



Investigation of the Morphological Changes in Nafion Membranes Induced by Swelling With Various Solvents

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and Nora C. Beck Tan

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Weapons and Materials Research Directorate, ARL

Abstract

The structure of Nafion 117 perfluorosulfonate ionomer membranes has been investigated using small-angle neutron-scattering techniques. Structural changes induced by swelling of the membranes with water, alcohols, and dipolar aprotic solvents were monitored, at solvent swelling levels ranging from ~2% to >50%, by volume. Membranes swollen up to ~50 volume-percent solvent exhibited two scattering maxima: one known to be associated with ionic regions of the membrane structure and one known to be associated with correlation distances between crystalline regions in the membrane structure. The positions of both maxima shifted toward lower q values as the solvent content in the membrane increased. The shift in the position of both maxima was linearly related to the volume fraction of solvent in the membrane. The Bragg spacings corresponding to both the ionic feature scattering maximum and the crystalline feature scattering maximum were plotted vs. volume fraction of solvent in the membranes and the data fit using linear regression. The slopes associated with the spacing vs. volume fraction solvent curves were greater for the crystalline feature spacing than for the ionic feature spacing for all solvents other than water, indicative of preferential segregation of non-aqueous solvents into regions of the structure not directly associated with the ionic scattering maximum.

Acknowledgments

The authors would like to acknowledge the use of the facilities at the National Institute of Standards and Technology (NIST) Center for Neutron Research in Gaithersburg, MD, where all of the 30-m small-angle neutron-scattering (SANS) experiments were performed. In addition, the American Association for Engineering Education Post-Doctoral Research Associate Program and the U.S. Army Natick Soldier Center are acknowledged for financial support to author Sandra K. Young. Also, helpful technical discussions with Dr. Donald Rivin of the U.S. Army Natick Soldier Center are gratefully acknowledged.

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1. Introduction

Perfluorosulfonate ionomer membranes are materials of considerable commercial significance due to their use as solid polymer electrolytes in fuel cells and various other applications in electrochemistry and separation technologies. It is generally believed that the useful properties of these materials are a result of their structure, which is known to be heterogenous on the submicron or nanometer scale. However, despite nearly 20 years worth of investigation, there still remains considerable uncertainty regarding the details of this structure.

Most of the commercial perfluorosulfonate ionomers are based on chemistry similar to that of the Nafion membranes produced by DuPont, the general formula of which is represented in Figure 1. The membranes most extensively studied are those in sheet form, in which the sulfonate group is introduced via conversion of a sulfonyl fluoride after extrusion processing. The sulfonate group may be present in sulfonic acid form, or converted to ionomer form by exchange of the acidic proton with organic, alkali, or transition metal cations. For the current purposes, the sulfonate groups will be referred to generically as the ionic groups.

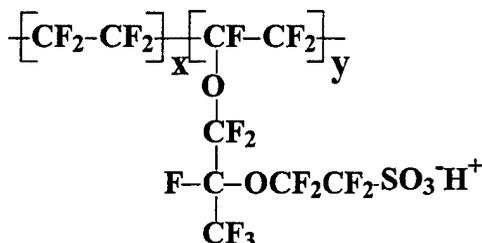


Figure 1. Chemical structure of the Nafion ionomer.

The structure of Nafion membranes is most often investigated using small-angle scattering (SAS) methods. Numerous SAS studies by a variety of research groups [1-10] have consistently produced characteristic patterns from perfluorosulfonate ionomer membranes having three basic features: (1) a scattering maximum occurring at momentum transfer vector (q) values in excess of 0.1\AA^{-1} that has been associated with aggregation of the ionic groups, (2) a scattering maximum occurring at $q \sim 0.04\text{\AA}^{-1}$ that has been associated with crystalline features of the structure, and (3) an upturn in intensity in the very low q region ($q < 0.01\text{\AA}^{-1}$). Structure of the crystalline regions has also been

investigated using x-ray diffraction techniques [2, 11, 12]. As the membranes are swollen with water vapor, liquid water, or methanol, the scattering maximum associated with the ionic aggregates increases in intensity and shifts to lower q values [1-4, 8-10, 13, 14].

The controversy regarding the structure is primarily concerned with the details of the organization of the ionic groups. Two basic types of models have emerged concerning the organization of ionic groups within the perfluorosulfonate ionomer membranes: cluster models and layer models. By far, the most attention has been given to the former. In the cluster models, electrostatic interactions hold the ionic groups into regions that are roughly spherical in shape and on the order of tens of angstroms in size and spacing [1-4, 7-10, 12-14]. The electron density difference between the regions of high sulfonate group concentration and the rest of the material is believed to be responsible for the appearance of a maximum in the SAS range. Cluster models were first introduced to explain the behavior in simpler ionomers, such as sulfonated polystyrene. The possibility of similar clustering phenomena occurring in perfluorosulfonate ionomer membranes was proposed in early studies of Nafion perfluorosulfonate ionomers by Roche and et al. [1] and by Gierke et al. [2].

Shortly after the idea of clustering in Nafion membranes was suggested, a number of investigations began that focused on the applicability of various versions of the cluster models to the description of the structure of Nafion. These investigations focused primarily on distinguishing between the various cluster models, and determining which model was likely to yield a better description of the nanoscale structure in perfluorosulfonate membranes. Different research groups differ in their opinion as to which model gives the best fit. Attractive features of the cluster models are that they account for the ionic cluster peak and have the ionic groups arranged such that interfacial energy in the system is minimized. They do not take crystalline fractions of the structure into account. The more controversial aspect of the cluster models is the difficulty in reconciling their predictions with certain experimentally observed scattering features. For example, several groups have noted that a linear relationship exists between the shift in position of the ionic cluster peak and the volume of water absorbed by the membranes upon swelling [2, 4, 15], which cannot be accounted for with a cluster model. In addition, in order to account for Porod behavior that indicates the total surface area in water swollen membranes is independent of the water volume fraction [10], it is necessary to impose a complicated, dynamic equilibrium on the system in which both the size and number of clusters in the membrane changes continuously as the membrane swells. This equilibrium would require significant molecular rearrangement during swelling that is difficult to envision given the crystalline features of the system [15].

An alternative description of the structure in perfluorinated ionomer membranes has also been proposed. This second model is based on the idea of the ionic groups being organized into layered structures of very thin crystalline regions whose surfaces are covered with the ionic groups. Both disk-like, chain-folded lamellae [15, 16] and bilayers of backbone chains [5–6, 11] have been proposed. In the case of layers, the scattering contrast comes from the density difference between the crystalline regions and the side chain regions, and the observed scattering would be representative of Bragg scattering from a periodic layered assembly. The first layer-type model was proposed by Starkweather [11] in 1982, and variations have been considered more recently by Ozerin et al. [5, 6] and Litt [15]. The strongest evidence for the layered model comes from the observation that the characteristic spacing associated with the ionic region increases linearly with the volume fraction of water or alcohol absorbed by the membranes in the region below 50% absorption [2]. This behavior is consistent with a layered structure, in which the interlayer spacing is increased as the liquid expands the ionic layers. Litt [15] has also argued that mechanical performance and volumetric measurements are also more in agreement with expected behavior from a layered structure than from a clustered structure. The primary attractive features of the layered model are its relative simplicity and its agreement with the observed linear dependency of ionic spacing with volume fraction solvent. Criticisms include lack of accountability for the observed upturn in scattering intensity at very low angles, lack of agreement between solvent induced-shift dependency of the ionic peaks and the small-angle crystalline peaks [9–10], plus some controversy surrounding the linearity of the relationship between solvent volume fraction and ionomer peak spacing [9–10].

In this study, the focus has been on increasing knowledge of the nanoscale structure in Nafion membranes by conducting extensive experiments on membranes in a variety of ion-exchanged forms and swollen with a variety of solvents to various levels. The extension of structural studies to membranes swollen with solvents other than water allows for investigation of conventionally processed membranes in highly swollen states, i.e., to solvent volume fractions above ~35% achievable by immersion in water. Employing non-aqueous solvents also allows for probing of those regions of the membrane structure not specifically associated with the ionic scattering feature and for identifying solvent partitioning effects. The results indicate that the characteristic dimensions of the membrane structure associated with both ionic features and crystalline features shift linearly as the volume fraction of solvent in the membrane increases. The linear dependence holds for a range of solvents of varying polarity up to volume fractions of ~0.5; however, the magnitude of the slopes corresponding to the dependence of the characteristic dimensions on solvent volume fraction vary from solvent to solvent.

2. Experimental

2.1 Materials

Perfluorosulfonate membranes (1100 equivalent weight, 7 mil thick) in the SO₃H form (Nafion 117) were obtained from C. G. Processing, Inc.* Concentrated hydrochloric acid and concentrated nitric acid were obtained from VWR Scientific† and used as received. All water utilized was distilled or deionized. Methanol (MeOH), ethanol (EtOH), propanol (PrOH), tetrahydrofuran (THF), dimethylformamide (DMF), and 3-Å molecular sieves were obtained from Sigma-Aldrich Chemicals.‡ Dimethylmethylphosphonate (DMMP) was obtained from Lancaster Chemicals.§

2.2 PFSI Membrane Initialization

All membranes were preconditioned and converted to the sulfonic acid form in an initialization procedure reported previously by Davis et al. [17]. Membranes were exchanged to the acid form by refluxing in 50% HCl:50% HNO₃ solution (v:v), leaching out excess acid in deionized water reflux (3x), and finally vacuum drying at 125 °C. All membranes were exchanged to this standard initial state prior to counterion exchange and evaluated using prompt-γ activation analysis in order to assure maximum sample reproducibility [18].

2.3 Small-Angle Neutron-Scattering (SANS) Evaluations

SANS measurements were performed at the National Institute of Standards and Technology (NIST) Center for Neutron Research in Gaithersburg, MD, using the 30-m SANS spectrometer located at NG-7.

Membranes were dried immediately before preparation for the scattering experiments at 125 °C and 4 kPa for 24 hr to remove as much residual atmospheric water as possible. Membranes were then weighed on an OHAUS GA200 analytical balance, containing a beaker of molecular sieves, in a room at 22 °C and 55% relative humidity. Solvent swollen samples were prepared by immersing the membranes in a vial containing the solvent and molecular sieves. Once removed from the vial, after patting the surface of the membrane dry, membranes were quickly weighed. For samples being evaluated at less than full solvent uptake, solvent was removed through heated evaporation to the desired volume fraction in a closed chamber containing a beaker of sieves to minimize

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‡ Aldrich Chemical Company, 1001 W. St. Paul Avenue, Milwaukee, WI 53233-2641.

§ Lancaster Synthesis, Inc., P.O. Box 1000, Windham, NH 03087-9972.

contamination by water. Since the boiling point is too high to easily remove it from the membrane, DMMP samples were made by calculating the amount of solution needed based on the weight of the membrane and adding it to the membrane. Once the samples were adjusted to a specific solvent volume fraction, they were immediately enclosed in 1-mm path length quartz cells and maintained at 25.0 ± 0.2 °C. The samples were typically made 24 hr prior to SANS measurements, allowing the solvent to equilibrate within the membranes. In addition, membranes were weighed after the experiments to verify that the solvent within the membrane had not escaped the confines of the sealed quartz cell.

The scattering intensity was measured as a function of q , the magnitude of the scattering vector. q is related to the scattering angle, θ , by the relationship $q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$, where λ is the wavelength of the incident neutron beam ($\lambda = 6$ Å for these experiments). The detector was a 64×64 cm² He-3 position-sensitive proportional counter with 1-cm² resolution. Scattered intensity was measured at q values ranging from ~ 0.002 Å⁻¹ to ~ 0.6 Å⁻¹. This was accomplished by placing the detector at various distances from the sample. The positions of the circular pinholes before the sample were adjusted to match the resolution of the detector configuration. Data were corrected for the scattering from an empty quartz sample cell, detector background and sensitivity, and the transmission value of each sample. Absolute scattering intensities were obtained by reduction of the raw data through calibration with the measured incident neutron intensity.

3. Results and Discussion

SANS experiments were performed on Nafion swollen in a variety of solvents. The scattering curves showed the features that are known to be characteristic of Nafion membranes; a low-angle intensity upturn, a broad peak around 0.04 Å⁻¹ that has been associated with crystalline regions of the structure [1-3], and a peak around 0.1 - 0.2 Å⁻¹ that has been associated with the ionic regions [1-3]. These features are seen regardless of the swelling solvent (Figure 2) and for membranes in the acid form and ion-exchanged forms (Figure 3). It might be noticed that the THF SANS spectra is not presented in the data. The THF sample appeared to polymerize, causing gelation of the solution in the vial. The acid sites within the Nafion membrane possibly caused this phenomena, as they could initiate the ring-opening polymerization of THF. Though the structural features are consistent regardless of counterion or solvent type at a given volume fraction of absorbed solvent, the total solvent uptake reached is strongly

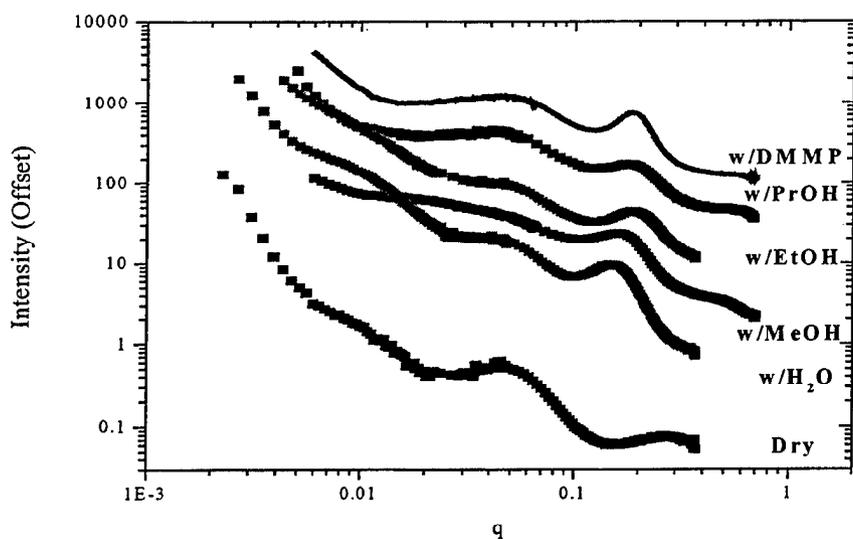


Figure 2. SANS intensity vs. scattering vector for Nafion membranes from bottom to top: (a) dry, (b) 32% water, (c) 34% methanol, (d) 38% ethanol, (e) 35.4% propanol, and (f) 35% DMMP. Intensities have been offset for clarity.

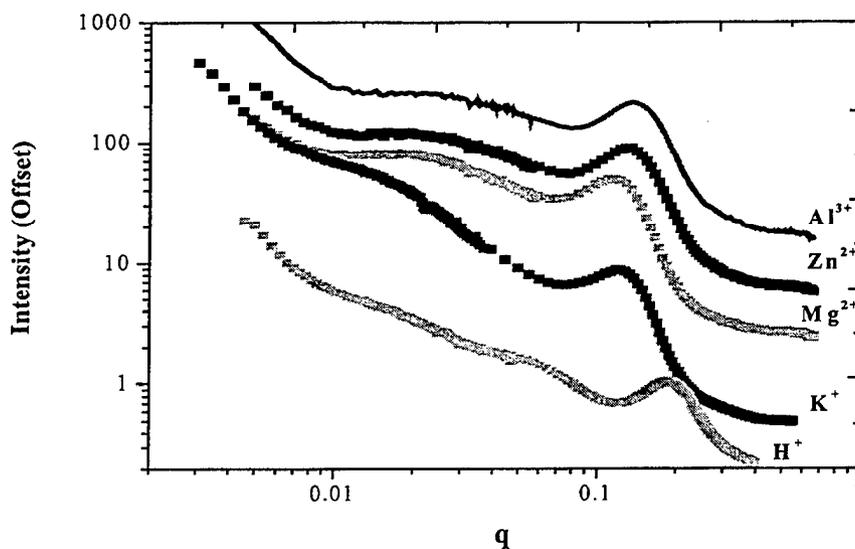


Figure 3. SANS intensity vs. scattering vector for water-swollen Nafion membranes with various counterions from bottom to top: (a) H⁺, 20.7% water, (b) K⁺, 15.9% water, (c) Mg²⁺, 31.2% water, (d) Zn²⁺, 24.8% water, and (e) Al³⁺, 21.9% water. Intensities have been offset for clarity.

dependent on the chemistry of the swelling solvent and the counterion of the sulfonic acid group (Table 1). Similar results have been reported previously [19].

Table 1. Maximum solvent uptake on immersion for Nafion 117 membranes with various counterions in water, methanol, ethanol, propanol, and DMMP.

Solvent ⇌ Counterion↓	Water (%)	Methanol (%)	Ethanol (%)	Propanol (%)	DMMP (%)
H ⁺	20.64	55.84	57.14	56.59	106.26
K ⁺	15.93	7.09	6.84	6.71	90.38
Ca ²⁺	24.73	26.46	23.03	—	65.53
Mg ²⁺	31.19	11.00	26.25	24.48	72.88
Zn ²⁺	24.82	29.17	26.81	26.34	66.32
Al ³⁺	21.88	22.47	23.58	22.13	15.22

Both the mid- q peak, (or crystalline peak), and the ionic peak shift in position as a function of the volume fraction of solvent absorbed by the membrane. Examples for selected solvents are shown in Figures 4–6. The positions of the ionic and crystalline peaks have been determined by fitting using a normalized Gaussian for the peak description, and a power function of q to represent the background (Figure 7). The physical dimension or spacing, d , associated with the peak position was calculated using the Bragg relationship, $d = 2\pi/q$. The ionic peak shifts to lower q values (higher d spacing) as the volume fraction of solvent in the membrane increases, in agreement with the results of other researchers [2, 3, 10]. This shift is consistent across the entire range of solvents studied; however, the magnitude of the shift at a given volume fraction of solvent is solvent dependent. This result is illustrated by Figure 8 and Table 2, in which the d spacings associated with the ionic peaks for membranes swollen with various solvents have been plotted against the volume fraction of solvent in the membrane and fit using linear regression. Two interesting observations may be made from Figure 8. First, the Bragg spacing corresponding to the ionic peak position increases linearly with the volume fraction of solvent absorbed by the membrane, regardless of solvent type, at solvent concentrations between ~2% and ~50%. Second, the slope of the spacing vs. volume fraction curve is different for different solvents. Each observation has implications with regard to the various structural models proposed for Nafion membranes.

The implications of the linear relationship between the Bragg spacing corresponding to the ionic peak and the volume fraction of solvent in the membrane have been the subject of considerable recent controversy. As mentioned in the introduction, the significance of a linear relationship is that it is

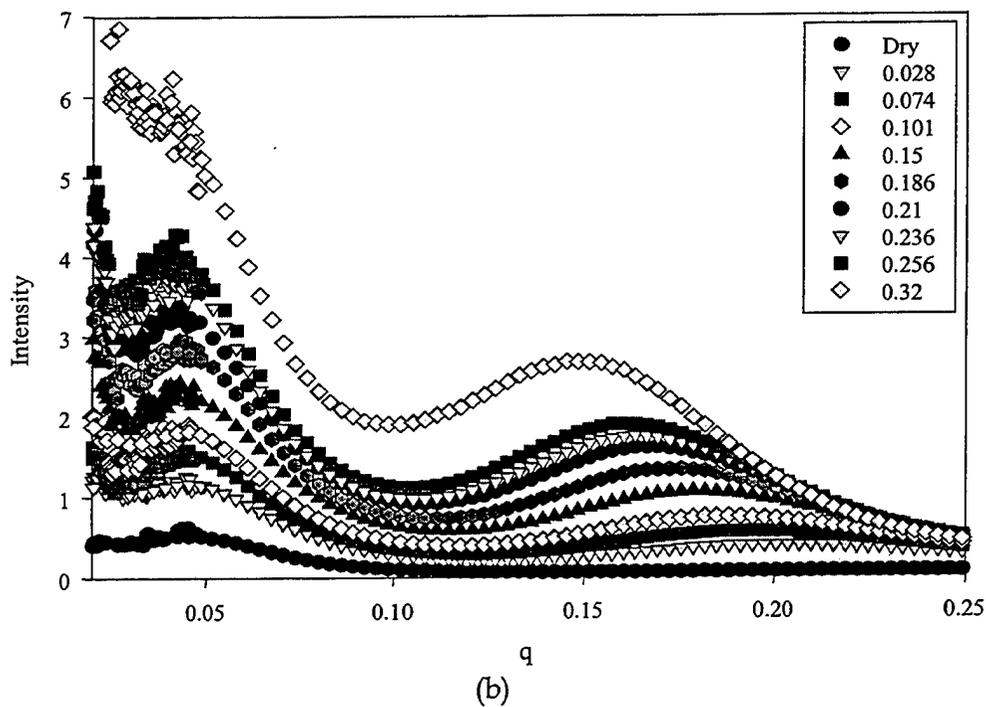
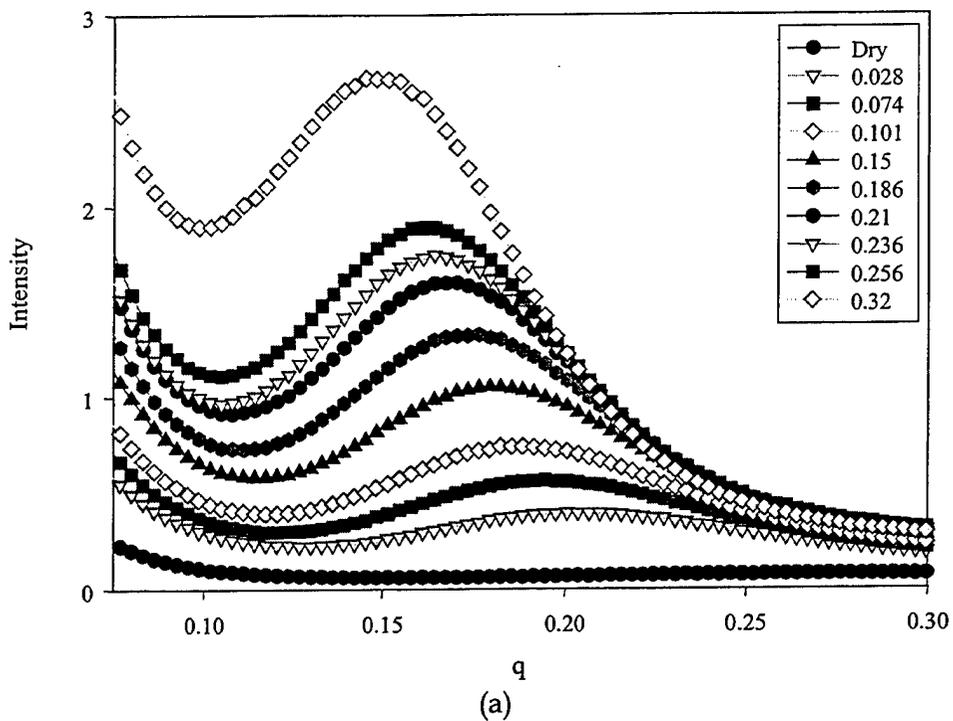


Figure 4. SANS intensity vs. scattering vector for water-swollen Nafion membranes as a function of volume fraction of water in the membrane; (a) peaks corresponding to the ionic feature in the system are evident, and (b) peaks corresponding to the crystalline (lower q) and ionic (higher q) features are evident. (Legend corresponds to graph from bottom to top.)

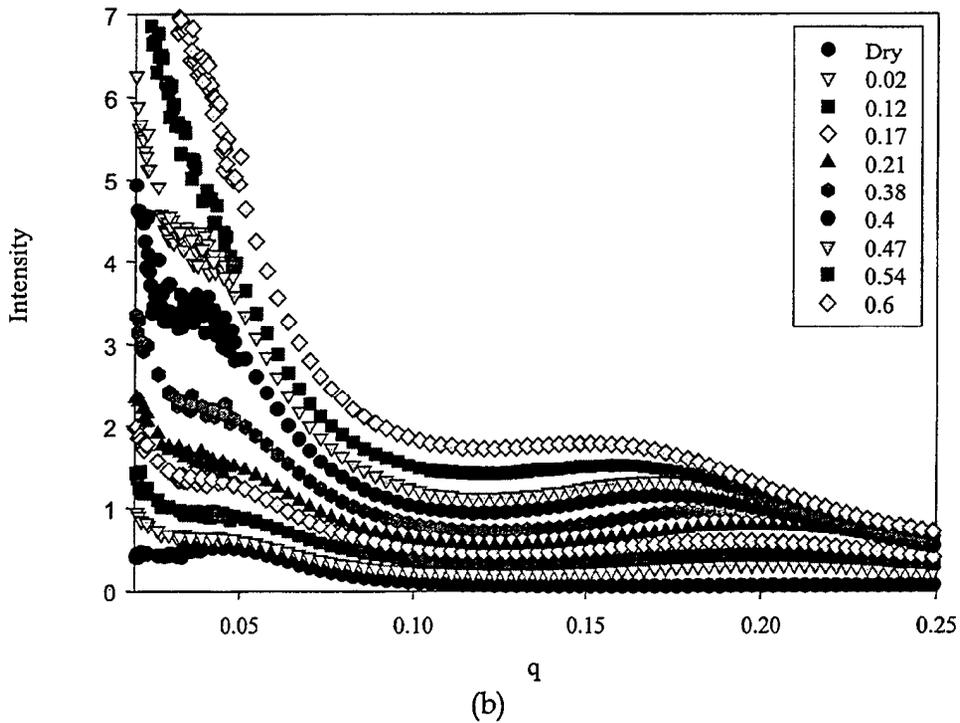
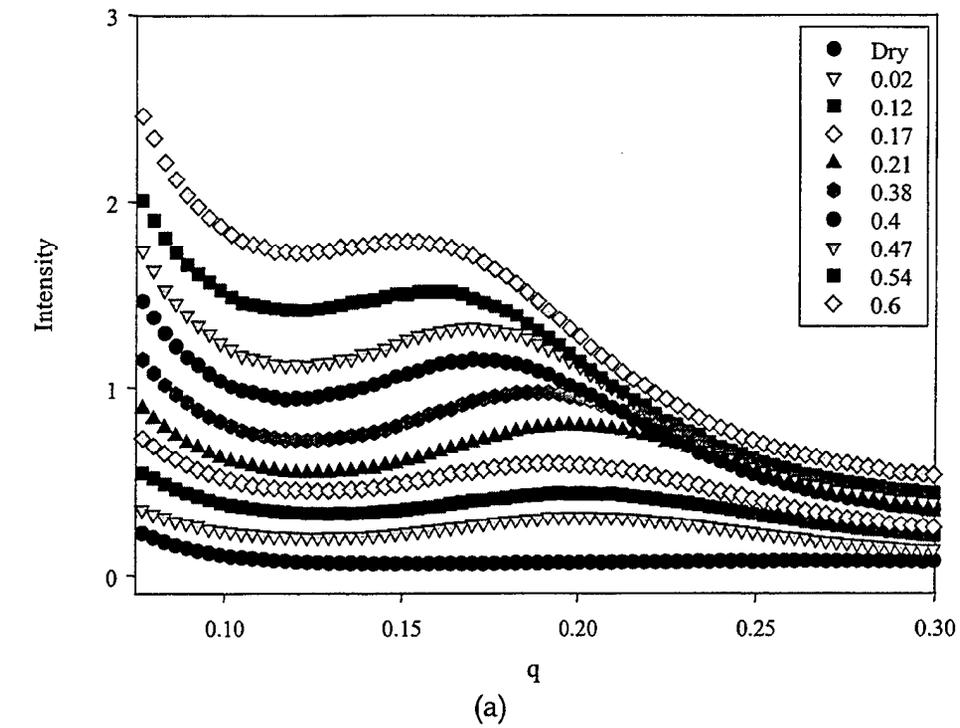


Figure 5. SANS intensity vs. scattering vector for ethanol-swollen Nafion membranes as a function of volume fraction of ethanol in the membrane; (a) peaks corresponding to the ionic feature are evident, and (b) peaks corresponding to the crystalline (lower q) and ionic (higher q) features are evident. (Legend corresponds to graph from bottom to top.)

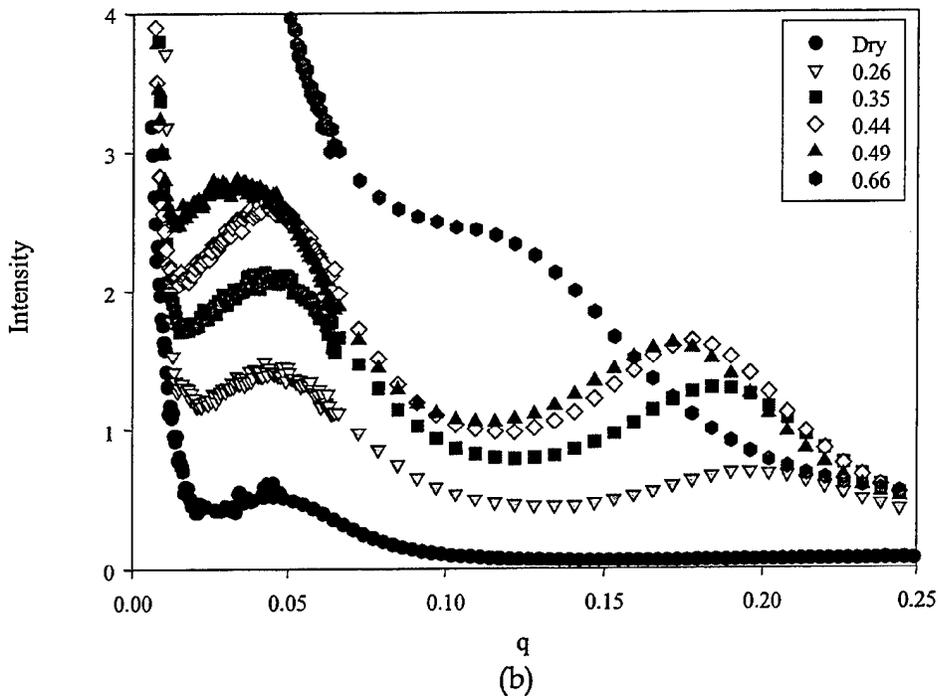
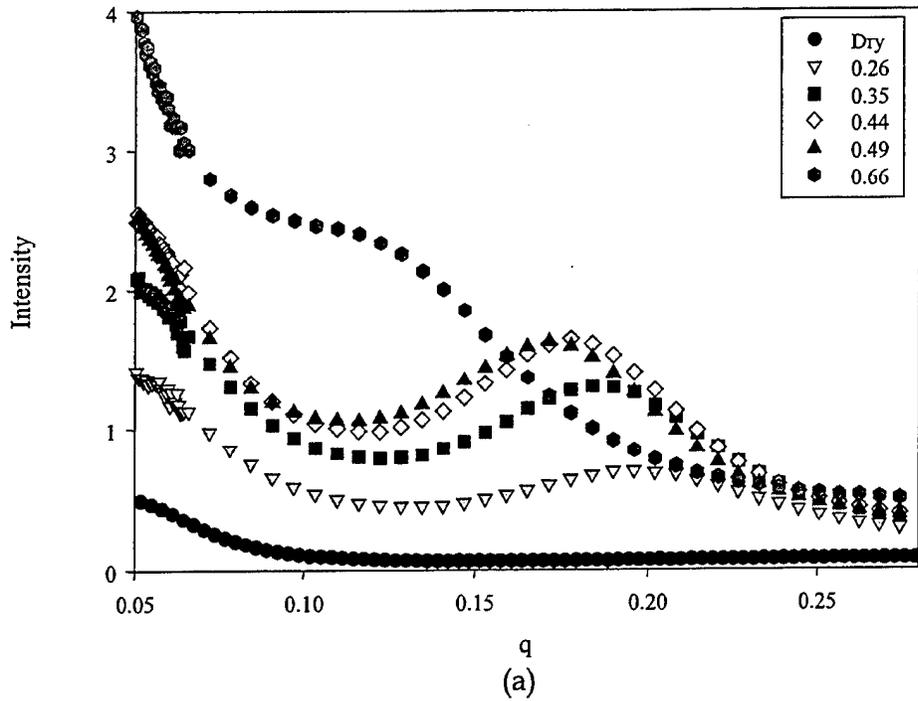


Figure 6. SANS intensity vs. scattering vector for water-swollen Nafion membranes as a function of volume fraction of DMMP in the membrane; (a) peaks corresponding to the ionic feature are evident, (b) peaks corresponding to the crystalline (lower q) and ionic (higher q) features are evident. (Legend corresponds to graph from bottom to top.)

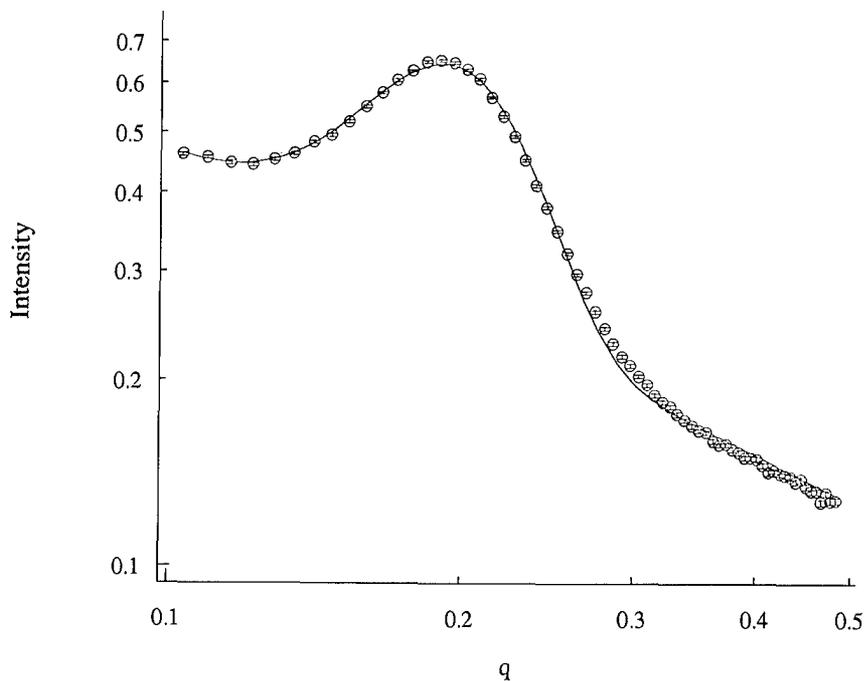


Figure 7. Gaussian curve fit with a power function background (line) to the ionic scattering peak in the SAS intensity vs. scattering vector data (open circles) for a Nafion membrane swollen to 0.11 volume fraction methanol.

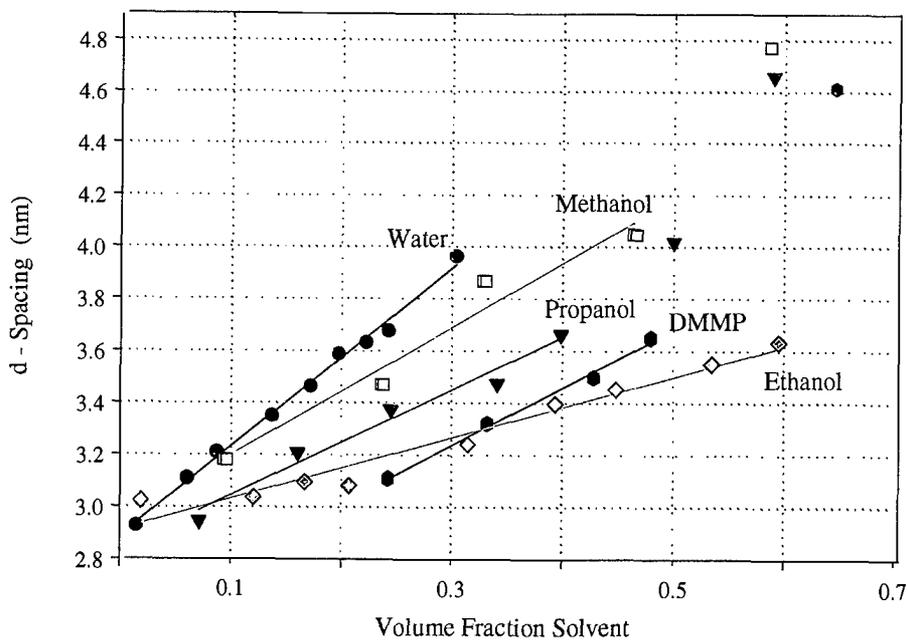


Figure 8. Bragg spacing corresponding to the ionic cluster peak vs. volume fraction solvent for Nafion membranes swollen with various solvents. Lines represent best fit from linear regression. Associated curve fitting parameters are listed in Table 2.

Table 2. Parameters from a linear fit of the curves of spacing corresponding to the ionic peaks vs. the volume fraction of solvent in Nafion membranes swollen with water, methanol, ethanol, propanol, and DMMP.

Solvent	No. of Points Used in Statistics	Volume Fraction Range	y-Intercept	<i>m</i> , Slope	<i>r</i> , Correlation Coefficient
Water	9	0-0.32	2.85	3.72	0.99125
Methanol	4	0-0.48	2.43	4.88	0.93781
Ethanol	7	0-0.47	2.90	1.24	0.92549
Propanol	5	0-0.41	2.73	1.67	0.99826
DMMP	4	0-0.49	2.60	2.05	0.99734

that it is inconsistent with a cluster-type model for the membrane structure, and consistent with a layer model. Recent results of a Porod analysis of SANS investigation of water-swollen Nafion membranes indicates that the specific surface area in the system does not change as water volume fractions increase from ~ 0.08 to >0.50 [10], which is also consistent with expectations from a layered system. Recently, the linearity of that relationship has been challenged by Gebel [10], who reported exponents closer to 1.3 for water-swollen membranes, in contrast to the results of several other groups that have reported a linear relationship [2, 4] for solvent-swollen membranes. Regardless, the data collected has been limited in previous investigations largely to membranes swollen only with water or methanol. The data collected in the current study is more extensive than that previously reported, and it covers a broad range of solvents. The agreement across solvents of varying polarity and dielectric content with a linear variation of ionic spacing with volume fraction of solvent between $\sim 2\%$ and $\sim 50\%$ swelling is strong evidence for a layered structure in the regime where the polymer represents the primary component in the membrane/solvent system. It should be noted that this investigation did not probe the structure of membranes at solvent levels below $\sim 2\%$. Any initial structural changes occurring in morphology of the membranes between the dry state and conditions in which the solvent content reached $\sim 2\%$, such as coalescence of clusters into layers or channels, have not been considered.

It is interesting to note that the position of the scattering feature associated with the crystalline regions also shifts linearly with volume fraction of solvent (Figures 4-6 and 9). Limited results on a similar membrane-water system reported previously are in general agreement with this observation [9]. Since the mid- q peak represents correlation between crystalline regions within the membrane, its motion yields information about the nature of the swelling within the non-crystalline regions of the membrane separating the crystalline regions. The slope of the "crystal-spacing" vs. volume fraction solvent curves exceed those of the "ionic-spacing" vs. volume fraction solvent curves except for the

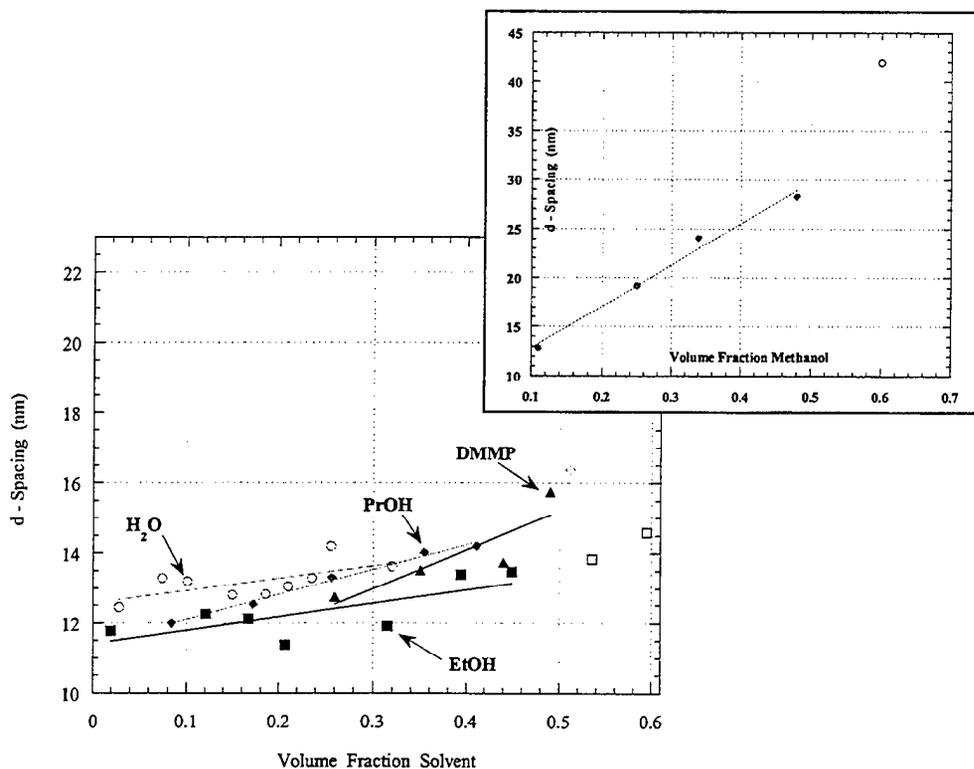


Figure 9. Bragg spacing corresponding to the crystalline peak vs. volume fraction solvent for Nafion membranes swollen with various solvents. Lines represent best fit from linear regression for data up to 0.50 volume fraction solvent. Associated curve fitting parameters are listed in Table 3.

case in which water is the solvent (Tables 2 and 3). For the water-swollen membranes, the slopes of both curves are similar, though there is considerable scatter in the data on the crystalline feature spacing. For membranes swollen with any of the alcohols considered or DMMP, the slopes of the crystalline feature spacing vs. volume fraction solvent curves are at least twice those of the ionic feature spacing vs. volume fraction solvent curves. In the extreme case of methanol, the solvent shows a strong preference for the portions of the structure not represented by the ionic peak. This result may have implications for design of polymer-based fuel cell membranes, in that reduction of susceptibility to methanol crossover problems is likely to require significant modification of the non-crystalline phase in the material.

The change in the slope of the spacing vs. volume fraction curves may be interpreted as evidence of the solvent partitioning into different regions of the membrane's structure. For example, for membranes with 20 volume-percent

Table 3. Parameters from a linear fit of the curves of spacing corresponding to the crystalline feature peaks vs. the volume fraction of solvent in Nafion membranes swollen with water, methanol, ethanol, propanol, and DMMP.

Solvent	No. of Points Used in Statistics	Volume Fraction Range	y-Intercept	<i>m</i> , Slope	<i>r</i> , Correlation Coefficient
Water	9	0-0.32	12.572	3.548	0.654
Methanol	4	0-0.48	8.572	44.446	0.993
Ethanol	7	0-0.47	11.416	3.840	0.739
Propanol	5	0-0.41	11.401	7.099	0.995
DMMP	4	0-0.49	9.639	11.137	0.878

solvent, the spacing corresponding to the ionic regions is greater for the membranes swollen with water than for the membranes swollen with the alcohols or DMMP. This indicates that the water partitions more effectively into the layer-like regions of the structure than the other solvents. Correspondingly, the slope of the crystalline feature spacing vs. volume fraction curve is the smallest for water, indicating poorer penetration of the non-crystalline portions of the structure by water in comparison to the alcohols or DMMP. The partitioning effect is illustrated further in Figure 10, in which the microscopic volumetric expansion for membranes swollen to their full capacity is calculated assuming a fully layered structure and plotted against the total volumetric swelling of the membrane. For those membranes swollen with water, the microscopic swelling calculated from the change in the ionic feature spacing exceeds the total swelling in the system calculated from the solvent uptake, regardless of counterion. For other solvents, the microscopic volumetric swelling is less than would be predicted based on the total swelling of the membranes. This indicates considerable partitioning into the portion of the structure not represented by the ionic peak, in agreement with the results based on comparison of the slopes of the crystalline and ionic feature spacing vs. solvent volume fraction curves (Figures 8 and 9). It should be noted that the nature of the counterion has a significant effect on partitioning in membranes swollen with solvents other than water. For example, for membranes swollen with ethanol or propanol, the expansion predicted from the ionic feature spacing decreases in the order $Zn^{2+} > Al^{3+} > Mg^{2+}$, though the total swelling experienced by the membrane is similar for all three counterions (Figure 10). This behavior may have implications for the modification of membranes for use with liquid fuels.

Though not addressed as part of this investigation, the partitioning effect has been observed by other researchers for membranes swollen with water/alcohol mixtures, in which the alcohol was found to plasticize the Nafion matrix enhancing macroscopic swelling relative to that achievable in either pure solvent [20].

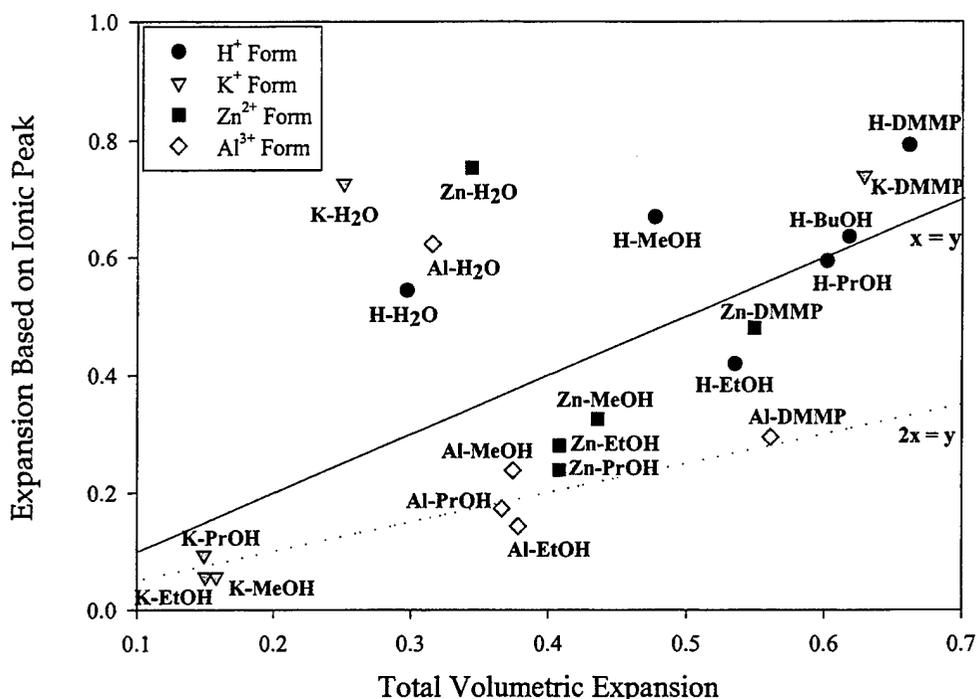


Figure 10. Microscopic volumetric swelling in Nafion membranes calculated from the increase in the ionic feature spacing vs. total volumetric swelling in the membranes calculated from weight uptake of solvent. (Counterions and solvents as indicated.)

As previously noted [10, 11], the slopes of both curves (ionic spacing vs. volume fraction solvent, crystal peak spacing vs. volume fraction solvent) would have to match if the structure were to be envisioned as wholly comprised of crystalline platelets separated by ion-rich channels. Only in the water swollen samples are the slopes comparable. However, the structure could alternatively be envisioned as having isolated ordered regions with a highly ordered layered crystalline-type structure (such as those suggested by Starkweather [11], Litt [15], Ozerin et al. [5, 6], or Rebrov et al. [16]), dispersed within a matrix of less well-ordered material. A general structural interpretation of this sort is easily reconciled with reported crystallinity values from x-ray diffraction in the 10-15% range [2, 11] and consistent with reports of a networked channel structure in the membranes [21]. For a dispersed layered crystalline-phase model, the disparity in the ionic feature spacing and crystalline feature spacing slopes would be indicative of the preference of the particular solvent for the matrix relative to the layered-crystalline regions rather than evidence against a layered structure.

Finally, the behavior beyond the point at which the solvent exceeds 50% of the volume of the system must be considered. For membrane-solvent systems in

which the total solvent swelling in the system naturally exceeds 50% on immersion, such as methanol, propanol, and DMMP, a discontinuity in the relationship between the ionic feature spacing and the solvent volume fraction occurs in the vicinity of the 50% swelling point (Figure 8). Though the data available are very limited, this discontinuity is consistent with the appearance of a second structural regime, as recently described by Gebel [10]. This second regime occurs after a phase inversion takes place, and in this regime the structure of the membrane-solvent system has been described as a connected network of polymer rods [10], which is the precursor to the formation of the rod-like micellular structure that has been identified in Nafion solutions. In this investigation, the discontinuous jump in the dimension of the ionic feature was observed for all solvents that were capable of swelling the membranes to levels higher than 50% except ethanol. This discrepancy may be related to the lesser capacity of ethanol for partitioning into, and presumably eventually disrupting, the layered regions of the membrane structure as evidenced by the comparatively small slope in the ionic feature vs. volume fraction solvent curve for ethanol (Tables 2 and 3).

Various SANS structural evaluations were performed on Nafion counterion membranes. These membranes were completely swollen and swollen to varying volume fractions just like the acid-form membranes discussed in this report. X-ray diffraction (XRD) and dynamic mechanical analysis (DMA) data were also taken on acid-form and counterion-form membranes. In addition, various conductivity and methanol crossover studies on Nafion are currently ongoing or the data are being evaluated for acid-form and counterion-form membranes. These data will be discussed in future works.

4. Conclusions

SANS investigations of Nafion 117 membranes swollen with a variety of solvents have been performed. Scattering curves show features typical of swollen perfluorosulfonate ionomer membranes, such as a maximum associated with ionic regions of the structure and a maximum associated with crystalline regions of the structure. Both maxima are observed to shift toward lower scattering vector positions as the membranes swell for all solvents tested. For solvent volume fractions up to ~50%, positions of both maxima decrease linearly as the solvent content in the membrane increases. Correspondingly, the real-space dimensions or Bragg spacings corresponding to these maxima increase linearly with solvent content in the membranes at solvent levels up to ~50 volume-percent. The slopes of the curves of spacing vs. volume fraction solvent differ for the ionic feature spacing and the crystalline feature spacing, with the slope of the crystalline feature spacing vs. volume fraction curve exceeding that of the ionic

feature spacing vs. volume fraction curve for all solvents except water. This is taken to be indicative of the non-aqueous solvents partitioning preferentially into the regions of the structure that do not give rise to the ionic scattering maxima. A comparison of the microscopic swelling estimated from changes in the ionic feature spacing vs. the total volumetric swelling in the system based on total solvent uptake also indicates preferential segregation of non-aqueous solvents into regions of the structure not represented by the ionic feature scattering. For membranes swollen with solvents other than water, irrespective of the counterion associated with the acidic group, the total swelling in the membranes was found to exceed the microscopic swelling. For water-swollen membranes, the microscopic swelling is similar to the total volumetric swelling. Finally, for membranes swollen to solvent levels exceeding 50 volume-percent, evidence of significant structural changes have been found that are consistent with recent predictions of phase inversion and the formation of a connected rod-like structure in this solvent regime [10].

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