0±0.1 |
| Solcast 1 | - | 11-43 | - |
| Solcast 2 | - | 20-120 | - |
| Solcast 3 | - | 10-180 | - |
| Solcast 3a | 0.58±0.26 | - | - |
| Solcast 3b | 0.16±0.02 | - | - |
| Solcast 4 | - | 25-40 | - |
| Solcast 4a | 0.16±0.02 | - | 9.3±0.1 |
| Solcast 4b | 0.41±0.06 | - | 5.4±0.3 |
| Solcast 5 | - | 20-100 | - |
| Solcast 5a | 0.78±0.02 | - | 5.2±0.1 |
| Solcast 5b | 0.53±0.02 | - | 7.0±0.1 |
| Solcast 6 | - | 20-150 | - |
| Solcast 6a | 0.69±0.03 | - | 9.8±0.1 |
| Solcast 6b | 1.4±0.15 | - | 8.4±0.1 |
| Solcast 7 | - | 20-60 | - |
| Solcast 9 | - | 15-50 | - |
| Solcast 10 | - | 110-230 | - |
| Solcast 11 | - | 30-50 | - |
| Solcast 12[a] | 0.70±0.02 | 80-230 | 28±0.1 |
| Solcast 13[a] | 0.86±0.01 | 250-400 | 20±0.1 |
| Solcast Average | 0.69±0.32 | - | 10±4.7 |

a. Films cast from water/methanol solutions. All other films cast using water/propanol solutions.

Figure 4.1 – Perfluoro carboxylate solcast 3 and Nafion FTIR comparison (dry $H^+$ form).



A range of film thicknesses were produced by varying the ratio of Flemion/water/isopropanol starting solution and the DMF before drying. Continuous films were required for both pressure and pervaporation transport experiments and it was initially difficult to generate the defect-free product. Heating the solution quickly or evaporating the solution at an increased vacuum (greater than 2 in. Hg) resulted in perforated cast membranes, but as the casting procedure evolved, the methodology needed to produce defect-free product was discovered. The final evolution of the casting procedure required that the solution be heated in three-3 hour stages (at temperatures of 100, 130 and 150 °C) under 1-2 in. Hg vacuum, in a flat-bottom casting vessel, and in a level oven.

### *4.1.2 Small Angle X-ray Scattering*

Solution cast perfluoro carboxylate ionomer films were subjected to small angle x-ray scattering (SAXS) tests in order to investigate basic material morphology. Shown in Figure 4.2 are curves for membrane solcast 6, dried at 130 °C, and for the same film (solcast 6A) following treatment at 150 °C. The SAXS data illustrates how the polymer structure was annealed at the higher drying temperature of 150 °C as the crystalline structure scattering maxima is only observed in solcast 6A. The lack of the characteristic crystalline shoulder in the SAXS data for the solcast material dried at the lower temperature, and the absence of a clear ionic cluster peak for both materials, is in agreement with SAXS data for the Flemion™ perfluoro carboxylate polymers indicating the existence of a similar crystalline structure in the solution cast films.[29] Further analysis of solcast 6A (Figure 4.3) shows the possibility of a second feature at approximately 1.2 $nm^{-1}$ to be discussed in detail below. From the peak locations of the solution cast film SAXS data shown in Figure 4.2 and 4.3 and using Equation 2.4, the crystalline feature is estimated to have dimensions of approximately 18 nm in diameter.

Two additional models were used to estimate feature sizes using the SAXS data generated for the solcast 6A ionomer films: The Guinier equation linear model (low angle linear model from the radius of gyration), and the uniform sphere model.[46,47,48] For the low-angle linear model, the radius of gyration is determined from the slope of linear sections of SAXS data when plotting ln($I(q)$) vs. $q^2$ (Equation 4.1)

$$I(q) = I_0 e^{\left[-q^2 R_g^2 / 3\right]} \qquad 4.1$$

where $I(q)$ is the x-ray intensity, $R_g$ is the radius of gyration, and q is the angular variable. The radius ($R$) of the spherical feature can then be calculated from the radius of gyration for spherical homogeneous bodies (Equation 4.2).

$$R = \sqrt{\frac{5}{3} R_g^2} \qquad 4.2$$

The polymer crystalline feature of membrane Solcast 6 was modeled by the Guinier equation (data curve section shown in Figure 4.2) and results indicate that the crystalline feature is approximately 9nm in diameter.

Figure 4.2 – SAXS data from perfluoro carboxylate solcast 6.

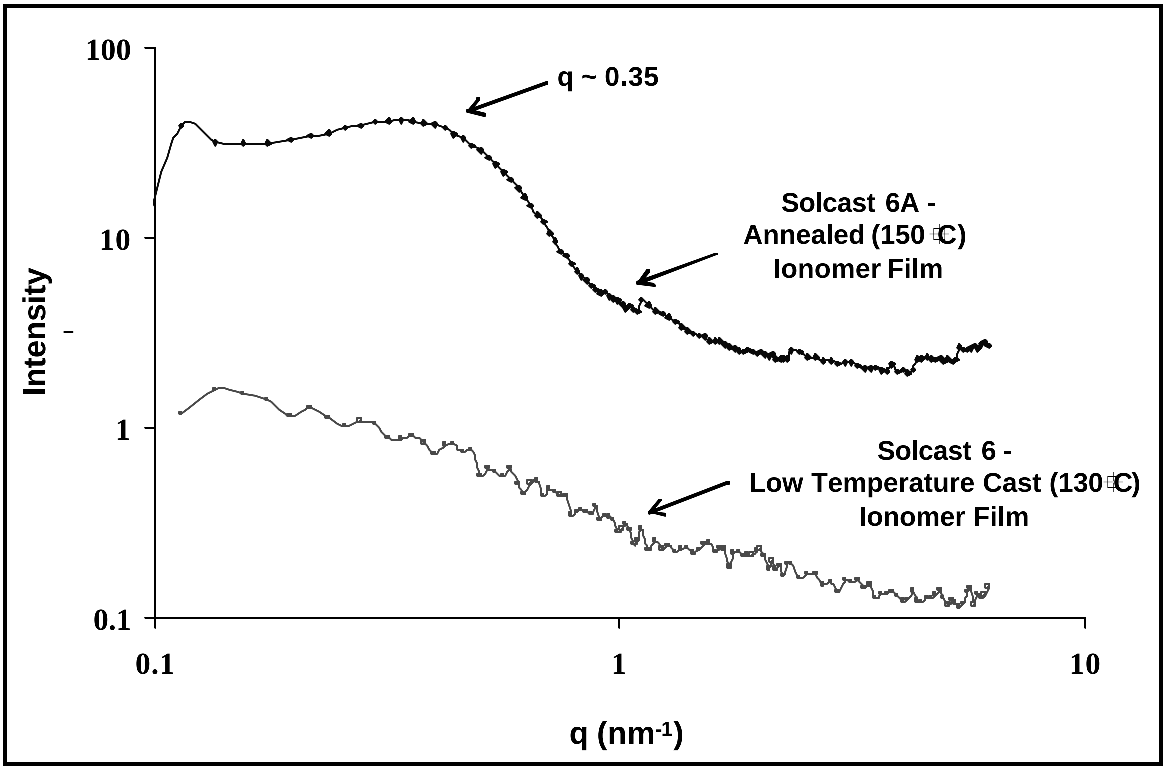
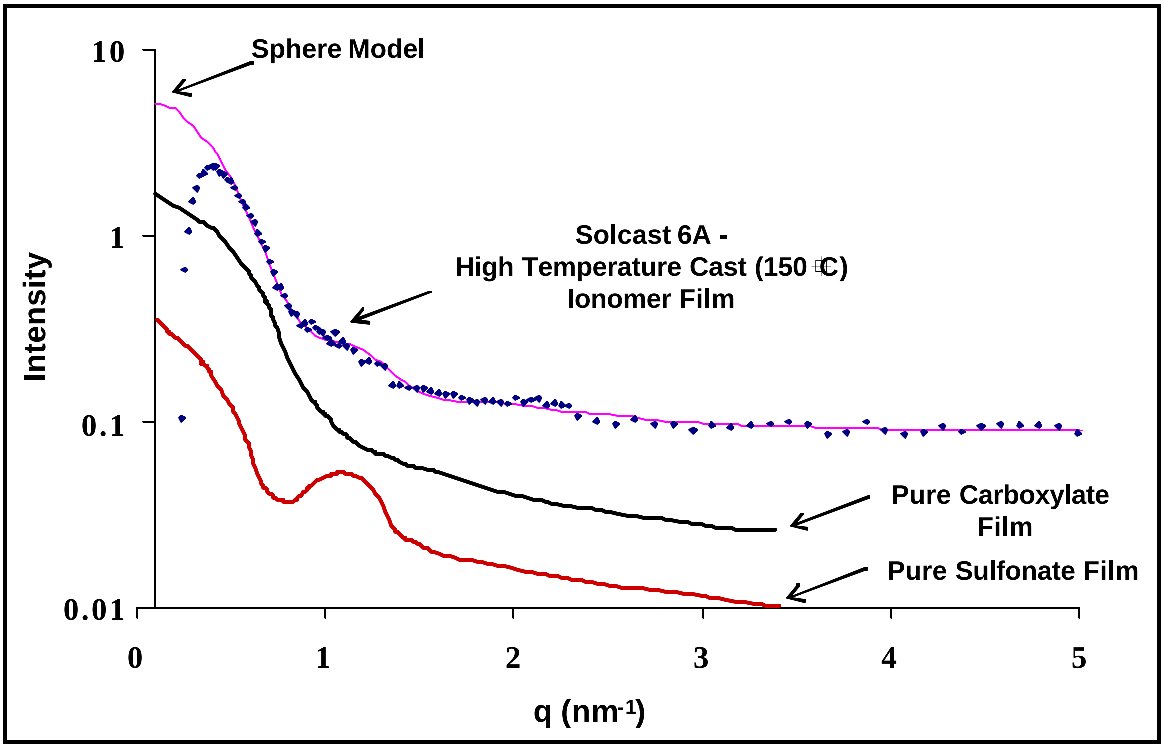


Figure 4.3 – SAXS data modeling.



Additionally the uniform sphere model was used to evaluate solution cast SAXS data. The methodology behind the model is to generate an x-ray scattering intensity curve from the cumulative curves of the radii from different homogeneous features. Equation 4.3 shows the formula used to calculate a curve for a sphere of a given radius

$$f^2(qR) = 9\left(\frac{\sin(qR) - (qR)\cos(qR)}{(qR)^3}\right)^2 \qquad 4.3$$

where $f(qR)$ is defined as the normalized scattering amplitude and is shown in Equation 4.4.

$$f(qR) = 3(qR)^{-3}[\sin(qR) - qR\cos(qR)] \qquad 4.4$$

Equation 4.5 details the corrected intensity ($I(q)$) where $I_m(q)$ is the raw intensity data for the given run, $I_d$ is the dark intensity (closed shutter), $I_s(q)$ is the scattering intensity of the substrate (polyethylene envelope), $m_f t_f$ is calculated from the ratios of the beam intensities for the direct beam through the sample film ($P_o exp(m_f t_f)$) and the direct beam through the background ($P_o exp(m_b t_b)$), and $P_o$ is the absolute direct beam intensity.

$$I(q) = \frac{[I_m(q) - I_d] - [I_s(q) - I_d]\exp(-m_f t_f)}{P_o m_f t_f \exp(-m_f t_f - m_b t_b)} \qquad 4.5$$

For comparison, two additional curves are shown in Figure 4.3 illustrating scattering data for typical pure perfluoro carboxylate and pure sulfonate polymer materials. The solid curve atop solcast 6A data shown in Figure 4.2 represents the uniform sphere model fit for Solcast 6 SAXS data and results indicate that a second feature occurs with dimensions between 2 and 5 nm, with the crystalline shoulder indicating a feature dimension of 9-10 nm in diameter. The smaller feature can be explained as representing the cluster feature, suggesting that some of our solution cast membranes contain a small percentage of sulfonate terminated pendent chains resulting in a small number of ionomer cluster features (and verified by FTIR spectroscopy, section 4.1.3). Table 4.2 summarizes the size-relative percentages of these features as indicated by the uniform sphere model.

Table 4.2 – Feature Size Distribution for Uniform Sphere Model

| Feature Diameter (nm) | Relative Percentage (%) |
|---|---|
| 2 | 17.5 |
| 5 | 20 |
| 9 | 30 |
| 10 | 32.5 |

### *4.1.3 Fourier Transform Infrared Spectroscopy*

Fourier transform infrared spectral analysis has been a vital tool in determining the chemical structure of perfluoro sulfinic, sulfonic and carboxylic ionomers for the last two decades. Recently, Perusich (2000) conducted a detailed analysis of Du Pont (long side chain) and Asahi Glass (short side chain) carboxylate films using this technique. For our analysis, FTIR-ATR spectra were collected for the potassium form of the “as received” Asahi Glass Flemion™ material and for solcast films. Both Asahi Glass Flemion™ materials and solcast spectras contain the same peak information as the Asahi Glass and DuPont material (Figure 4.4, methyl form) spectra generated by Perusich noting that all spectra peaks are skewed low for the solution cast films. These results are summarized in

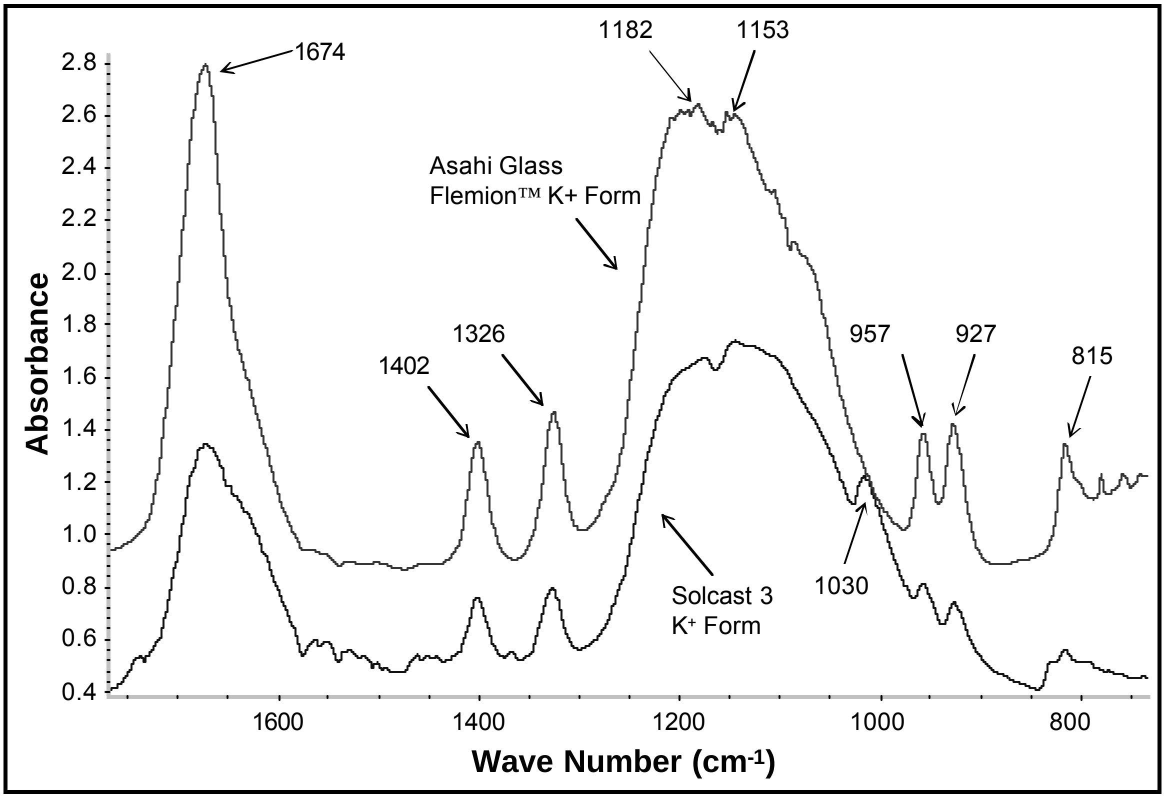
Figure 4.4 and a direct comparison is shown in Table 4.3. Results indicate that peak positions for both our dissolution feed material and the solcast films confirm the presence of carboxylate terminated side chains as hypothesized. For example, the peaks at 1674 and 1402 cm$^{-1}$ have been assigned to –C=O and –O-K groups, which confirms the presence of carboxylate terminated side chains.

Table 4.3 – Ionomer film FTIR comparison.

| Asahi Glass Feed Film (cm$^{-1}$, K$^+$ Form) | Solcast 3 Film (cm$^{-1}$, K$^+$ Form) | Perusich (2000) Asahi Glass Film (cm$^{-1}$, Methyl Form) | Nafion 115 Solution cast Film (cm$^{-1}$, H$^+$ form) | Peak Assignment |
|---|---|---|---|---|
| - | 2970 and 2850 | - | 2970 and 2850 | C-H stretch in $–CO_2CH(CH_3)_2$ And $–SO_3CH(CH_3)_2$ (proposed) |
| - | - | 2968 and 2860 | - | C-H stretch in $–CO_2CH_3$ |
| 1674 | 1674 | 1676 | - | C=O in $-CO_2K$ |
| 1402 | 1402 | 1408 | - | O-K in $-CO_2K$ |
| 1326 | 1327 | - | 1305 | $SO_3^-$ |
| 1182 | 1175 | 1200 | 1202 | C-F Bands |
| 1153 | 1144 | 1152 | 1142 | C-F Stretch |
| 957 | 957 | 1025 | - | C-O-C |
| - | 1026 | - | 1058 | $SO_3^-$ |
| 927 | 926 | 984 | - | C-O-C |
| 815 | 815 | 816 | 815 | $CF_2$ |
| - | - | - | 608 | $-SO_2F$ |

In addition, spectra from solcast 3 recast materials contain peak information at approximately 1030 and 1326 cm$^{-1}$ which suggests that small amounts of sulfonate terminated side chains might be present in the carboxylate material. Grot et al. (1985)

Figure 4.4 – Solcast 3 and Asahi Glass Flemion™ FTIR comparison (dry K$^+$ form).



and Boyle et al. (1983) speculate that carboxylate polymers converted from the perfluoro sulfonyl fluoride precursor always contain a trace of the sulfonate terminated pendent chains as seems to be the case with the solcast 3 membrane.

### *4.2 Solution Cast Membrane Transport Experimental Results*

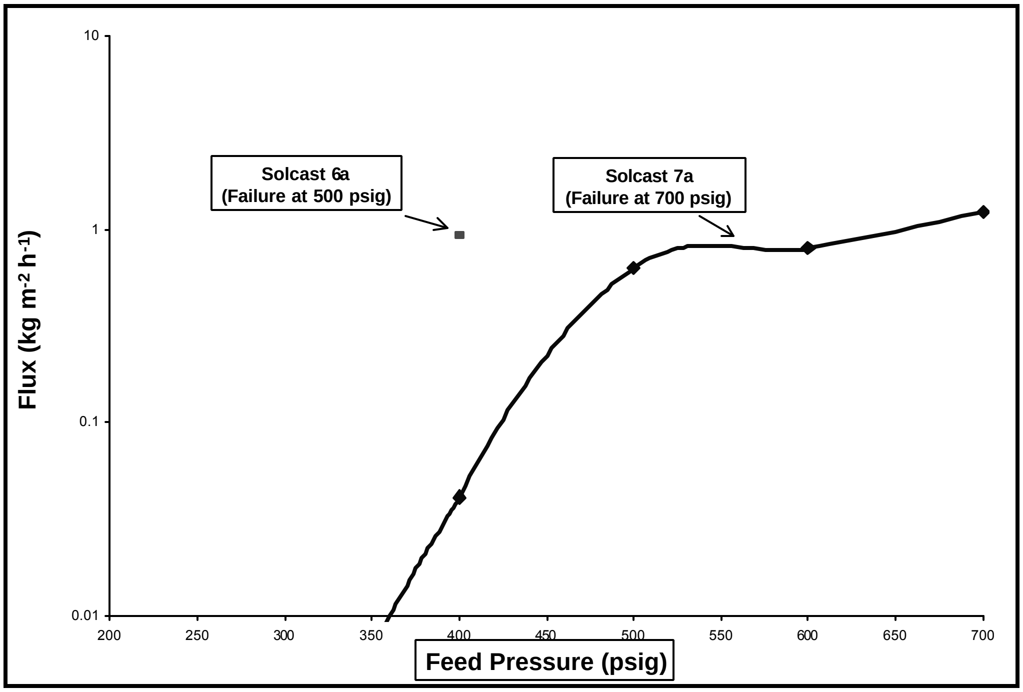
### *4.2.1 Pressure Transport*

A primary goal of our research was to generate solution cast membranes that were robust and could endure transport tests at low trans-membrane pressure driving forces (pervaporation) as well as large pressure differentials. A number of membranes were generated and tested, and seven films survived trans-membrane pressures to 200 psig, one to 500 psig (solcast 6a) and one to 700 psig (solcast 7a). Figure 4.5 shows pure water flux data for solcast 6a and 7a as a function of trans-membrane pressure. Pure water flux results show that the flow was non-existent at pressures below 300 psig after which fluxes increased dramatically with Solcast 7a showing a flux of approximately 1 kg $m^{-2}$ $h^{-1}$ at 700 psig. In comparison, Nafion™ 111 fluxes ranged from 0.6 to 2.2 kg $m^{-2}$ $h^{-1}$ for pressures ranging from 100 to 400 psig and membrane failure was consistently seen at pressures between 400 and 500 psig.

### *4.2.2 Pervaporation Transport*

Pervaporation transport tests were performed with both perfluoro carboxylate solcast and perfluoro sulfonate Nafion™ 111 material in the $H^+$ form and pretreated as described

Figure 4.5 – Solution cast film pure water pressure transport data at 25 °C.



in Appendix A. Nafion™ 111 was chosen for comparison because the product's thickness was similar to that of the solcast film examined. Nafion™ 111 had a membrane thickness of 25 μm as compared to 10-20 μm for the solution cast polymer films. Figure 4.6 illustrates the influence of the nitric acid feed composition on the total (or water) pervaporation flux and water separation factor for the two perfluoro membranes. Experimental results show that the flux for solution cast film solcast 3 was approximately two orders of magnitude lower than that for the perfluoro sulfonate ionomer, with carboxylate water fluxes ranging from 0.002 and 0.02 kg/m$^2$-h. Water separation efficiencies for the solution cast membrane was determined to be more than one order of magnitude larger than for the Nafion™ offering much smaller nitrate ionic permeability than the Du Pont sulfonate polymer. Specific separation efficiencies are detailed in Table 4.4. Figure 4.6 shows a maximum for both water separation and total flux at approximately 20 wt% nitric acid. Typically, similar plots for pure sulfonate membranes in binary systems show a steady decrease in flux (as well as separation factor) as the chemical potential is decreased with increasing nitric acid concentration. However, Sportsman (1998, 2002) demonstrated that the Nafion™ 90209 film also realized maximums in water permeance and water separation factors at 25 and 50 wt% nitric acid, respectively (see Figure 2.13). Sportsman attributes the maximums to non-idealities in the nitric acid/water/membrane system and experimental error.

Figure 4.6 – Solcast and Nafion™ 111 pervaporation data at 25 °C.

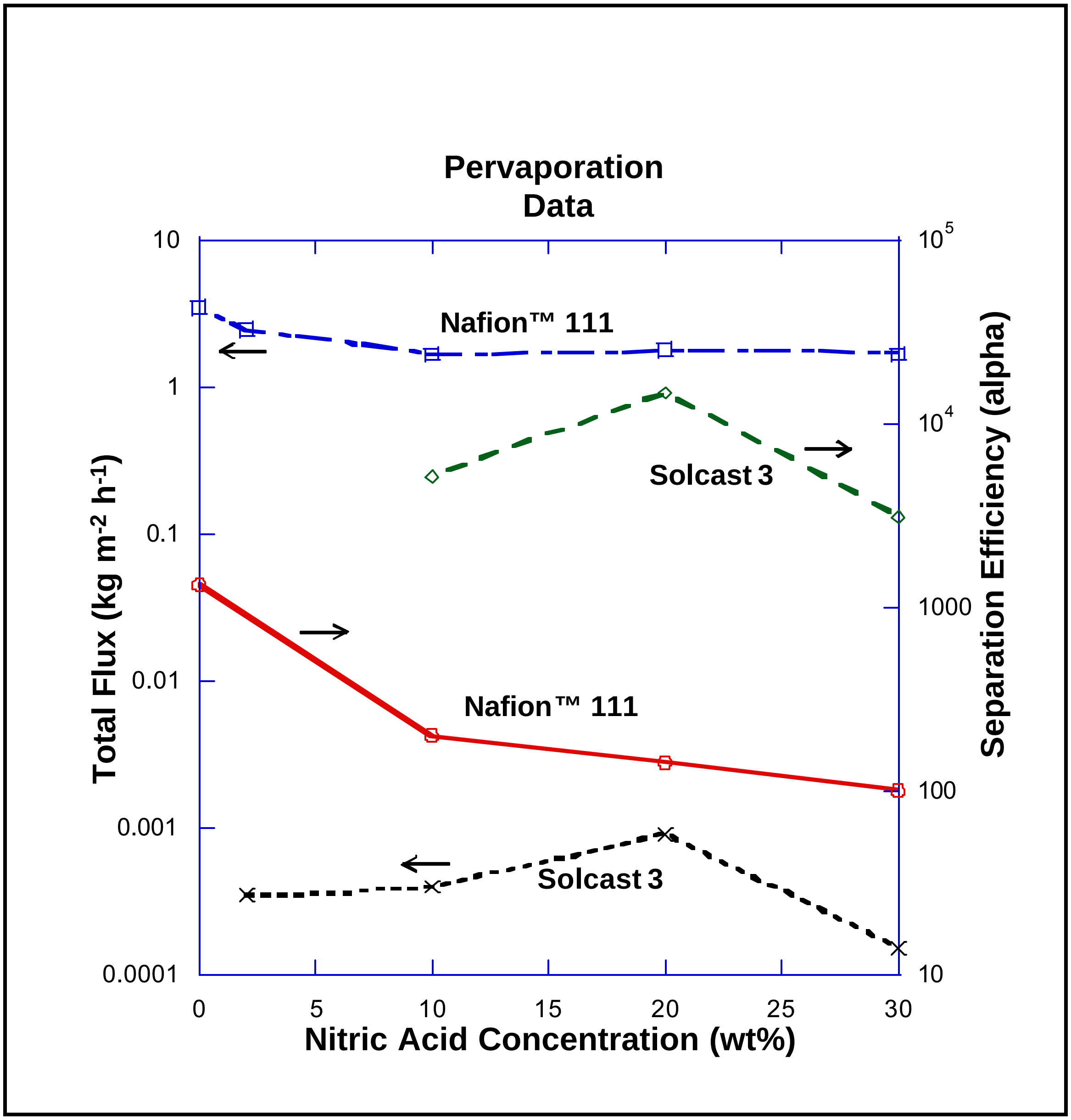


Table 4.4 – Ionomer film nitric acid separation efficiencies ($\alpha$).

| Nitric Acid Concentration (wt%) | Solcast 3 Separation Efficiency ($\alpha$) | Nafion™ 111 Separation Efficiency ($\alpha$) |
|---|---|---|
| 2 | - | 26.9 |
| 10 | 425 | 29.7 |
| 20 | 1736 | 58.2 |
| 30 | 714 | 14.0 |

Sportsman (2002) investigated the nitric acid transport properties for the perfluoro sulfonate/carboxylate ionomer film Nafion™ 90209 and predicted permeate flux and permeabilities for the carboxylate layer when combining experimentally demonstrated data for pure sulfonate material with his data. Based on transport modeling, he hypothesized that the water separation efficiency ($\alpha$) of the carboxylate layer was approximately two orders of magnitude higher than the sulfonate layer in the sulfonate/carboxylate composite membrane. When comparing solution cast transport property results to predicted perfluoro carboxylate ionomer film (Sportsman, 2002) properties, permeabilities for the solcast membrane were approximately one order of magnitude lower for 10 wt% nitric acid feed solutions. Although trends for both the Du Pont composite carboxylate layer and the solcast ionomer show an increase in water separation factor when compared to the sulfonate material, differences between the predicted and actual permeability data suggest that the morphology of the solution cast membranes are significantly different than that for the carboxylate layer in the Nafion™ 90209 composite films manufactured by Du Pont.

### *4.3 Summary*

Information was developed with an emphasis on the generation of thin solution cast films, characterization of the material, and dehydration of nitric acid using the thin perfluoro carboxylate ionomer polymers. Results showed that water fluxes for solution cast films were non-existent at pressures below 300 psig, which was consistent with data for thick, unmodified films produced by Asahi Glass™, after which fluxes increased dramatically then leveled to approximately 1.0 kg $m^{-2}$ $h^{-1}$. Nitric acid dehydration pervaporation results showed that water separation efficiencies ($\alpha$) for the solution cast films were more than one order of magnitude larger than for the Nafion™ ionomer films confirming predictions that the perfluoro carboxylate offers a higher water selectivity than the sulfonate material.[1,2,11,32,33] Differences between predicted water separation factors and actual results indicate that a difference in film morphology exists between solcast films and the perfluoro carboxylate layer in Nafion™ 90209 composite films.[1,2]

Primarily three analytical techniques were employed in characterizing the solution cast membranes during the investigation: Determination of equivalent weight (EW) using acid/base titration, analysis of the structure of the crystalline matrix with SAXS, and determination of chemical composition using FTIR-ATR. Solution cast film equivalent weights were relatively low (a result of the esterification of our solution cast films during the casting process) as cast polymer EWs averaged 0.69 meq. $g^{-1}$ when compared to 1.25 meq. $g^{-1}$ for unmodified perfluoro carboxylate films.

A review of SAXS information indicated that solcast films contained the characteristic crystalline structure scattering maxima for perfluoro carboxylate films. However, the crystalline structure was only observed at the higher drying temperature of 150 °C demonstrating the material's annealing characteristics, which is in agreement with SAXS scattering data for Nafion™ sulfonate solution cast ionomers generated by Moore et al. (1988) and identical to that for perfluoro carboxylate films from the manufacturer tested by Fujimura (1981). Evaluation of SAXS data using the uniform sphere model indicated that a feature may be present with a spherical diameter between 2 and 5 nm. If this feature does exist it could be explained as representing the cluster feature indicating that solution cast membranes contain sulfonate terminated pendent chains resulting in a small number of perfluoro sulfonate ionomer cluster features.

Both Asahi Glass Flemion™ materials and solcast FTIR-ATR spectra data contain the same peak information as the Asahi Glass and DuPont material spectra generated by Perusich (2000) confirming the presence of carboxylate terminated side chains in the solcast material as hypothesized. In addition, peak information exists indicating the presence of an ester form of the carboxylate terminated side chain which could possibly explain the reduction of EW resulting from the solcast dissolution and casting process.

# 5.0 MIXED PERFLUORO IONOMER FILMS FROM NAFIONÔ R1100

During experimentation with films synthesized using the Grot conversion procedure, results verified that the thin sulfonate and mixed ionomer materials could be produced from commercially available films, demonstrated nitric acid dehydration using the conversion products, and provided fundamental film morphological and chemical characterization. The core hypothesis of this research was based on the outcome of solution cast studies in that the solcast effort demonstrated a significant increase in nitric acid system water separation factors for perfluoro carboxylate membranes in comparison to those for similar perfluoro sulfonate films. Additionally, the hypothesis for the mixed ionomer was expanded to demonstrate that trans-membrane flux and separation efficiencies are a function of the ratio between sulfonate and carboxylate terminated side chains for mixed perfluoro sulfonate/carboxylate ionomer membranes.

Two synthesis techniques were used where thin perfluoro carboxylate/sulfonate ionomer films were made from Nafion™ perfluoro products. First, Nafion™ 111 (perfluoro sulfonate) was treated using a procedure developed by Fujimura et al. (1981).[24] Although this procedure was successful in converting the perfluoro sulfonate film to the sulfonyl form from which the product was generated, the treatment was expensive both in terms of resources and time. The second technique or procedure, developed by Grot et al. (1985), where Nafion™ R1100 sulfonyl fluoride sheet material was used as the precursor, was also successful in producing the desired product and proved to be simple in comparison to the Fujimura procedure. Therefore, the second procedure was adopted as the standard for our work (Appendix A.6).

### *5.1 Mixed Film Characterization*

Characterization of the mixed films was accomplished using the same techniques as utilized for the solution cast films. However, additional analytical techniques were employed to provide information such as the carboxylate to sulfonate terminated pendent chain ratios (x-ray fluorescence) for the purpose of proving or disproving our hypotheses.

### *5.1.1 General Characterization*

Perfluoro ionomer film thickness, water sorption, and equivalent weight (EW) characteristics were used to inventory the mixed films produced during these studies, and are listed in Table 5.1. Equivalent weights (meq. $g^{-1}$) were determined using a titration technique where films were pretreated by boiling the material in 1.0M nitric acid, rinsed with Milli-Q™ water, soaked in 0.01 M KOH, and finally, the EW was determined following titration of the KOH solution with $HNO_3$ (Appendix A.2). On average, mixed ionomer film EW compared well with the pure perfluoro sulfonate material where sulfonate and mixed film equivalent weights were determined to be 0.91 and 1.06 meq.-$g^{-1}$, respectively. Water sorption measurement results showed that the average perfluoro sulfonate/carboxylate polymer water content (9.3 wt%) was significantly lower than that for the unprocessed Nafion™ 111 material (23 wt%) and slightly higher than the as received Flemion™ ionomer film (8.0 wt%). All films were examined in the acid ($H^+$) counter-ion form.

Table 5.1 – Mixed ionomer film general characterization data.

| Sample | EW (meq $g^{-1}$) | Water Sorbed in $H^+$ Form (wt%) |
|---|---|---|
| Flemion™ | 1.25* | 8.0±0.1 |
| Nafion™ 111[19,44] | 0.91 | 23.0* |
| Grot 2ab | 0.84±0.07 | 7.1±0.3 |
| Grot 2bb | 0.93±0.06 | 7.6±0.3 |
| Grot 2cb | 1.05±0.14 | 3.1±0.6 |
| Grot 2db | 0.85±0.08 | 4.7±0.4 |
| Grot 5ab | 0.97±0.07 | 11.8±0.3 |
| Grot 5bb | 1.04±0.10 | 10.2±0.4 |
| Grot 6ab | 0.80±0.09 | 6.9±0.4 |
| Grot 7ab | 1.29±0.11 | 7.9±0.5 |
| Grot 7bb | 1.32±0.07 | 12.8±0.3 |
| Grot 8ab | 1.19±0.07 | 11.5±0.3 |
| Grot 9ab | 0.85±0.06 | 11.4±0.2 |
| Grot 9bb | 0.88±0.08 | 12.1±0.3 |
| Grot 10ab | 1.08±0.11 | 12.5±0.5 |
| Grot 10bb | 0.99±0.07 | 8.1±0.3 |
| Grot 11ab | 0.98±0.08 | 8.8±0.3 |
| Grot 11bb | 1.25±0.08 | 9.8±0.4 |
| Grot 12ab | 1.34±0.07 | 10.7±0.3 |
| Grot 12bb | 1.38±0.07 | 9.7±0.3 |
| Grot Film Average | 1.06±0.10 | 9.3±1.1 |

*Manufacturer equivalent weight data or water sorption data.

### *5.1.2 Fourier Transport Infrared Characterization*

Fourier transform infrared spectroscopy analysis (FTIR) was useful in qualitatively and semi-quantitatively determining the ratio of carboxylate to sulfonate terminated pendant chains in the mixed ionomer films. Using the relative absorbance intensities for peaks at approximately 1790 $cm^{-1}$ (carboxylate pendant side-chains) and 1060 $cm^{-1}$

(sulfonate terminated side-chains), it was determined immediately following the conversion process whether an individual run had generated the desired product. Additionally, if the conversion was incomplete perfluoro sulfonyl fluoride groups would be present and a peak would be observed at 608 $cm^{-1}$. Figure 5.1 provides complete example spectra for Nafion™ 111 and the Grot 8ab ionomer films. Figure 5.1.a shows that Nafion™ 111 contains only the sulfonated pendant chain indicated by the lack of a peak at 1790 $cm^{-1}$, whereas Figure 5.1.b illustrates the presence of both the carboxylate and the sulfonate side-chain for mixed ionomer film Grot 8ab. Figure 5.2 shows the focused spectra for four membranes with varying carboxylate content. This illustration clearly demonstrates the increase in intensity of the peak at 1790 $cm^{-1}$ (and subsequent decrease in intensity of the sulfonate peak at 1060 $cm^{-1}$) as the carboxylate content increases. For this example the Grot films can be arranged by increasing carboxylate content as 7ab<12bb<5ab<6ab, which has been verified quantitatively by XRF analysis.

### *5.1.3 Carboxylate Content (X-ray Fluorescence Characterization)*

Relative amounts of carboxylate and sulfonate terminated pendant chains were determined quantitatively in the mixed ionomer films using x-ray fluorescence (XRF). By chemically converting the ionomer material to the alkali salt form, potassium in this procedure, both the cation and sulfur constituent content was determined. The basis for calculating side-chain ratios included the assumptions that each potassium cation was associated with a single anion pendant chain, and that potassium cations not associated

`Figure 5.1 – Direct transmission FTIR of dried ionomer films: a. Pure sulfonate pendant side-chain Nafion™ 111, b. high carboxylate mixed film Grot 8 ab.

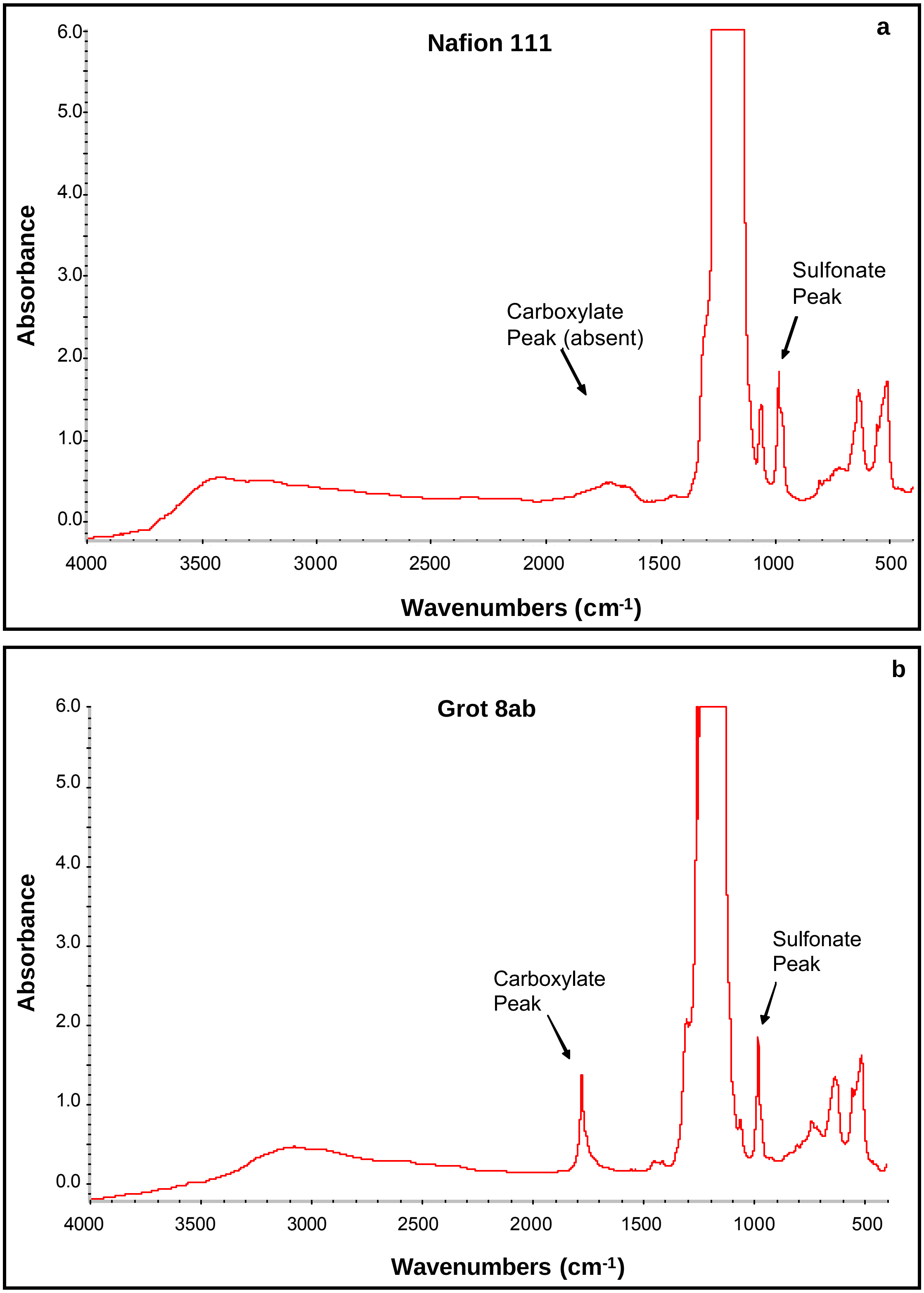
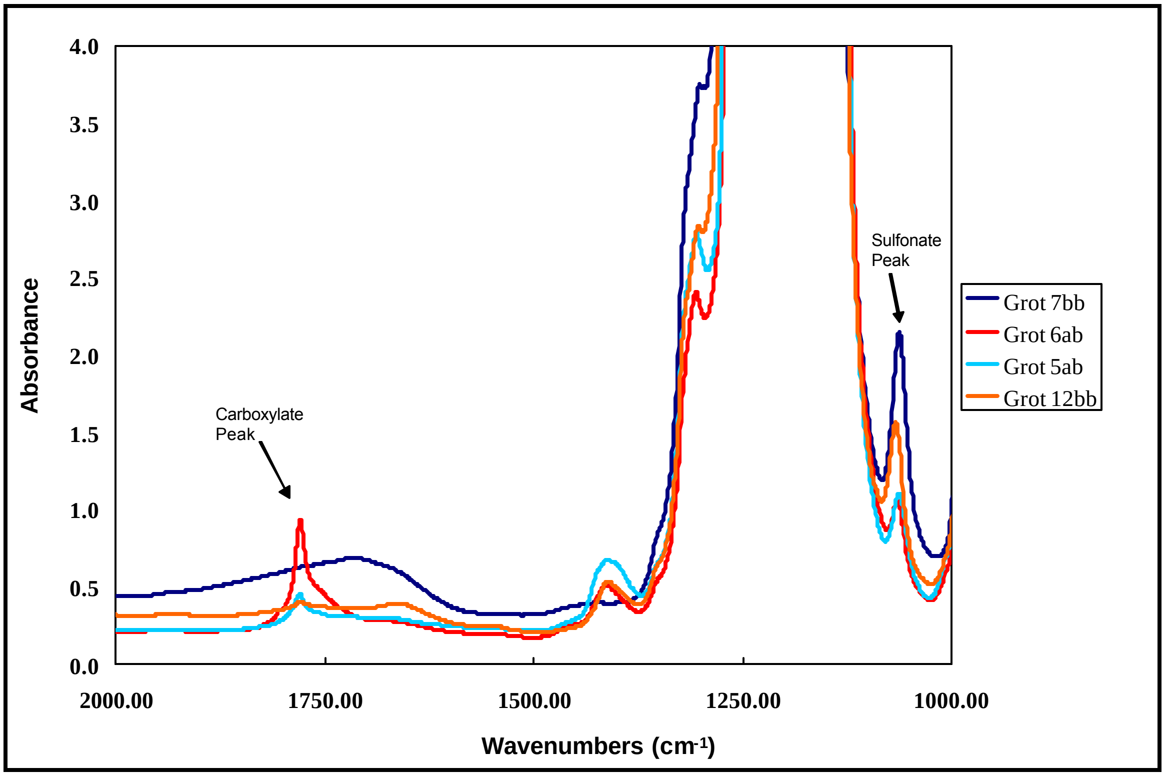


Figure 5.2 – FTIR intensity comparison for dry sulfonate and mixed carboxylate/sulfonate films.

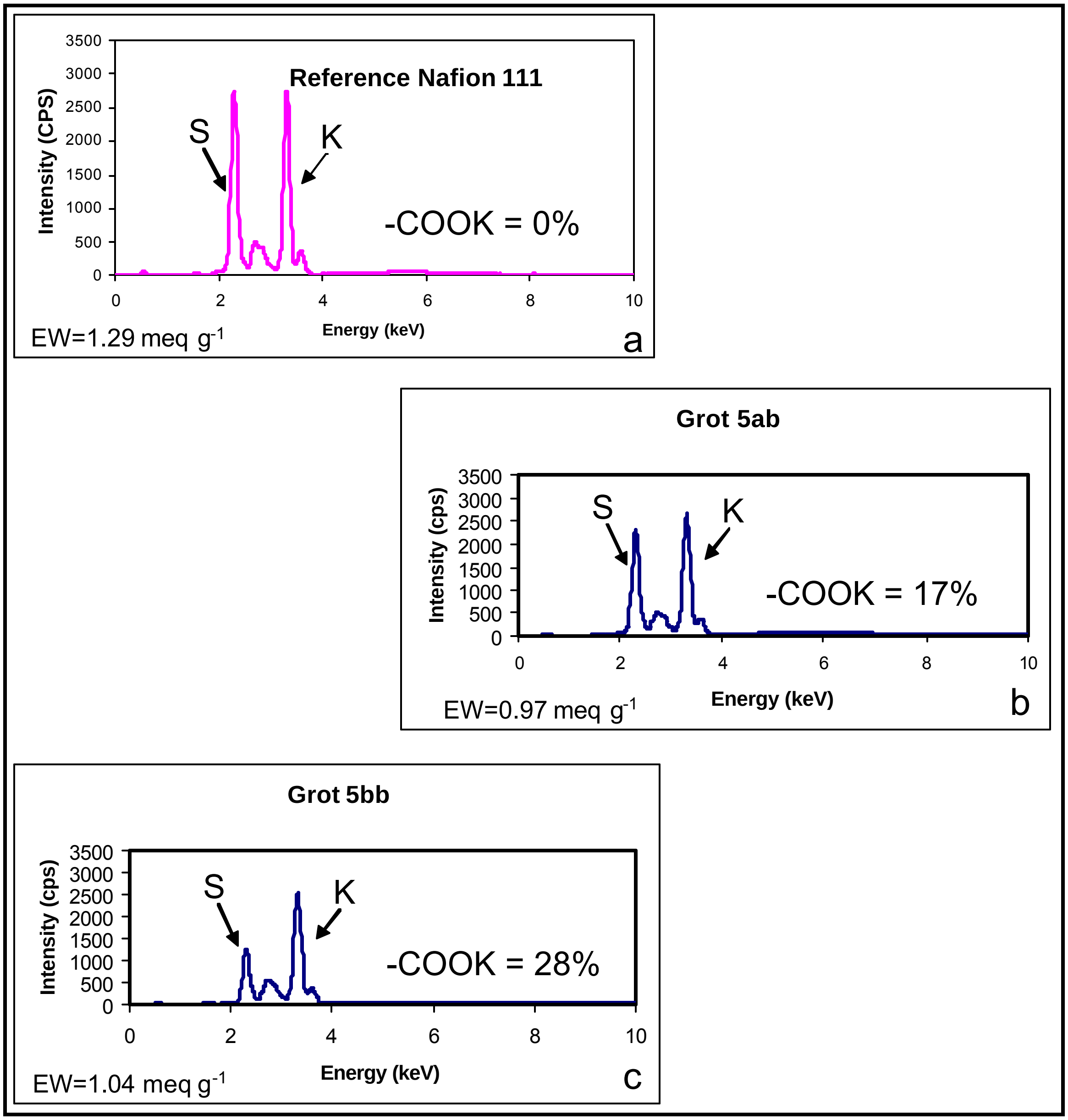


with the sulfur were associated with a carboxylate terminated side-chain.[11] An adjustment, or signal strength correction, was necessary for intensity variations between sulfur and potassium in the reference sulfonate materials. Figure 5.3 shows the XRF spectra for the dried Nafion™ 111 reference (Figure 5.3.a) and dried mixed ionomer samples Grot 5ab (Figure 5.3.b) and Grot 5bb (Figure 5.3.c). Carboxylate pendant chain content was calculated using Equation 5.1

$$\text{Mole }\%\left[-COOK\right]=\frac{I_K-(I_s)C_R}{I_K}\times 100 \qquad 5.1$$

where $I_K$ is the intensity of the sample potassium signal, $I_S$ the intensity of the sulfur signal, and $C_R$ the signal strength correction factor ($C_R = 1.17$) for the potassium based on reference sulfonate membranes Grot 7ab and 7bb. Figure 5.4 shows visual images of 50mm$^2$ (~8 × 6mm) samples for mixed ionomer films Grot 5ab and 5bb. The images have been enhanced such that darker colors (blue to black) show the lack of the sulfur or potassium, whereas lighter colors (orange to yellow) show higher concentrations of the particular element being measured. For example, comparing the image in Figure 5.4.a to the image in Figure 5.4.c, one can observe that the sulfur content in polymer Grot 5ab is higher than that for film Grot 5bb as indicated by the lighter color of the image for Grot 5ab. In addition, the images also illustrate the uniformity of the conversion process. When examining image 5.3.d one can interpret film Grot 5bb as having very uniform potassium content represented by the homogeneous color relative to that resulting from sample Grot 5ab. A summary of mixed ionomer membrane carboxylate pendant chain

Figure 5.3 – X-ray fluorescence spectra for reference and mixed ionomer films.

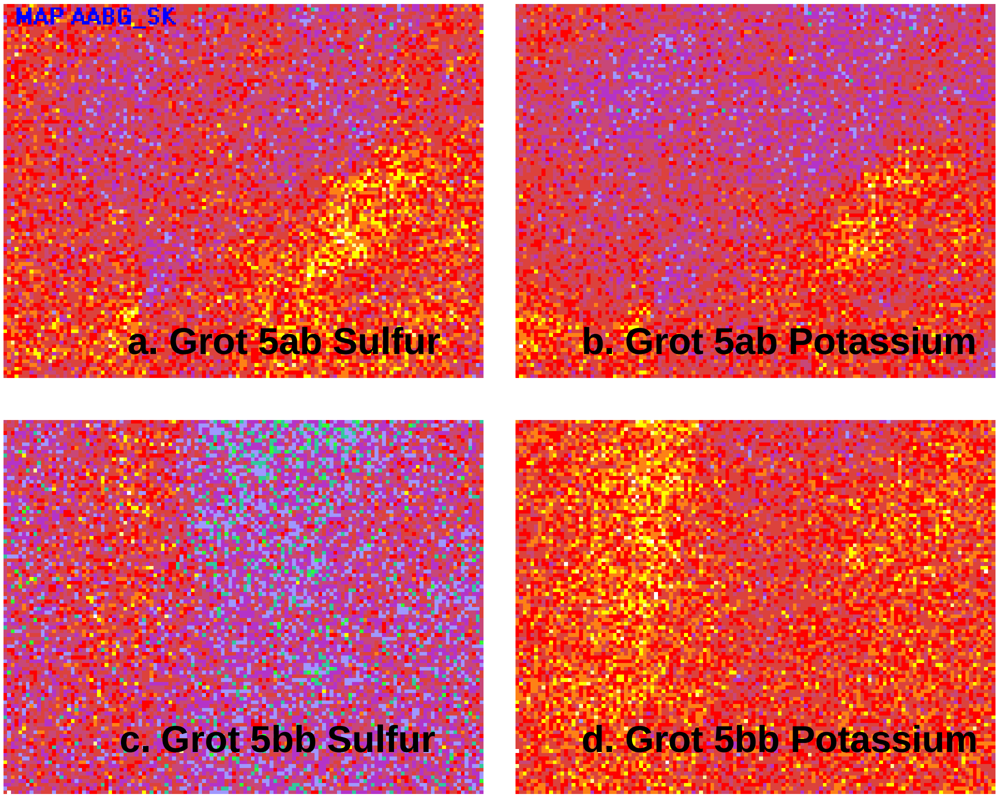


Reference Nafion 111

Grot 5ab

Grot 5bb

Figure 5.4 – Visual images of Grot 5ab (17mole% carboxylate) and Grot 5bb (28mole% carboxylate) XRF spectra.



a. Grot 5ab Sulfur

b. Grot 5ab Potassium

c. Grot 5bb Sulfur

d. Grot 5bb Potassium

content calculated using Equation 5.1 is given in Table 5.2. Results indicate that use of the procedure developed by Grot et al. (1985) allowed us to generate films with as much as 71 mole% and as little as 3mole% carboxylate pendant chain. However, the Grot conversion films always contained a significant quantity of the sulfonated pendant chain. A comparison was made between carboxylate pendant chain content determined by XRF and the content determined by FTIR, and an excellent correlation was found between the results from the two analytical techniques as is shown in Table 5.2.

Table 5.2 – Carboxylate content of conversion films as determined by XRF and FTIR.

| Sample | Carboxylate Content By XRF (mole%) | Carboxylate content by FTIR (mole%)* |
|---|---|---|
| Flemion™ | ~100 | ~100 |
| Nafion™ 111[20,49] | 0 | 0 |
| Grot 2ab | 23 | - |
| Grot 2cb | 15 | - |
| Grot 5ab | 17±13 | 25 |
| Grot 5bb | 28±6 | 31 |
| Grot 6ab | 41±5 | 38 |
| Grot 7ab | 0 | 0 |
| Grot 7bb | 0 | 0 |
| Grot 8ab | 53 | - |
| Grot 9ab | 3.0±3 | 4 |
| Grot 9bb | 13 | - |
| Grot 10ab | 32±7 | 30 |
| Grot 10bb | 71±2 | 75 |
| Grot 11ab | 0 | 0 |
| Grot 11bb | 5.0 | 0 |
| Grot 12ab | 3.4 | 0 |
| Grot 12bb | 10±3 | 5 |

*Error in curve fitting less than 8%.

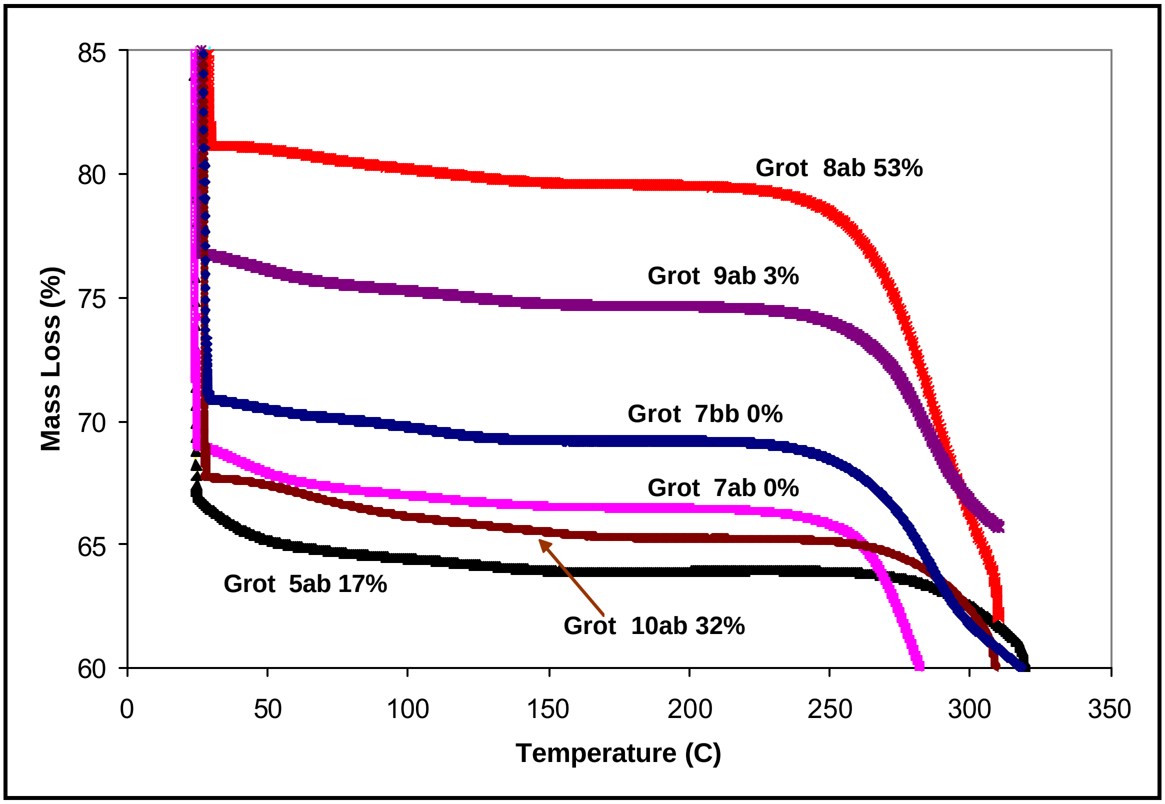
Perfluoro carboxylate content for FTIR was determined from the ratio of the area under the carboxylate (1790cm-1) and the sulfonate (1060cm-1) peaks, each film was measured once (one data point for each film listed), and curve fitting error was determined to be less than 8%.

Worth noting is that there does not appear to be a relationship between EW and carboxylate pendant side-chain content (or sulfonate content) with the average EW being $1.06 \pm 0.10$ meq.-$g^{-1}$.

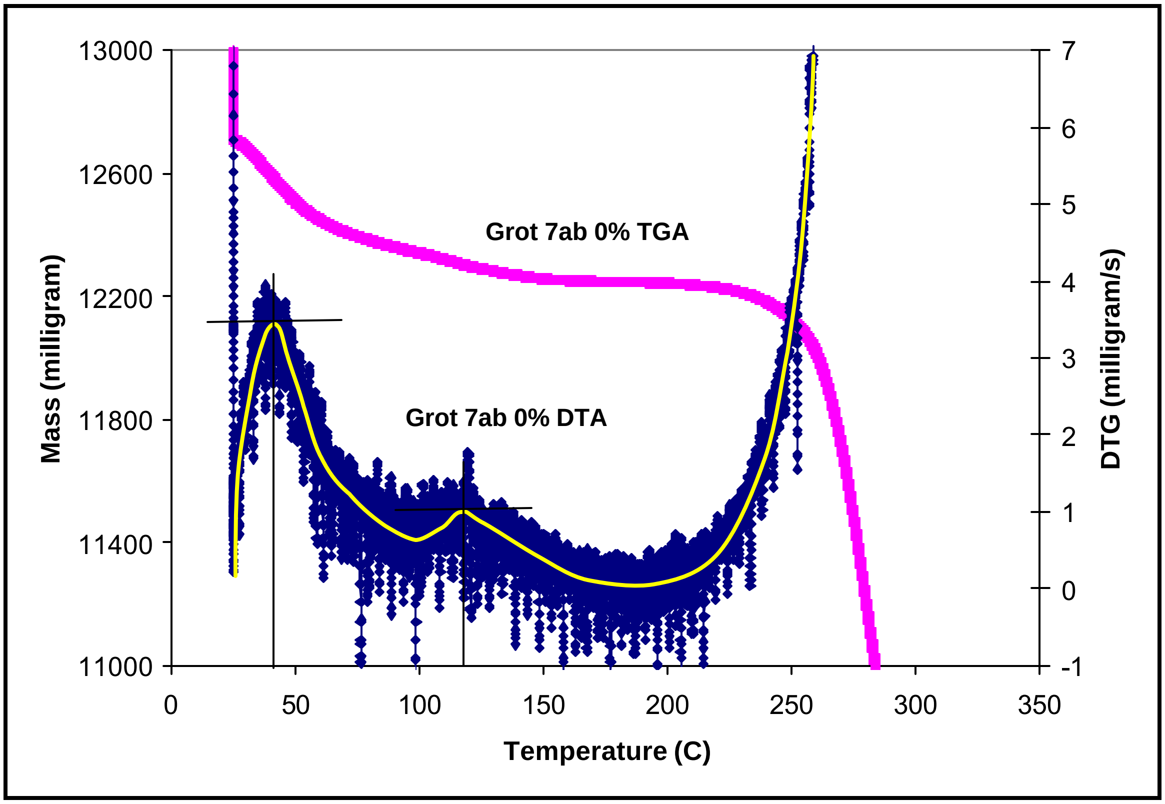
### *5.1.4 Thermal Gravimetric Analysis (TGA) and Ionomer Water Loss*

Boyle et al. (1982, 1983) experimentally determined that water diffusivities in pure perfluoro carboxylate and carboxylate/sulfonate composite materials were comparable to those in pure sulfonated Nafion™ product at similar membrane water content, but that the hydration limits for the pure carboxylate ionomer was as much as 50 % that of the content for similar sulfonate films. Yeager et al. observed in 1982 that the hydration of exchange sites for similar carboxylate and sulfonate terminated pendant chains was approximately 22 % lower for the carboxylate. Yeager attributed the reduction in hydration in the carboxylate films to the increased hydrogen bond strength between the hydroxyl carboxylate oxygen and water hydrogen (see section 2.2.5). Thermal gravimetric analysis of the hydrated Grot conversion procedure membranes was implemented in an attempt to explain observed water content and transport differences between pure sulfonate and mixed sulfonate/carboxylate films. The goal was to determine if a correlation existed between carboxylate content and the temperature at which water was thermally removed from the films. Figure 5.5 shows the TGA curves for two sulfonate reference (Grot 7ab-b and 7bb-b) and four mixed ionomer films scanning from room temperature to 320 °C. Our results show that changes in the mass loss per change in temperature occurs at two distinct temperatures for each of the ionomer films. The exact temperature at which these inflections occur was determined by plotting differential thermal gravimetric (DTG) data against temperature as seen in Figure 5.6 for pure sulfonate sample Grot 7ab-b. Table 5.3 lists the inflection point temperatures for all films tested with the discovery being that the lower inflection point was found to be at a lower temperature for the pure sulfonate films. The pure perfluoro sulfonate inflection was observed at 40 °C, whereas the mixed ionomer inflection point was observed at approximately 62 °C. The trend for location of the second inflection temperature on the DTG curve appears to be at a higher temperature for the mixed ionomer material, however, the inflection point for both types of membrane occur at statistically the same temperature. The conventional explanation for the two different mass loss rates is given as the existence of two distinct types of water in the membranes, absorbed and bonded water. Absorbed water is evolved at the higher rate (up to the lower DTG inflection temperature) and the bonded water is evolved at the slower rate (up to the higher DTG inflection temperature). Given this theory, these data indicate that the films even containing small percentages of carboxylate terminated pendant chains retain

Figure 5.5 - Thermal gravimetric analysis of perfluoro ionomer films.



5.6 – Differential thermal gravimetric determination of inflection points for sulfonate film Grot 7ab-b.



absorbed water to higher temperatures when compared to those films with only sulfonate terminated pendant chains. This TGA/DTG information is consistent with previously published water content characterization data, and with pure water flux information as seen with both the solution cast (section 4.2) and mixed films (section 5.2 below). In summary, materials containing carboxylate terminated side chains show higher resistance to hydraulic flux, lower water content, and show a trend for retaining water at higher temperatures consistent with increased bonding strengths between the hydroxyl oxygen and water hydrogen in the carboxyl materials when compared to pure sulfonate materials. In addition, water retention at higher temperatures might be an indication that the carboxylate films have potential for higher conductivities at higher temperatures than sulfonate films, an attribute essential for efficient fuel cell development.

Table 5.3 – TGA summary of perfluoro sulfonate and mixed films.

| Sample | Carboxylate Content (Mole%) | Absorbed Water Transition Temperature (°C) | Bonded Water Transition Temperature (°C) |
|---|---|---|---|
| Sulfonate pendant chain | | | |
| Grot 7ab-b | 0 | 40 | 115 |
| Grot 7bb-b | 0 | 40 | 110 |
| Average | 0 | 40±6 | 113±45 |
| Carboxylate pendant chain | | | |
| Grot 5ab-b | 17 | - | 125 |
| Grot 8ab-c | 52 | 65 | 115 |
| Grot 9ab-a | 3 | 57 | 120 |
| Grot 10ab-b | 32 | 64 | 130 |
| Average | 26 | 62±13 | 123±20 |

### *5.1.5 Proton Diffusivities from Nuclear Magnetic Resonance (NMR)*

Nuclear magnetic resonance ($^1$H pulse gradient spin-echo NMR) analysis was utilized for the purpose of quantitatively determining hydrogen ion diffusion coefficients in hydrated commercially manufactured and mixed films. Table 5.4 lists diffusivities for those films tested. NMR proton diffusion coefficient results for mixed films (Grot 7bb and Grot 11ab) show that generating the film using the chemical conversion procedure gives rise to a film with diffusivities on the order of 25 % the magnitude of those created by the manufacturer (Nafion™ 111).

Table 5.4 – Perfluoro ionomer diffusivities
for water saturated films as determined by NMR.

| Sample | Carboxylate Content (Mole%) | Diffusion Coefficient (D, $\times 10^7$ cm$^2$-s$^{-1}$)* |
|---|---|---|
| Nafion™ 117 | 0 | 48.0[34,35] |
| Nafion™ 111 | 0 | 51.5 |
| Flemion™ | 100 | 39.6 |
| Grot 5ab | 17 | 5.1 |
| Grot 6ab | 41 | 5.4 |
| Grot 7bb | 0 | 8.5 |
| Grot 10ab | 32 | 7.1 |
| Grot 11ab | 0 | 10.3 |
| Grot 12 bb | 10 | 7.5 |

*Less than 10% error in diffusion coefficients from NMR analysis.

However, for the films modified in-house, the proton diffusivities are significantly smaller for those containing carboxylate terminated side-chains when compared to the ionomer material with only sulfonate terminated side-chains. This same trend exists when comparing diffusivities for both water and nitrate ion for pure sulfonate and mixed sulfonate/carboxylate membranes. Additionally, our proton diffusion coefficient results for Nafion™ 111 from NMR compare well with those determined for Nafion™ 117.[34,35]

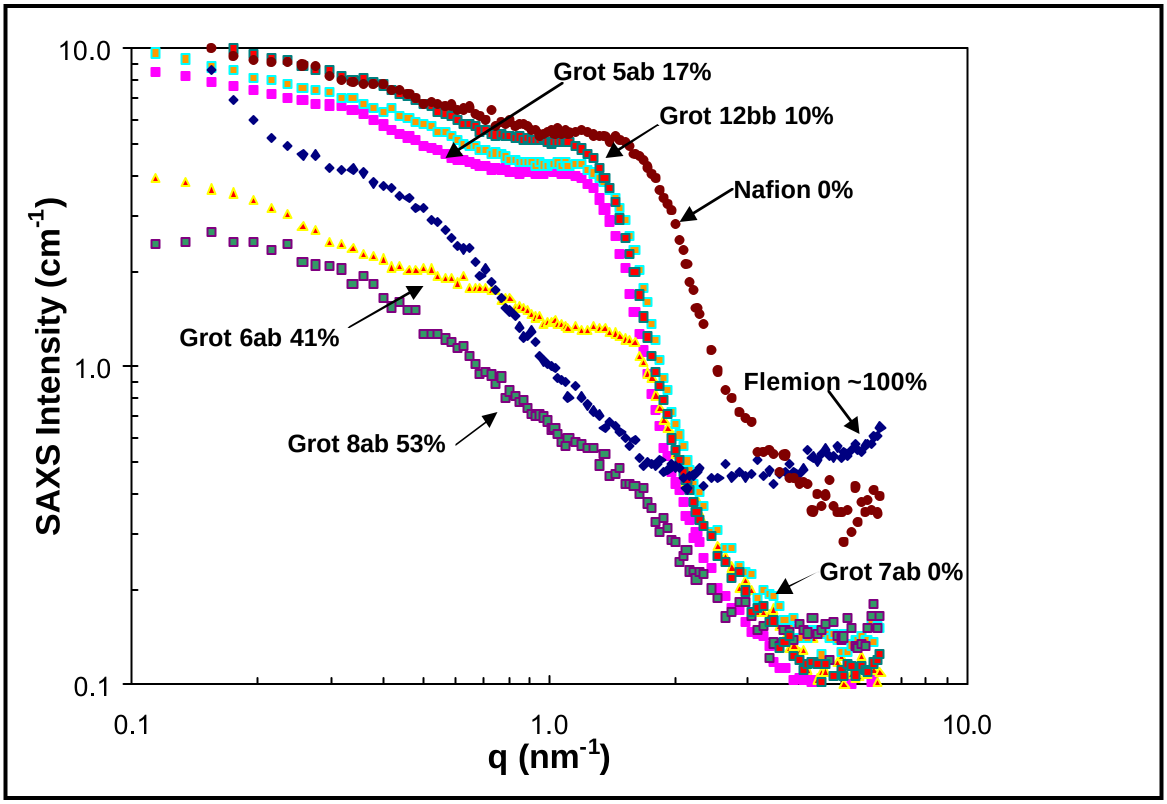
### *5.1.6 Small Angle X-ray Scattering in Mixed Ionomer Films*

A series of Grot procedure synthesized polymer samples were analyzed by SAXS for the purpose of determining morphological differences between perfluoro sulfonate and mixed sulfonate/carboxylate films.

In preparation for SAXS analysis, film samples were hydrated and sealed in a polyethylene (PE) holder and, when processing the scattering data, a background subtraction was required based on the empty holder (or blank). In the course of the measurements it became clear that the background contributions from the blanks were not all the same even though they were fabricated from the same polyethylene sheet material. Based on measurements of 4 different blanks it was determined that two distinct types of background were involved. The blanks for Grot 2ab and Grot 7ab were obtained by cutting the samples open and removing the actual samples (after measuring the SAXS data for the ionomer samples). Based on the two types of blank scattering curves it was clear which blank background was appropriate for processing the data from each sample. Some had a clear feature near $q = 0.35\ nm^{-1}$ (blank data were used) and some had no feature near $0.35\ nm^{-1}$ (Grot 2ab blank or Grot 7ab blank data were used).

Figure 5.7 shows the processed SAXS data (corrected for the PE holder) for 5 samples where the intensities are in absolute units. One can see systematic differences in the

Figure 5.7 - Processed SAXS data from Grot samples.



SAXS curves that appear to be due to scattering associated with a feature (well-defined shoulder) characteristic of the hydrated sulfonate pendant chain cluster just above 1 nm$^{-1}$. In order to get an idea of the size of the scattering feature causing this shoulder, model fits were made of spherical objects to simulate the part of the curves near and above 1 nm$^{-1}$ and these yielded estimates of an average feature diameter (nm). Also, the quantitative amount of scattering was calculated in the form of the integrated SAXS (see sections 2.1.3 for fundamental SAXS information and 4.1.2 for uniform sphere model details) which should be proportional to the volume fraction of the scattering objects. Table 5.5 shows the results of these fits and calculations.

Table 5.5 - SAXS analytical results for mixed films

| Sample | Background sample used | Cluster Feature Diameter (nm) | Q -Scattering (absolute units) |
|---|---|---|---|
| Grot 5ab | Blank | 4 | 13.8 |
| Grot 6ab | Blank | 3 | 7.7 |
| Grot 7ab | Grot 7ab Blank | 4 | 17.3 |
| Grot 8ab | Grot 2ab Blank | 4 | 2.8 |
| Grot 12bb | Grot 2ab Blank | 4 | 18.6 |

Results illustrated in Figure 5.7 show that as sulfonate pendant chain content increases there is an increase in the intensity of the cluster feature shoulder located just above 1 nm$^{-1}$. The inference is that as the sulfonate content increases, the intensity of characteristic sulfonate cluster morphology shoulder is seen. Likewise, as the carboxylate pendant content increases, this feature decreases and all but disappears as shown in the previously mentioned literature. These data substantiate the hypothesis that mixed sulfonate/carboxylate films can be synthesized from the Nafion R1100 perfluoro sulfonyl fluoride precursor using the proposed procedure and correlate well with the content analysis data developed using x-ray fluorescence.

### *5.2 Transport Experimental Results*

Pure water and nitric acid transport results for mixed perfluoro sulfonate/carboxylate ionomer membranes are described in detail below.

#### *5.2.1 Pervaporation*

Pure water and nitric acid dehydration pervaporation transport tests were conducted with films generated using the standard chemical conversion process described above. Pervaporation feed solutions consisted of pure water, 1, 2 and 5 % nitric acid. The system permeate pressure was maintained at 10 torr, permeate vapor was condensed and collected in a liquid nitrogen cooled vacuum trap system, whereas the feed solution system was maintained at approximately 24 °C (see Figures 2.11 and 3.3). Both total mass flux and permeate nitrate concentration were measured during experimentation resulting in the ability to calculate water separation factors ($a$) for each feed concentration. Table 5.6 lists flux and water separation factor data for each of the membranes tested. Figure 5.8 illustrates the total flux as a function of nitric acid concentration for the film transport data listed in Table 5.6 with the result being a

Figure 5.8 – Pure water and nitric acid pervaporation flux through perfluoro ionomer membranes.

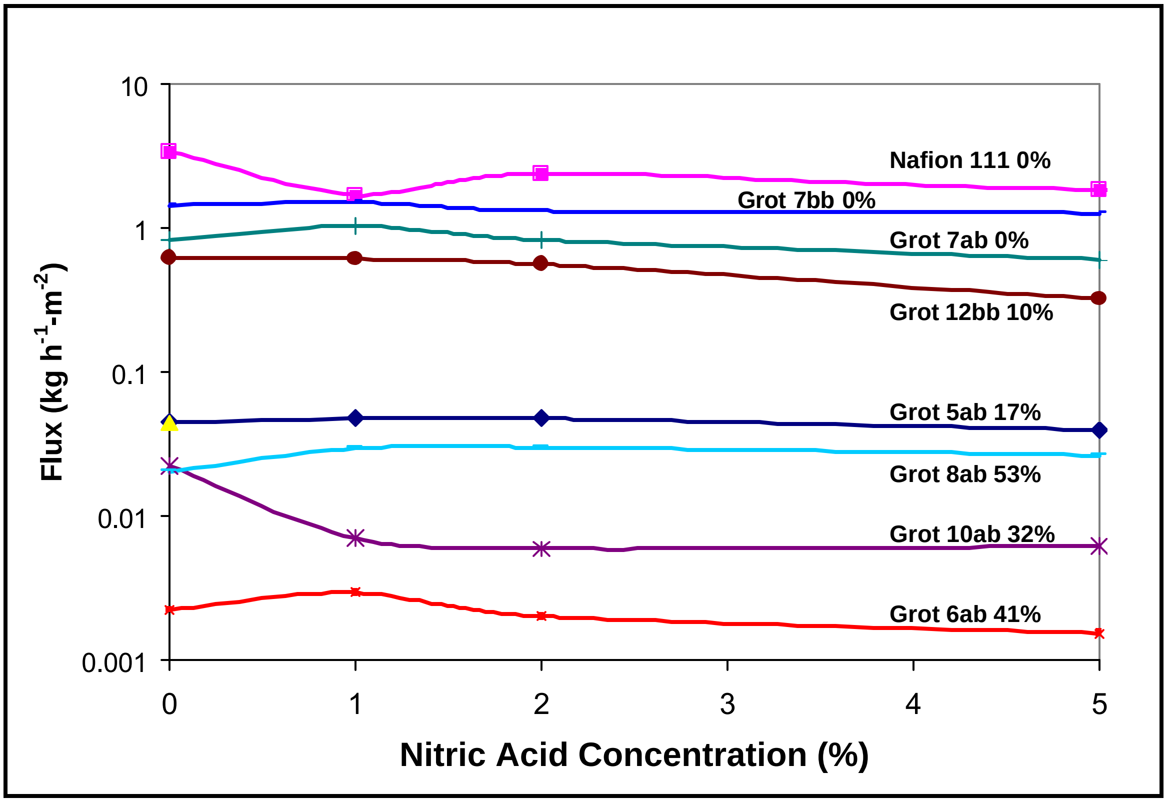
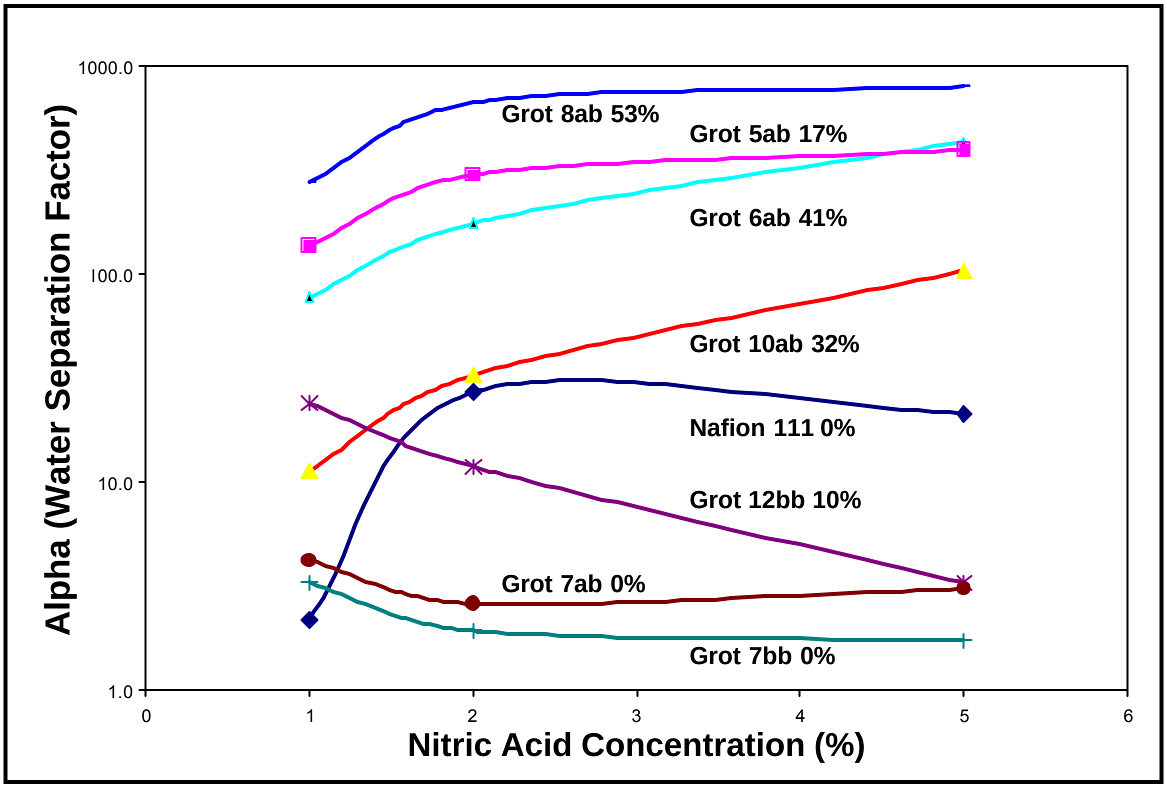


Figure 5.9 – Pervaporation water separation factors in nitric acid for perfluoro ionomer membranes.



dramatic decrease of approximately three orders of magnitude in flow as perfluoro carboxylate side-chain content is increased from 0 to 41 mole%. The two extremes can be seen in films Grot 7bb and Grot 6ab showing a very strong correlation between carboxylate content and decrease in total mass flux. Total flux is strongly a function of polymer carboxylate content, but is not a function of the acid concentration as is shown by the horizontal nature of all plots (Figure 5.8) for the dilute acid concentrations tested. Also of interest is the observation that overall mass fluxes for the Nafion 111 films ($H^+$ form) are approximately 100% higher than those for the pure sulfonate side-chain films generated using the chemical conversion procedure developed by Grot et al. (Grot 7ab and 7bb).

Table 5.6 – Mixed film ($H^+$ form) flux and water separation data.

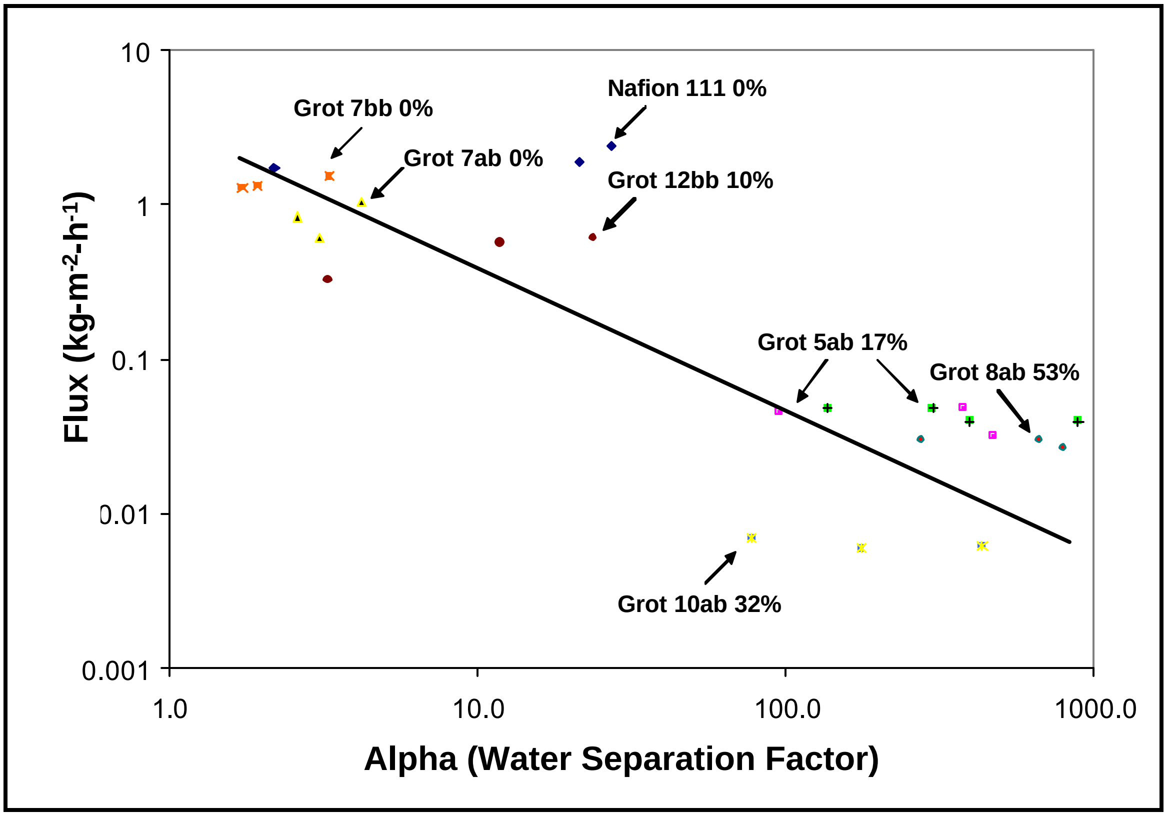
| Run | Carboxylate Content (mole%) | Flux (kg $m^{-2}$ $h^{-1}$) at given nitric acid concentration (%)* | | | | Water separation ($\alpha$) at given nitric acid concentration (%)* | | |
|---|---|---|---|---|---|---|---|---|
| | | 0 | 1 | 2 | 5 | 1 | 2 | 5 |
| Nafion™ 111 | 0 | 3.4 | 1.7 | 2.4 | 1.9 | 2.2 | 26.9 | 21.3 |
| Grot 5ab | 17 | 0.045 | 0.046 | 0.048 | 0.032 | 94.9 | 376 | 469 |
| Grot 6ab | 41 | 0.0023 | 0.003 | 0.0020 | 0.0015 | 11.3 | 32.5 | 103 |
| Grot 7ab | 0 | 0.83 | 1.1 | 0.84 | 0.61 | 4.2 | 2.6 | 3.1 |
| Grot 7bb | 0 | 1.5 | 1.5 | 1.3 | 1.3 | 3.3 | 1.9 | 1.7 |
| Grot 8ab | 53 | 0.21 | 0.030 | 0.030 | 0.027 | 274 | 666 | 796 |
| Grot 10ab | 32 | 0.022 | 0.0070 | 0.0060 | 0.0062 | 77.3 | 176 | 433 |
| Grot 12bb | 10 | 0.63 | 0.62 | 0.57 | 0.33 | 23.8 | 11.8 | 3.3 |

* Error in flux less than 21 % and in water separation factors less than 12 % and detailed in Appendix C.

Water separation factors ($\alpha$) in relation to feed acid concentration detailed in Table 5.6 is also illustrated in Figure 5.9. Results indicate that the magnitude of the water separation factors increase by two orders of magnitude as the carboxylate side-chain content increases from pure sulfonate (Grot 7ab and 7bb) to 55 mole% (Grot 8ab). Worth noting is that the shape of the water separation curves differs between individual films. Ideally, the shape of these curves should be identical as all films are water selective in this system, but due to non-idealities and experimental error over the narrow range of acid feed concentrations, curve shapes varied to a great extent.

Presented in Figure 5.10 are water separation characteristics in relation to bulk solution flux for six Grot membranes and Nafion™ 111 at nitric acid feed concentrations of 1, 2 and 5 wt%. The plot shows that water separation capacity, which is strongly proportional to the carboxylate content, is inversely proportional to the flux for this set of mixed ionomer films. Figure 5.10 demonstrates a trade-off in terms of application of this film to the dehydration of nitric acid: When high water separation factors are required, low trans-membrane fluxes will be expected. This information reveals the flexibility of the material in that the carboxylate content can be manipulated in order to generate a film with a given water separation capability, provided that the materials flux is adequate for the application. The decrease in total flux with carboxylate content appears to complement basic information developed by Boyle et al. (1982, 1983) and Yeager et al.(1982) in terms of a reduction in overall water content and water diffusivities. Both total flux and water separation data supports speculation by Sportsman (1998, 2002) that the reduction of total flux and the increase in water separation factor (nitric acid solutions) is due to the presence of perfluoro carboxylate ionomer material. In summary,

Figure 5.10 – Flux-separation trade-off for conversion films
(1, 2 and 5wt% Nitric Acid).



of greatest importance is that experimental results confirmed the hypothesis given for this effort: Mixed ionomer film bulk fluxes dramatically decreased and that water separation factors increased as the carboxylate side-chain content was increased from 0 (pure sulfonate film) to 55 mole%.

### *5.2.2 Pressure Experimental Results*

Pressure tests were attempted with films generated using the chemical conversion procedure as well with Nafion™ 111 ionomer films. None of the Grot conversion films showed any water transport (at or above our detection limit of $10^{-4}$ kg $m^{-1}$ $h^{-1}$) at trans-membrane pressures above 20 psig, including the pure sulfonate films generated by this procedure. One speculation for no transport was that the film might be compressing and blocking the perforated holes of the support screen in the test cell so different membrane cell experimental configurations were tested with the purpose of mechanically supporting the thin mixed ionomer film (for example using Nafion™ 111), but again, no pressure transport was observed. A possible explanation of this result might be that the films generated using the procedure developed by Grot et al. (1985) are far more compressible than those generated by E. I. Du Pont de Nemours, and when small compression forces are applied across the film, the cluster and connecting pathways collapse preventing any solution transport. A literature search for evidence of this phenomena occurring in perfluoro sulfonate or perfluoro carboxylate ionomer film pressure transport research did not yield any similar instances or additional explanations of the results. Pressure system pure water flux and permeability data were obtained for the Nafion™ 111 films ($H^+$ form) in hopes of being able to compare the information to similar results for perfluoro ionomer films generated using the Grot conversion procedure. This information and comparison to similar data for Nafion™ 112 is detailed in Appendix B.

### *5.3 Summary*

During this portion of our investigation the procedure by which perfluoro sulfonate and mixed sulfonate/carboxylate films could be modified in-house was demonstrated, synthesized films were characterized, and transport data supported the proposed hypotheses. The in-situ conversion procedure used to synthesize the films from the Nafion™ R1100 sulfonyl fluoride precursor (proposed by Grot et al., 1985) proved to be simple and could be completed in a relatively short period of time of approximately two days.

Synthesized ionomer materials were subject to general characterization which included ionomer equivalent weight and water sorption measurements. On average, mixed film equivalent weights compared well with perfluoro sulfonate ionomer films where sulfonate and mixed ionomer equivalent weights were determined to be 0.91 and 1.06 meq.-$g^{-1}$, respectively. Water sorption measurements (completely hydrated material) results showed that the average mixed ionomer perfluoro sulfonate/carboxylate water content (9.3 wt%) was significantly lower when compared with unprocessed

Nafion™ 111 material (23 wt%) and slightly higher than the as received Flemion™ ionomer film (8.0 wt%).

Immediately following the conversion process, relative FTIR absorbance peak intensities were used to qualitatively determine whether an individual run had generated the desired mixed ionomer perfluoro product. Relative amounts of carboxylate and sulfonate terminated pendant chains were determined quantitatively using x-ray fluorescence (XRF). In total, 16 of the films were subject to the XRF analysis process confirming the in-situ conversion procedure as a valid procedure for the intended purpose of generating films with a range of carboxylate content. X-ray fluorescence results indicated that film carboxylate content ranged from pure sulfonate to approximately 71 mole% of the total pendant chain concentration. A comparison was made between carboxylate pendant chain content determined by XRF and the qualitative content determined by FTIR, and an excellent correlation was found between the two analytical techniques.

Thermal gravimetric analysis data indicated that the films containing even small percentages of carboxylate terminated pendant chains retain absorbed water to higher temperatures when compared to those films with only sulfonate terminated pendant chains. Additionally, nuclear magnetic resonance ($^1$H pulse gradient spin-echo NMR) was utilized for the purpose of quantitatively determining hydrogen ion diffusion coefficients in hydrated commercially manufactured and mixed ionomer films. Results showed that mixed ionomer film proton diffusivities were significantly smaller for those containing carboxylate or a mixture of sulfonate and carboxylate terminated side-chains when compared to our chemically converted polymer with only sulfonate terminated side-chains. Thermal gravimetric analysis results and NMR proton diffusivity information was consistent with previously published water content, water and ion diffusivity data, and with pure water flux information as seen with both the solution cast and mixed films. Our results from DTA and NMR, combined with water content data, support the theory postulated by Yeager et al. (1982) that the observed reduction in water flux in perfluoro carboxylate ionomer material can be attributed, at least in part, to the reduction in hydration in the carboxylate polymer material. In addition, our data seems to be consistent with the explanation that the relative decrease in water flux is due to the increased hydrogen bond strength between the carboxylate hydroxyl oxygen and water hydrogen (or purely the hydrogen, as is the case with proton diffusivity measurements) relative to that in the pure sulfonate material.

Small angle x-ray scattering experimental analysis was performed on seven membranes converted using the in-situ procedure developed by Grot et al. (1985). As with commercially manufactured films, SAXS data showed that the characteristic sulfonate feature of the cluster morphology existed for films with sulfonate pendant chains. Our data demonstrate how the intensity of this feature is proportional to the sulfonate content in the mixed sulfonate/carboxylate pendant chain films with pure sulfonate and low carboxylate films having the most intense shoulder.

Most important, the pervaporation transport data obtained shows that the flux decreased by approximately three orders of magnitude and the water separation factor increased by as much as two orders of magnitude as the carboxylate side-chain content was increased from 0 (pure sulfonate) to 53 mole% carboxylate.  Transport results support the hypothesis that trans-membrane flux and separation efficiencies are a function of the ratio of sulfonate to carboxylate terminated pendant chains in the mixed perfluoro ionomer.

# 6.0 SUMMARY AND CONCLUSIONS

Results from investigations involving solution cast perfluoro carboxylate membranes provided support for continued research and development of the ionomer films as applied to the dehydration of nitric acid, as well as for the advancement of fundamental characterization of the films. The primary goals of the solcast effort were to develop a procedure for fabricating thin perfluoro carboxylate films in house and a summary of the accomplishments achieved toward these goals is as follows:

- A number of solution cast membranes were generated using a procedure based on dissolution and casting techniques generated for perfluoro sulfonate ionomer films. Manufacturing carboxylate solcast membranes, which would survive high trans-membrane pressures, proved to be difficult. However, seven films survived pressures to 200 psig, one to 500 psig (solcast 6a) and one to 700 psig (solcast 7a). The solcast films produced had an average EW of 0.69 meq. $g^{-1}$, with an average water saturation near 10 wt%.
- Results indicated that sulfonate terminated side chains might exist in the solution cast films generated for this study. Evaluation of SAXS data using the uniform sphere model demonstrated that a feature exists (spherical diameter between 2 and 5 nm) suggesting that the sulfonate cluster feature is present in solution cast

membranes. This information is consistent with claims published by Grot (1985) and by Boyle et al. (1983).

- Pure water flux for thin solcast films (10-20 µm) as a function of trans-membrane pressure showed that water fluxes were non-existent at pressures below 300 psig. These results are consistent with experimental results for water transport in thick (162 µm) perfluoro carboxylate membranes as published by Sportsman (2002).
- Perfluoro carboxylate solcast film bulk solution flux was determined to be approximately two orders of magnitude lower than for the Nafion™ 111 sheet ionomer. When comparing pervaporation results for solution cast membranes to those predicted for the perfluoro carboxylate ionomer in Nafion™ 90209 by Sportsman, (2002), permeabilities for the solcast membranes were approximately one order of magnitude lower for feed concentrations of 10wt% nitric acid. These results are a good indication that a difference in film morphology exists between solcast films and the perfluoro carboxylate layer in Nafion™ 90209 composite films.
- Nitric acid dehydration experimental results using pervaporation showed that water separation efficiencies for the solution cast membranes were more than one order of magnitude larger than for the Nafion™ 111, confirming the prediction by Sportsman (2002) that the carboxylate form of the ionomer offers higher water

selectivity than for those membranes containing purely the sulfonate terminated pendant chains.

For in-situ conversion investigations the initial hypothesis was expanded to include a demonstration that trans-membrane flux and separation efficiencies were dependant on the ratio between sulfonate and carboxylate terminated side chains in the perfluoro ionomer. Investigations included development and demonstration of a procedure by which perfluoro sulfonate and mixed sulfonate/carboxylate ionomer films could be modified in house, manufactured materials could be characterized, and transport data obtained to support or disprove the proposed hypotheses. A summary of the accomplishments achieved toward the goals of this effort is as follows:

- An in-situ conversion procedure (Grot conversion procedure) was successfully demonstrated which used Nafion™ R1100 sulfonyl fluoride sheet polymer as precursor to material to the generation of perfluoro sulfonate and mixed perfluoro sulfonate/carboxylate films.
- Basic characterization results included EW and water sorption. Mixed ionomer film equivalent weights compared well with the perfluoro sulfonate ionomer films with equivalent weights were determined to be 1.06 and 0.91 meq. $g^{-1}$, respectively. Water sorption measurement (hydrated films in the acid form) results showed that the average mixed perfluoro

sulfonate/carboxylate film water content of 9.3 wt% as compared to 23 wt% for Nafion™ 111.

- Fourier transform infrared spectroscopy was determined to be a valuable tool by providing immediate qualitative information as to carboxylate content of the membranes following synthesis. The spectroscopic results were also used to check XRF results for consistency.
- Films generated were subject to XRF analysis in order to determine perfluoro carboxylate content and confirm the viability of the Grot conversion process. Nineteen films were analyzed with results being qualitative information for films with carboxylate pendant chain content ranging from 0 (pure sulfonate) to 71 mole%.
- Thermal gravimetric analysis was conducted with hydrated ionomer material generated using the Grot conversion process. Results verified the existence of both absorbed and bonded water, that evolution temperatures differed for absorbed water in the sulfonated and mixed carboxylate/sulfonate films, but that water evolution temperatures for bonded water were essentially the same for the two types of membranes.
- Nuclear magnetic resonance ($^1$H pulse gradient spin-echo NMR) was used to generate proton diffusivities in hydrated conversion films for comparison with water (self-diffusion) and other ion diffusivities. Results from the analysis showed that proton diffusion coefficients decreased in carboxylate

materials, relative to pure perfluoro sulfonate polymers, which was similar to diffusivity trends seen for water and for the sodium ion in the hydrated film.

- Small angle x-ray scattering analysis confirmed the presence of the characteristic cluster morphology for films with sulfonate pendant chains. Our data demonstrated how the intensity of the feature decreased with decreased sulfonate content in the sulfonate/carboxylate polymers. Pure sulfonate and low carboxylate content films were shown to have cluster features with the highest intensity.
- Of great significance was the verification that pervaporation bulk solution flux decreased by approximately three orders of magnitude, and water separation factors increased by as much as two orders of magnitude, as the carboxylate side-chain content is increased from 0 (pure sulfonate) to 53 mole% carboxylate in the mixed ionomer polymers.

In review, solution cast nitric acid dehydration pervaporation and pressure system experimental results confirmed the hypothesis that trans-membrane fluxes decrease and water separation efficiencies increased in carboxylate terminated pendant chain ionomers when compared to sulfonate perfluoro ionomer material. This effort showed that thin carboxylate films could be made using a solution cast procedure similar to that demonstrated for perfluoro sulfonate ionomer material. In addition, most analytical characterization used throughout this work was demonstrated and refined using the solution cast films synthesized during preliminary experimentation. Analytical information produced for the solution cast films showed that equivalent weights for the films were diminished and that there were indications of perfluoro sulfonate terminated pendant chains present in the films. Finally, the information obtained was valuable in a number of ways, including that the film casting procedure was difficult and suggestions that mixed carboxylate/sulfonate membranes could be easily generated from commercially available materials.

Mixed sulfonate/carboxylate film pervaporation experimental results validated the theory that as the carboxylate concentration increases, the bulk flux decreases and the water separation factors increase. General characterization of the mixed ionomer films gave EW, water saturation, general morphology (SAXS), and gross carboxylate content (FTIR) through analytical techniques learned during solution casting efforts. Also, techniques not previously utilized were used to reveal quantitative carboxylate content (XRF), water retention of films at increased temperatures (TGA), and water proton diffusivity (NMR) data. All in all, the information gathered during mixed film investigations verified stated hypotheses, tested and confirmed the validity of the conversion procedure, and provided a great deal of material morphological, chemical, and nitric acid dehydration performance data.

# 7.0 RECOMMENDATIONS

A great deal of experimental data was obtained from which general hypotheses were verified during the effort detailed above. However, as with all research and development, each question answered seemed to spawn another dozen questions destine for future projects, and this work is no exception. What follows are a list of areas where our data could be refined, improved or expanded if resources become available.

First, efforts should concentrate on refinement of the mixed ionomer conversion process procedure, operating parameters, and characterization. Chemical conversion system and operating parameters in need of attention include batch reaction equipment modifications, experimentation with new reduction, oxidation and hydrolysis reagents, optimization of reagent concentrations and reaction times, and optimization of operating temperatures and annealing times. In terms of characterization, in addition to using direct transmission FTIR and XRF for overall chemical composition determination, we recommend the use of FTIR-ATR in an attempt to profile the materials at different film depths.

Also, the generation of additional statistical data on mixed ionomer film conversion yields as related to reaction conditions could be conducted. Each one of the films tested as part of this effort can be considered only a single data point as no two films generated and tested had the same carboxylate content due to processing time constraints. Continued efforts should center on replicating the transport results with films having identical carboxylate content (different conversion runs). Ideally, repetition would eliminate films that appear to be anomalies (transport experimental results) and fall outside of general trends demonstrated by all other data.

Optimization of carboxylate/sulfonate mixture for water separation and flux would be extremely useful. Figure 5.10 details how bulk fluxes and water separation factors vary with mixed ionomer film carboxylate concentration. This figure also illustrates the trend toward low fluxes and high separation with films containing small concentrations of the carboxylate terminated pendant chain. A plot of this data on a linear-linear scale shows that films with carboxylate pendant side chain content at and above 17mole% have relatively no flux but high water separation capability. On the other hand, with the films having 10mole% carboxylate or less, fluxes are reasonable (with 1 kg $m^{-2}$ $h^{-1}$ being an industrial rule of thumb for a film flux to be useful in industrial applications) yet the separation factors are small. These two clusters of data seem to have a boundary somewhere between 10 and 17 mole% carboxylate content. Additional studies are recommended to determine if there is a genuine carboxylate content where the flux and separation capabilities are both acceptable.

At some point following the continued development detailed above, and as part of the natural progression of development, the generation of pilot and full scale unit operation equipment should be pursued. Application of this new technology is a goal for the Los Alamos National Laboratory and movement in the direction of testing scale and full-size acid dehydration units on waste streams in plant facilities would be of benefit even if results proved the system unfit for production applications. Engineering system modeling, such as ASPEN, might be useful in determining optimum acid recycle equipment configuration and operating parameters when the addition of a membrane unit operation is attempted.

As a whole, completion of procedural and operating parameter refinement and optimization, completion of nitric acid and water transport characterization, development of more optimal films for water separation, and full-scale demonstration would facilitate the complete evaluation of the applicability of mixed ionomer films to the dehydration of acid wastes. However, in part or in total, the value of continued investigations is encouraged and will, undoubtedly, advance the cause of perfluoro ionomer science.

Finally, the production and characterization of the mixed ionomer films has resulted in great interest in investigating the use of the films as proton exchange membranes (PEM) in developing fuel cell industry. The reduction in water flux, as well as continued high proton diffusivities, created an enthusiastic push for additional research in that these membranes have high potential to provide better performance than the fuel cell industrial standard PEM perfluoro sulfonate polymers. Initial scoping studies have provided interesting methanol transport and conductivity (water and methanol) data, and continued investigations are recommended and encouraged based on these preliminary results.

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# APPENDIX A – OPERATING PROCEDURES

## *A.1 Solution cast (solcast) Ionomer Film Production*

Solution cast membranes were synthesized using the dissolution and casting procedures described below.

### *A.1.1 Dissolution*[27,28]

1. Obtain perfluoro carboxylate feed material required for desired concentration.
2. In a clean, glass dissolution vessel, mix 15 mL of de-ionized water and 15 mL isopropanol, and 10 clean glass beads.
3. Preheat oven to 190 °C.
4. Place glass liner/solution in Parr reactor, seal the reactor, and place the sealed reactor in the oven for 4 hours.
5. Remove the reactor from oven and allow it to cool at to room temperature for 6 hours.
6. Disassemble the reactor and remove solution from reactor and store in a glass sample container. Determine mass of any solids not dissolved.
7. Clean and dry entire reactor vessel in preparation of next run.

### *A.1.2 Casting*[28,29]

1. Obtain perfluoro carboxylate feed solution required for desired film thickness given glass casting vessel dimensions.
2. In a clean, glass casting vessel, add feed solution and an equal volume of DMF (,$N^1$-dimethylformamide).
3. Verify that the furnace is level.
4. Start vacuum pump, preheat oven to 100 °C, and adjust system to indicate 1-2” Hg vacuum.
5. Place casting vessel/solution in vacuum furnace and hold at 100 °C for 3 hours. Monitor vacuum and temperature and adjust vacuum pump and furnace controls as needed.
6. Increase temperature to 130 °C and hold for 3 hours.
7. Increase temperature to 150 °C and hold for 3 hours, or hold at temperature 1 hour if dryness has been achieved.
8. Weigh dried vessel/film.
9. In order to hydrate the film, add 100 ml of de-ionized water to vessel containing the film, place on a hot plate at 40 °C for 1 hour (or until membrane begins to float).
10. Dry the casting vessel, weigh and determine dry film weight.

11. Store film in de-ionized water.

## *A.2 Ion Exchange Capacity (Equivalent Weight) Analysis*

1. Dry Perfluoro ionomer film for 24 hours at 100 °C for 24 hours. Weight the dried material.
2. Hydrate the material by soaking the film in de-ionized (DI) water for 24 hours.
3. Place the film in the acid form by boiling (90-95 °C) the material in gently stirred, 1.0 M $HNO_3$ for 4 hours.
4. Rinse the ionomer film 3 times with DI water.
5. Soak the film in 0.01 M KOH at 40 °C for 24 hours.
6. Rinse film with DI water and combine rinse solution with KOH solution from step 5.
7. Back-titrate the combined solution with $HNO_3$.
8. Calculate EW as moles KOH used to neutralize acid per gram dry ionomer material (or meq. $g^{-1}$).

## *A.3 Nitrate Ion Analysis (Ion Specific Electrode)*

1. Prepare ion specific electrode (nitrate electrode 9307 does not require solution in the assembly process. and conductivity electrode as required by manufacturer. Probes will usually require cleaning and refilling of inner and outer chamber solutions. Assembly of the reference electrode is detailed in the double junction manual (Ag/AgCl manual A, pages 90-92).
2. Assemble system electrode stand and brackets, and gather supplies such as glassware, standard solutions, Milli-Q™ de-ionized water, concentrated nitric acid, and samples.
3. Conduct a self check on the meter as specified by the manufacturer (Orion 290A meter operations manual C, page 61).
4. Assemble the electrode system as specified by the manufacturer (assembly outlined in either electrode manual or Orion meter operations manual).
5. Check the electrode operations as detailed by the manufacturer (Nitrate electrode manual B, page 10) using prepared solutions 2 and 3.
6. Create a calibration curve bracketing the expected range of sample concentrations (Orion 290A meter manual C, page 74). Use a minimum of 3 calibration solutions (example solution preparation procedures are located in the nitrate electrode

manual B, page 33). When choosing calibration solutions, be aware that some samples may require dilution for proper concentration evaluation.

7. Prepare samples of 100 ml (maximum volume) to be measured including 1 mL of low ISA (20 ml of ISA dissolved in 100 ml of Milli-Q™ de-ionized water) and stir thoroughly.
8. Rinse the electrodes thoroughly with Milli-Q™ de-ionized water, blot (do not swipe) the electrodes dry with a clean tissue, and place the electrodes in the samples.
9. Continue to stir samples, wait for meter reading to stabilize and record nitrate concentration.
10. Electrodes can be stored for short periods (up to 1 week) in manufactures recommended solutions when not in use (the double junction reference electrode can be stored in Milli-Q™ water, whereas the nitrate specific electrode should be stored in 100ppm nitrate standard with ionic strength adjuster, ISA, solution).
11. Disassemble and clean electrodes as required buy the manufacturer when not in use.

### *A.4 Mass Transport System Operating Procedures*

Perfluoro ionomer membranes were tested in both pressure and pervaporation systems and procedures are described below.

### *A.4.1 Pressure System Operation*

1. Trim membrane, install membrane in Millipore™ cell (either 2 in. or 1 in. diameter cell can be used), and install cell in system.
2. Energize syringe pump and pump controller.
3. Verify that syringe pump is empty.
4. Set pump pressure on controller using setting control A and entering predetermined pressure.
5. Verify that approximately 500 ml of feed solution is in place, fill line is submerged in feed solution, and that fill valve is open.
6. Close retentate needle valve.
7. Fill syringe pump with feed solution. Bleed air (at pressure of 100psig or less) from the syringe pump system by opening both the feed and retentate valves simultaneously, engaging system, and verifying that all gas is removed from the system (liquid streams visible from both feed and retentate lines), and discontinuing the pump. Refill syringe pump and reset system pressure, if needed. Close both retentate and fill valve.
8. Activate the syringe pump and allow the system to reach the desired pressure.

9. Adjust feed flow rate by throttling the retentate needle valve and monitoring controller flow indicator.

10. Monitor permeate rate and accumulation, feed flow rate, and feed volume as needed.

11. Discontinue operation as appropriate, and inventory final permeate volume (mass).

12. Flush system as necessary by removing membrane cell, installing cell replacement line, purging syringe pump, refilling with de-ionized water (repeat flush twice when concentrated feed solutions are used).

13. De-energize system when not in use.

### *A.4.2 Pervaporation System Operation*

1. Assemble membrane cell with film to be tested.

2. Verify that feed system has been thoroughly flushed with de-ionized water.

3. Flush the feed-side system loop 3 times with approximately 100 ml of solution to be used for the given run, draining the solution between each flush and verifying that the feed tank is sealed when the pump is operating.

4. Fill feed tank with approximately 200 ml of feed solution and seal the tank.

5. Engage the feed pump (approximately 1 ml $s^{-1}$).

6. Verify that the condensation system is clean and dry.
7. Seal the permeate-side system and place both condensers in liquid nitrogen.
8. Open one permeate condenser to the system and start vacuum pump.
9. Adjust permeate side pressure to run conditions by throttling needle valve on vacuum pump while monitoring pressure readout.
10. Maintain conditions for 30 minutes for the purpose of establishing equilibrium then switch permeated system condenser to second chilled condenser.
11. Monitor permeate-side pressure and adjust as needed.
12. Maintain liquid nitrogen levels in on-line condenser system as required.
13. Record start and end run times, permeate accumulation and general observations.
14. Completely flush feed-side loop with de-ionized water following each run.

### *A.5 Fujimura Aqueous Film Conversion Procedure*[10,24]

1. The Nafion membrane is first treated with 2 N HC1 for 3 hours at 80 °C to prepare the sulfonic acid form, Nf-S$0_3$H. In this way we obtained a series of sulfonic acid forms.
2. The membrane is then washed with water for 3 hours.

3. The membrane is then reacted with 5 % $NH_4OH$ for 16 hours at room temperature to obtain Nf-$S0_2NH_4$.
4. The membrane is again washed with water for 4.5 hours.
5. The membrane is then dried under vacuum.
6. The membrane is then refluxed with 1:4 (v/v) $PCl_5/POCl_3$ for 70 hours to obtain Nf-$SO_2Cl$.
7. The membrane is then refluxed with $CCl_4$ for 18.5 hours and dried under vacuum.
8. The Nf-$SO_2Cl$ membrane is further reacted with HI at 80 °C for 115 hours to obtain the carboxylic acid form, Nf-COOH.
9. The membrane is then washed with methanol for 8 hours.
10. The membrane is then refluxed with a 10 % methanol solution of sodium hydroxide for 15 hours to prepare the sodium carboxylate form, Nf-COONa.
11. The membrane was then washed with water for 6 hours.
12. The membrane is then reacted with 2 N HCl at 80 °C for 16 hours to prepare the carboxylic acid form, Nf-COOH.
13. The membrane is then washed with water for 3 hours.
14. The membrane is then dried under vacuum at 130-140 °C for 18.5 hours to prepare the carboxylic acid form, Nf-COOH, for X-ray measurements.

15. The residual amount of sulfonate groups is quantitatively estimated to be minute by using fluorescent X-ray spectroscopy to analyze for sulfur before and after the chemical modification.

### *A.6 Grot Aqueous Film Conversion Procedure*[4]

1. Obtain perfluoro sulfonyl fluoride precursor material (Nafion™ R1100) for conversion.
2. The membrane is immersed in 85 % hydrazine hydrate (monohydrate) for a predetermined period for the purpose of generating the sulfinic acid form of the film. Increased exposure to hydrazine hydrate will result in greater conversion to the sulfinic salt eventually generating the perfluoro carboxylate form.
3. The film is then heated in 13 % KOH (aqueous) in 30 % dimethyl sulfoxide (DMSO) at 90 °C hydrolyzing the remaining unreacted sulfonyl fluoride terminated side-chains to the sulfonic acid.
4. The film is then cleaned by rinsing 3 times in Milli-Q water.
5. The membrane is then immersed at room temperature in a 20:100 volume mixture of concentrated HCl and concentrated glacial acetic acid for 20 minutes. In this procedural step the sulfinic acid is oxidized to the carboxylate form of the film.
6. The film is then cleaned by rinsing 3 times in Milli-Q water.

7. The film is then annealed in air at 130 °C for 16 hours.
8. The converted film is then prepared in either the acid form (for transport experimentation) or the potassium form (for EW analysis or XRF analysis), as needed.

### *A.7 Acid Pretreatment Procedure for Perfluoro Ionomer films*

1. If not already hydrated, soak the film in Milli-Q™ water for 24 hours.
2. Place the film in the acid form by boiling (90-95 °C) the material in gently stirred, 1.0 M $HNO_3$ for 4 hours.
3. Rinse the ionomer film 3 times with DI water.
4. Place the material in gently-stirred, boiling (90-95 °C) Milli-Q™ water for 4 hours.
5. Store in Milli-Q™ water as needed.

## APPENDIX B – NAFION™ 111 PRESSURE TRANSPORT DATA

Pressure system water flux data were obtained for the Nafion™ 111 films in hopes of being able to compare the information to similar results for perfluoro ionomer films generated using the Grot conversion procedure which was not possible. Pressure vs. pure water flux data curves are shown in Figure B.1 and give the comparison between Nafion™ 112 (thickness = 50.8 µm) data developed by Sportsman (2002) and Nafion™ 111 (thickness = 25.4 µm) illustrating that the thinner Nafion™ 111 and the Nafion™ 111 films have very similar water transport at given pressures.[1] Both films are in the $H^+$ form and were pretreated using the same procedure detailed in Appendix A.

Figure B.2 provides a comparison of the permeability verses trans-membrane pressure for the same Nafion™ films. Ideally if these two materials were identical then the permeabilities at any given pressure would be identical which, as seen from the comparison this figure provides, this is not the case. Additionally, Sportsman (2002) compared the pure water permeabilities at given pressures for Nafion™ 112, Nafion™ 115 and Nafion™ 117 films, and also identified difference in permeabilities for what the manufacturer describes as the same material. In light of this information the conclusion can be made that, if starting materials are identical, differences in the film permeabilities are likely due to morphological differences which are the result of variances in manufacturing procedure operating parameters or may be the result of quality control variations.

Figure B.1 – Nafion™ 111 and 112 Flux Comparison

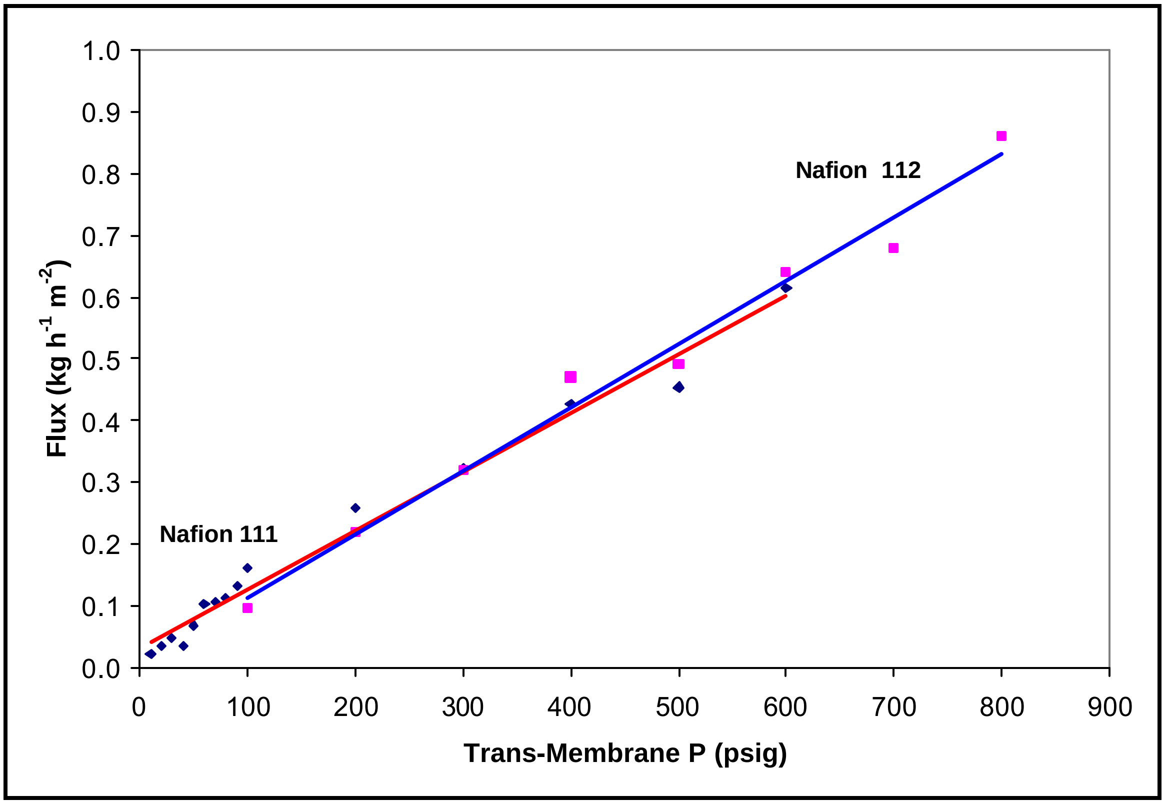
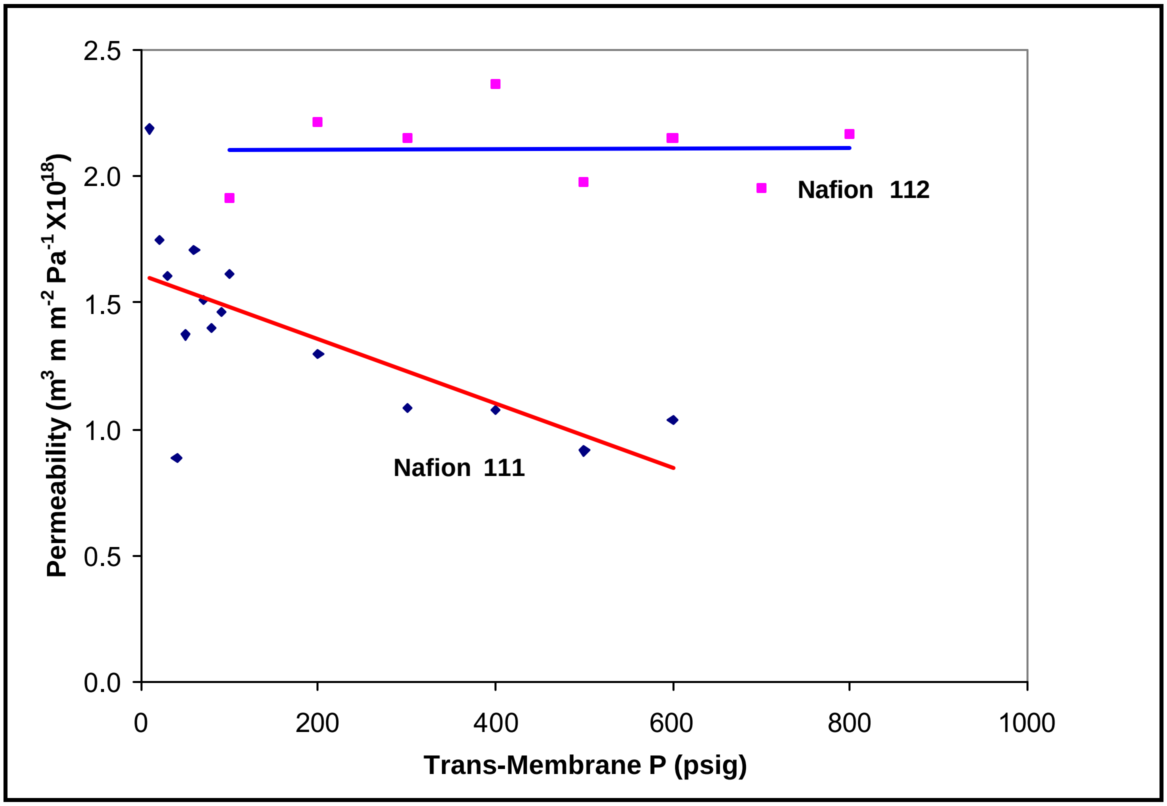


Figure B.2 – Nafion™ 111 and 112 Permeability Comparison



# APPENDIX C – FLUX AND SEPARATION FACTOR ERROR ANALYSIS

Table C.1 – Pervaporation Experimental Error

| Grot Run Number – Feed Acid (%) | Flux (kg/m$^2$-h) | Flux Error (%) | Separation Factor (α) | Separation Factor Error (±) |
|---|---|---|---|---|
| 5ab-0 | 0.0447 | 9.5 | | |
| 5ab-1 | 0.0455 | 6.9 | 94.6 | 10 |
| 5ab-2 | 0.048 | 6.9 | 377 | 42 |
| 5ab-5 | 0.0317 | 7.8 | 469 | 52 |
| 5ab-0B | 0.0451 | 5.6 | | |
| 5ab-1B | 0.0482 | 3.0 | 136 | 15 |
| 5ab-2B | 0.048 | 3.6 | 300 | 33 |
| 5ab-5B | 0.0398 | 3.6 | 689 | 76 |
| 6ab-0 | 0.00226 | 4.2 | | |
| 6ab-1b | 0.00295 | 9.3 | 11.2 | 1.3 |
| 6ab-2 | 0.00202 | 3.9 | 32.5 | 3.6 |
| 6ab-5 | 0.00154 | 2.5 | 103 | 11 |
| 7ab-0 | 0.829 | 17 | | |
| 7ab-1 | 1.052 | 17 | 4.16 | 0.46 |
| 7ab-2 | 0.835 | 17 | 2.61 | 0.29 |
| 7ab-5 | 0.611 | 13 | 3.06 | 0.34 |
| 7bb-0 | 1.454 | 17 | | |
| 7bb-1 | 1.533 | 20 | 3.28 | 0.36 |
| 7bb-2 | 1.33 | 17 | 1.93 | 0.21 |
| 7bb-5 | 1.286 | 17 | 1.72 | 0.19 |
| 8ab-0 | 0.0206 | 4.1 | | |
| 8ab-1 | 0.0298 | 4.0 | 274 | 30 |
| 8ab-2 | 0.0302 | 5.1 | 666 | 73 |
| 8ab-5 | 0.0267 | | 795 | 87 |
| 10ab-0 | 0.0224 | 3.4 | | |
| 10ab-1 | 0.00701 | 3.4 | 77.1 | 8.3 |
| 10ab-2 | 0.00597 | 2.6 | 176 | 19 |
| 10ab-5 | 0.00621 | 3.4 | 433 | 47 |
| 12bb-0 | 0.631 | 18 | | |
| 12bb-1 | 0.6173 | 8.8 | 24 | 3 |
| 12bb-2 | 0.567 | 8.4 | 12 | 1 |
| 12bb-5 | 0.326 | 11 | 3.27 | 0.36 |

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