Small-Angle Neutron Scattering Investigation of Structural Changes in Nafion Membranes Induced by Swelling with Various Solvents

SANDRA K. YOUNG, S. F. TREVINO, NORA C. BECK TAN

U.S. Army Research Laboratory, Weapons & Materials Research Directorate, AMSRL-WM-MA/Building 4600,
Aberdeen Proving Grounds, Maryland 21005-5169

Received 4 May 2001; revised 14 November 2001; accepted 16 November 2001

ABSTRACT: The structure of Nafion-117 perfluorosulfonate ionomer membranes was investigated with small-angle neutron scattering techniques. Structural changes induced by the swelling of the membranes with water, alcohols, and dipolar, aprotic solvents were monitored at solvent-swelling levels ranging from approximately 2 vol % to greater than 50 vol %. Membranes swollen up to approximately 50 vol % 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 scattering vector values as the solvent content in the membrane increased. The shift in the position of both maxima was linearly related to the solvent volume fraction in the membrane. The Bragg spacings corresponding to both the ionic-feature scattering maximum and the crystalline-feature scattering maximum were plotted versus the solvent volume fraction in the membranes, and the data fit with linear regression. The slopes associated with the curves of the spacing versus the solvent volume fraction were greater for the crystalline-feature spacing than for the ionic-feature spacing for all solvents other than water; this was indicative of preferential segregation of nonaqueous solvents into regions of the structure not directly associated with the ionic scattering maximum. © 2002 John Wiley & Sons, Inc. J Polym Sci Part B: Polym Phys 40: 387–400, 2002; DOI 10.1002/polb.10092

Keywords: ionomers; Nafion; polymer membranes; small-angle neutron scattering; fluoropolymers

INTRODUCTION

Perfluorosulfonate ionomer membranes are materials of considerable commercial significance because of 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 heterogeneous on a submicrometer or nanometer scale. However, despite nearly 20 years of investigation, there still remains considerable uncertainty regarding the details of this structure.

Most commercial perfluorosulfonate ionomers are based on a chemistry similar to that of the Nafion membranes produced by DuPont, the general formula of which is represented in Figure 1.

Certain commercial products are identified in this article to specify the experimental procedures in adequate detail. This identification does not imply recommendation or endorsement by the authors or by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

Correspondence to: N. C. B. Tan, W. L. Gore & Associates, 501 Vieve's Way, Elkton, MD 21922 (E-mail: nbecktan@wlgore.com)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 40, 387–400 (2002)

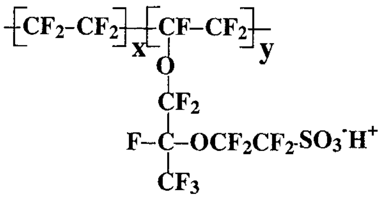


Figure 1. Chemical structure of the Nafion monomer.

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 into ionomer form by an exchange of the acidic proton with organic, alkali, or transition-metal cations. For our purposes, the sulfonate groups will be generically called the ionic groups.

The structure of Nafion membranes is most often investigated with small-angle scattering methods. Numerous small-angle scattering studies by a variety of research groups[1–10] have consistently produced characteristic patterns from perfluorosulfonate ionomer membranes with three basic features: (1) a scattering maximum occurring at momentum transfer vector (**q**) values in excess of 0.1 $Å^{-1}$ that has been associated with aggregation of the ionic groups, (2) a scattering maximum occurring at **q** $\sim$ 0.04 $Å^{-1}$ 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 $Å^{-1}$). The structure of the crystalline regions has also been investigated with X-ray diffraction techniques.[2,11,12] As the membranes are swollen with water vapor, liquid water, or methanol (MeOH), 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 in 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 small-angle scattering range. Cluster models were first introduced to explain the behavior in hydrocarbon ionomers, such as sulfonated polystyrene.[15] The possibility of similar clustering phenomena occurring in perfluorosulfonate ionomer membranes was proposed in early studies of Nafion perfluorosulfonate ionomers by Roche et al.[1] and 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 so 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 the position of the ionic cluster peak and the volume of water absorbed by the membranes upon swelling,[2,4,16] which cannot be accounted for with a cluster model. In addition, 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 change 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.[16]

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 disklike, chain-folded lamallae[16,17] and bilayers of backbone chains[5,6,11] have been proposed. For 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 in 1982,[11] and variations have been considered more recently by Rebrov and coworkers[5,6] and Litt.[16] 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[16] also argued that mechanical performance and volumetric measurements are 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 the solvent volume fraction. Criticisms include lack of accountability for the observed upturn in scattering intensity at very low angles, lack of agreement between the solvent-induced-shift dependency of the ionic peaks and the small-angle crystalline peaks,[9,10] and some controversy surrounding the linearity of the relationship between the 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 through 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, that is, to solvent volume fractions above that achievable by immersion in water (~0.35). Employing nonaqueous solvents also allows for probing 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 solvent volume fraction in the membrane increases. The linear dependence holds for a range of solvents of various polarities up to volume fractions of approximately 0.5; however, the magnitudes of the slopes corresponding to the dependence of the characteristic dimensions on the solvent volume fraction vary from solvent to solvent.

EXPERIMENTAL

Materials

Perfluorosulfonate membranes (equivalent weight = 1100, thickness = 7 mil) in the SO_3H form (Nafion-117) were obtained from C.G. Processing, Inc. Concentrated hydrochloric acid (EM Science) and concentrated nitric acid (J.T. Baker) were obtained from VWR Scientific and used as received. All water was distilled or deionized. MeOH, ethanol (EtOH), propanol (PrOH), dimethylformamide, and 3-Å molecular sieves were obtained from Sigma–Aldrich Chemicals. Dimethylmethylphosphonate (DMMP) was obtained from Lancaster Chemicals.

Perfluorosulfonate Ionomer (PFSI) Membrane Initialization

All membranes were preconditioned and converted into the sulfonic acid form in an initialization procedure reported previously by Mauritz et al.[18] Membranes were exchanged to the acid form through refluxing in 50/50 (v/v) HCl/HNO_3 solutions, the leaching of excess acid in deionized water reflux (3×), and vacuum drying at 125 °C. All membranes were changed into this standard initial state before counterion exchange and were evaluated with prompt γ-activation analysis to ensure maximum sample reproducibility.[19]

Small-Angle Neutron Scattering (SANS) Evaluations

SANS measurements were performed at the National Institute of Standards and Technology Center for Neutron Research (Gaithersburg, MD) with 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 h 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 the immersion of the membranes in a vial containing the solvent and molecular sieves. Once removed from the vial, after their surfaces were patted dry, the membranes were quickly weighed. For samples being evaluated at less than the full solvent uptake, the solvent was removed through heated evaporation to the desired volume fraction in a closed chamber containing a beaker of sieves to minimize contamination by water. Because the

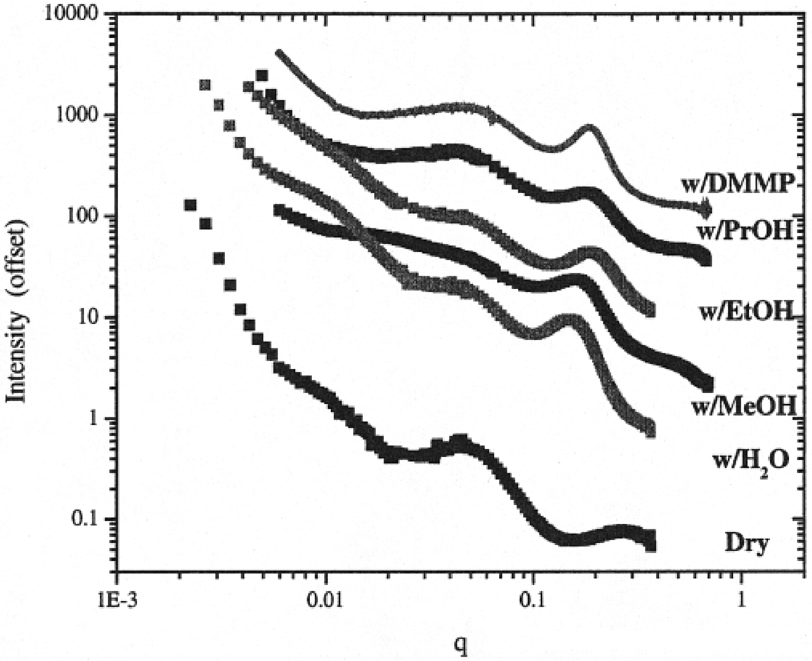


Figure 2. SANS intensity versus **q** (Å^{-1}) for Nafion membranes: (a) dry, (b) 32% water, (c) 34% MeOH, (d) 38% EtOH, (e) 35.4% PrOH, and (f) 35% DMMP. The intensities are offset for clarity.

boiling point was too high to easily remove the solvent from the membrane, DMMP samples were made by calculation of the amount of solution needed based on the weight of the membrane and by its addition 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 h before SANS measurements, which allowed the solvents to equilibrate within the membranes. In addition, membranes were weighed after the experiments to verify that the solvents within the membranes 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 $\mathbf{q} = (4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength of the incident neutron beam ($\lambda = 6$ Å for these experiments). The detector was a 64-cm × 64-cm He-3 position-sensitive proportional counter with 1-cm^2 resolution. The scattered intensity was measured at **q** values ranging from approximately 0.002 to 0.6 Å^{-1}. This was accomplished by the detector being placed 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, the 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.

RESULTS AND DISCUSSION

SANS experiments were performed on Nafion swollen in a variety of solvents. The scattering curves show the features known to be characteristic of Nafion membranes: a low-angle intensity upturn, a broad peak around 0.04 Å^{-1}, and an ionic peak around 0.1–0.2 Å^{-1}. These features are seen regardless of the swelling solvent (Fig. 2) and for membranes in the acid form and ion-exchanged forms (Fig. 3). Although the structural features are consistent regardless of the counterion or solvent type at a given volume fraction of absorbed solvent, the total solvent uptake reached is strongly dependent on the chemistry of the swelling solvent and the counterion of the sulfonic acid group (Table I). Similar results have been reported previously.[20]

Both the mid-**q** peak (or crystalline peak) and the ionic peak shift in position as a function of the

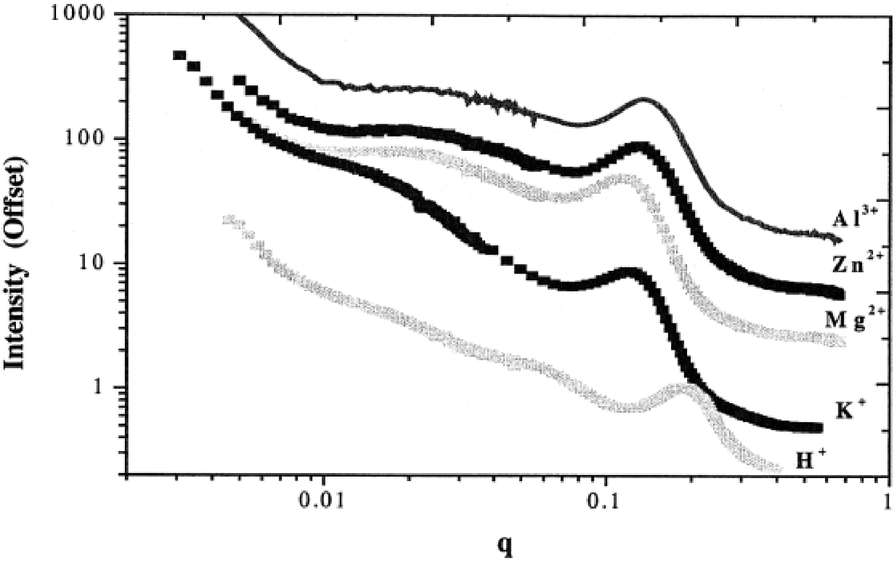
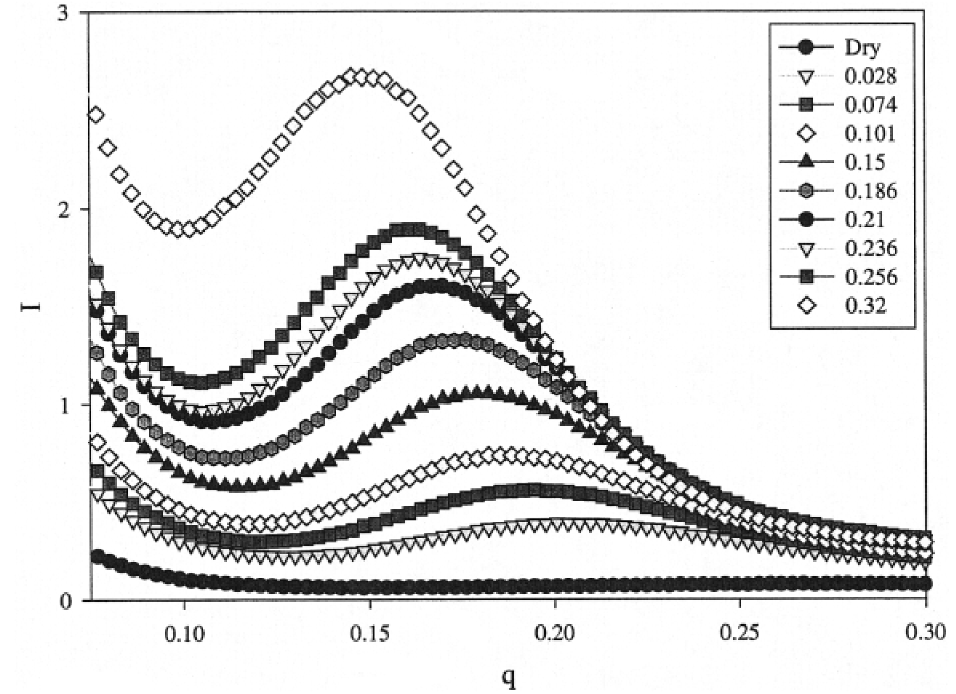


Figure 3. SANS intensity versus **q** (Å^{-1}) for water-swollen Nafion membranes with various counterions: (a) H$^+$, 20.7% water; (b) K$^+$, 15.9% water; (c) Mg^{2+}, 31.2% water; (d) Zn^{2+}, 24.8% water; and (e) Al^{3+}, 21.9% water. The intensities are offset for clarity.

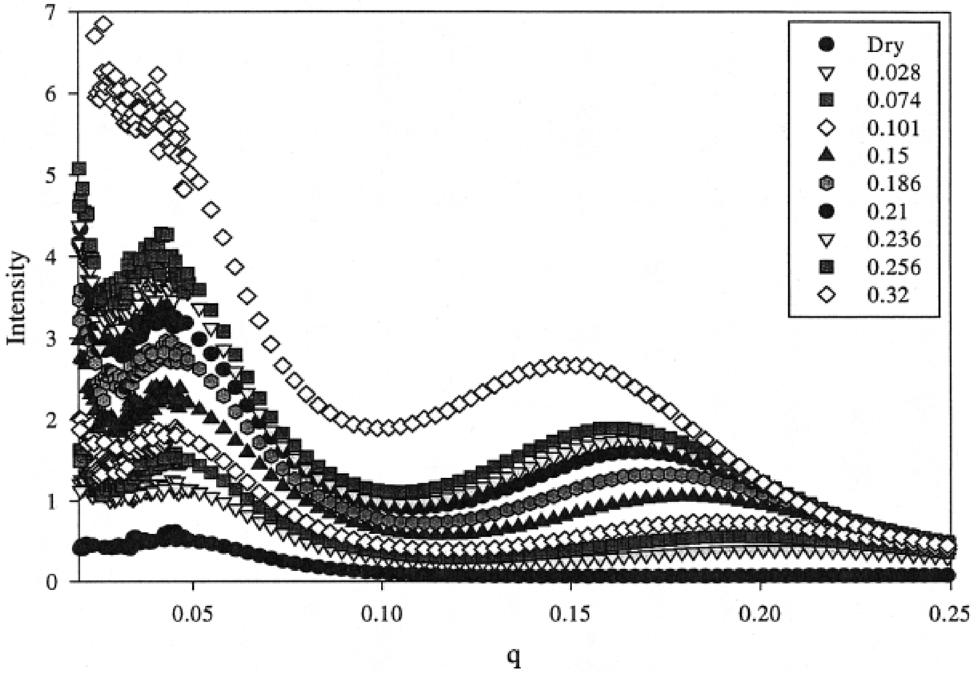
volume fraction of solvent absorbed by the membrane. Examples for selected solvents are shown in Figures 4–6. The positions of the ionic and crystalline peaks have been determined through fitting with a normalized Gaussian for the peak description and a power function of **q** to represent the background (Fig. 7). The physical dimension or spacing (d) associated with the peak position has been calculated with the Bragg relationship, $d = 2\pi/\mathbf{q}$. 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 II, 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 with 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 approximately 2 and 50%. Second, the slope of the curve of the spacing versus the volume fraction is different for different solvents. Each observation has implications with

Table I. Maximum Solvent Uptake on Immersion for Nafion-117 Membranes with Various Counterions in Water, MeOH, EtOH, PrOH, and DMMP

	Solvent				
Counterion	Water (%)	MeOH (%)	EtOH (%)	PrOH (%)	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



(a)



(b)

Figure 4. SANS intensity versus **q** (Å^{-1}) for water-swollen Nafion membranes as a function of the volume fraction of water in the membrane: (a) peaks corresponding to the ionic feature and (b) peaks corresponding to the crystalline (lower **q**) and ionic (higher **q**) features.

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 relation-

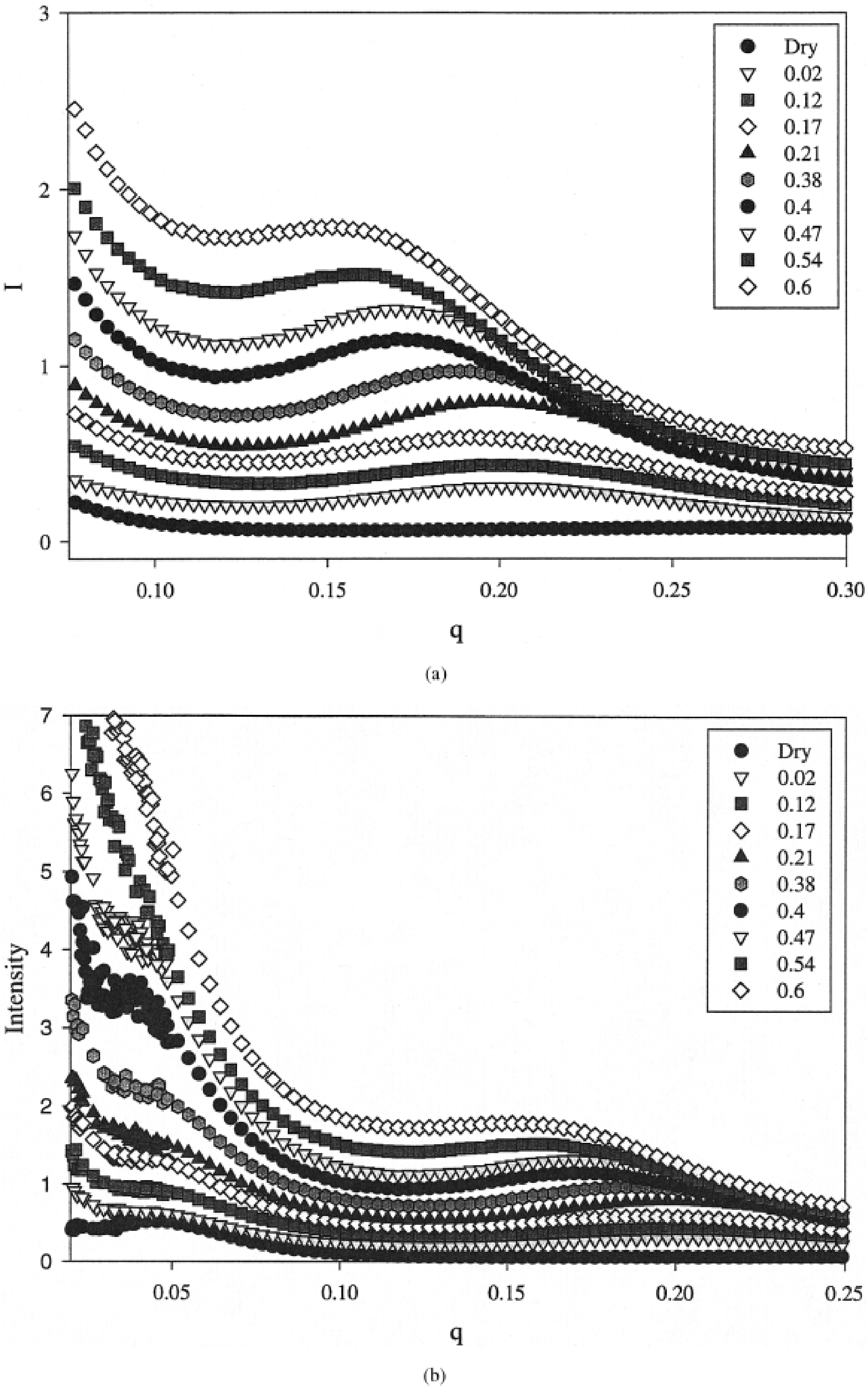
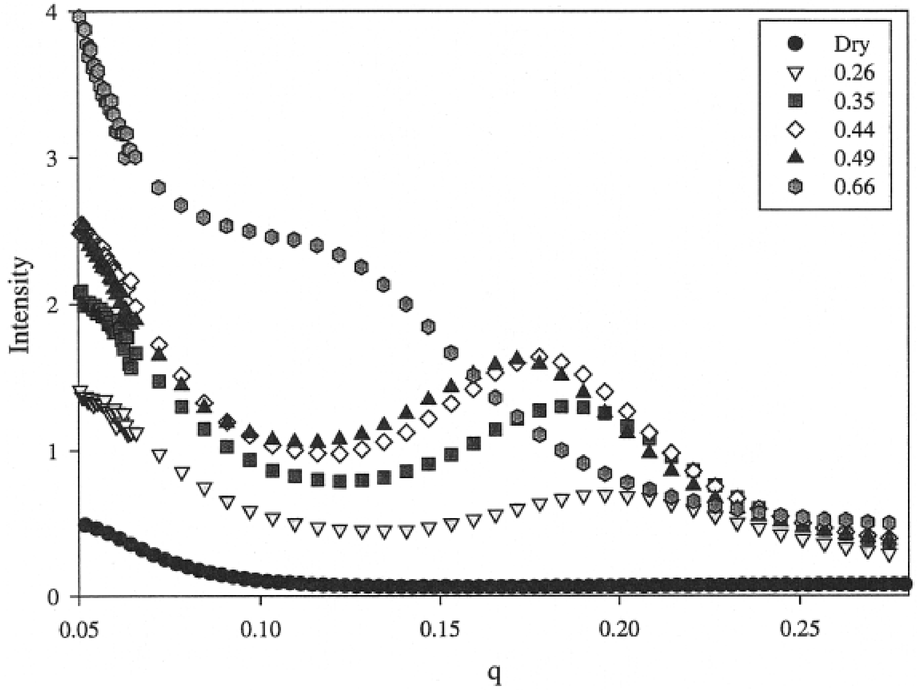
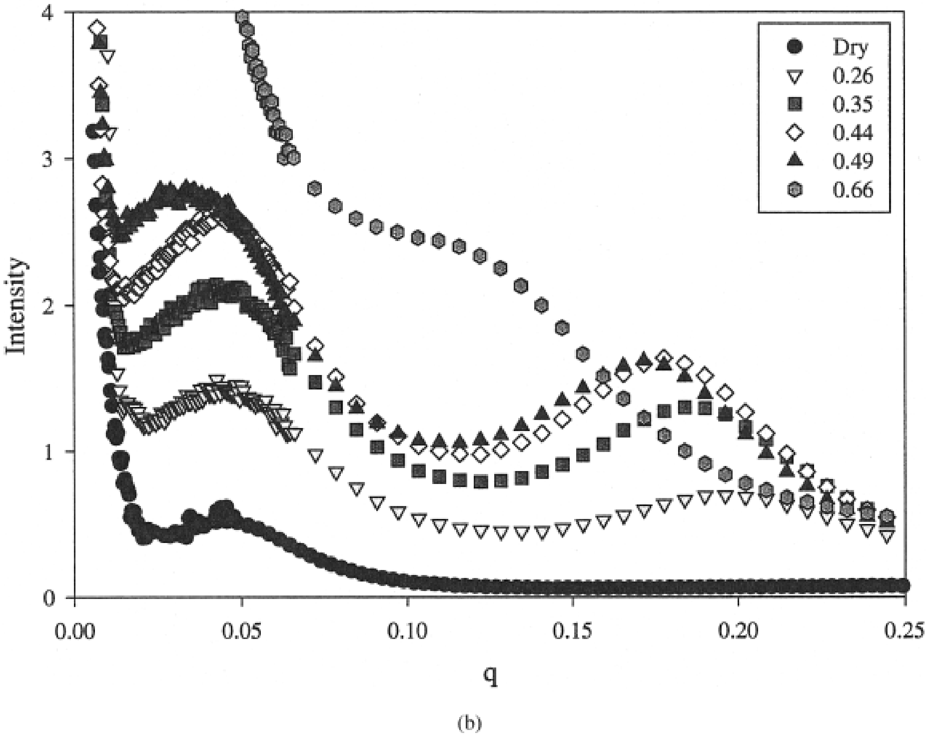


Figure 5. SANS intensity versus **q** (Å^{-1}) for EtOH-swollen Nafion membranes as a function of the volume fraction of EtOH in the membrane: (a) peaks corresponding to the ionic feature and (b) peaks corresponding to the crystalline (lower **q**) and ionic (higher **q**) features.

ship is that it is inconsistent with a cluster-type model for the membrane structure but is consistent with a layer model. Recent results of a Porod analysis of SANS investigation of water-swollen Nafion membranes indicate that the specific surface area in the system does not change as the



(a)



(b)

Figure 6. SANS intensity versus **q** (Å^{-1}) for DMMP-swollen Nafion membranes as a function of the volume fraction of DMMP in the membrane: (a) peaks corresponding to the ionic feature and (b) peaks corresponding to the crystalline (lower **q**) and ionic (higher **q**) features.

water volume fractions increase from approximately 0.08 to greater than 0.50,[10] which is also consistent with expectations from a layered system. Recently, the linearity of that relationship was challenged by Gebel,[10] who reported exponents closer to 1.3 for water-swollen membranes,

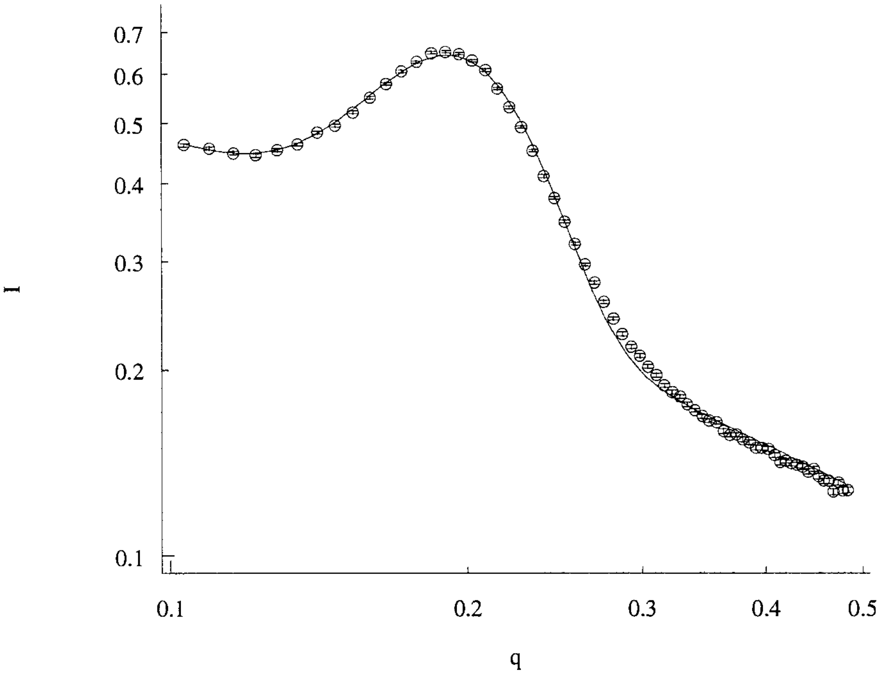


Figure 7. Gaussian curve fit with a power function background (line) to the ionic scattering peak in the data of the small-angle scattering intensity versus **q** (open circles) for a Nafion membrane swollen to a 0.11 volume fraction of MeOH.

in contrast to the results of several other groups that have reported a linear relationship[2,4] for solvent-swollen membranes. Nevertheless, the data collected have been limited in previous investigations largely to membranes swollen only with water or MeOH. The data collected in this study are more extensive than those previously reported and cover a broad range of solvents. The agreement across solvents of various polarities and dielectric constants with a linear variation of ionic spacing with a solvent volume fraction between approximately 2 and 50% swelling is strong evidence for a layered structure in the regime in which the polymer represents the primary component in the membrane–solvent system. This investigation did not probe the structure of membranes at solvent levels below approximately 2%. Any initial structural changes occurring in the morphology of the membranes between the dry state and conditions in which the solvent content reached approximately 2%, such as coalescence of clusters into layers or channels, were not considered.

The position of the scattering feature associated with the crystalline regions also shifts linearly with the volume fraction of solvent (Figs. 4–6 and 9). Limited results on a similar membrane–water system reported previously are in general agreement with this observation.[9] Because the mid-**q** peak represents correlation between crystalline regions within the membrane, its motion yields information about the nature of the swelling within the noncrystalline regions of the membrane separating the crystalline regions. The slope of curves of the crystal spacing versus the solvent volume fraction exceed those of the curves of the ionic spacing versus the solvent volume fraction, except for the case in which water is the solvent (Tables II and III). For the water-swollen membranes, the slopes of both curves are similar, although 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 curves of the crystalline-feature spacing versus the solvent volume fraction are at least twice those of curves of the ionic-feature spacing versus the solvent volume fraction. In the extreme case of MeOH, the solvent shows a strong preference for the portions of the structure not represented by the ionic peak. This result may have implications for the design of polymer-based fuel-cell membranes, in that the reduction of susceptibility to MeOH crossover problems is likely to require significant modification of the noncrystalline phase in the material.

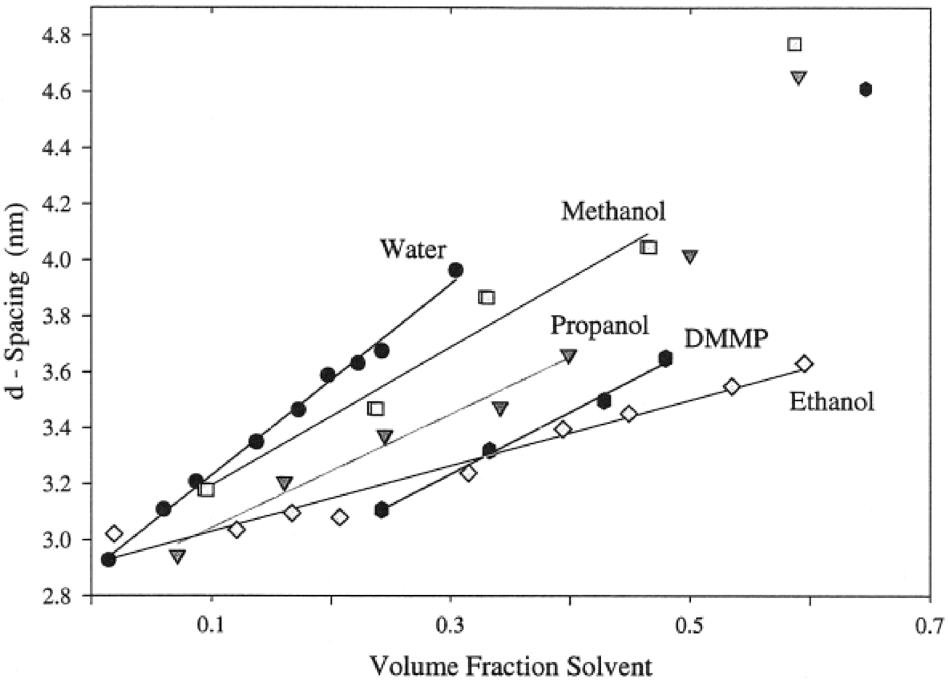


Figure 8. Bragg spacing corresponding to the ionic-feature peak versus the solvent volume fraction for Nafion membranes swollen with various solvents. The lines represent best fits from linear regression for data up to a 0.50 solvent volume fraction. Associated curve-fitting parameters are listed in Table II.

The change in the slope of the curves of the spacing versus the volume fraction may be interpreted as evidence of the solvent partitioning into different regions of the membrane structure. For example, for membranes with 20 vol % 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 water partitions more effectively into the layerlike regions of the structure than the other solvents. Correspondingly, the slope of the curve of the crystalline-feature spacing versus the volume fraction is the smallest for water, indicating poorer penetration of the noncrystalline portions of the structure by water in comparison with 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 under the assumption of 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 the counterion. For other solvents, the microscopic volumetric swelling is less than would be predicted according to the total swelling of the membranes. This indicates considerable

Table II. Parameters from a Linear Fit of the Curves of Spacing Corresponding to the Ionic Peaks versus the Volume Fraction of the Solvent in Nafion Membranes Swollen with Water, MeOH, EtOH, PrOH, and DMMP

Solvent	Points Used in Statistics	Volume Fraction	y Intercept	m (Slope)	(Correlation Coefficient)
Water	9	0–0.32	2.85	3.72	0.99125
MeOH	4	0–0.48	2.43	4.88	0.93781
EtOH	7	0–0.47	2.90	1.24	0.92549
PrOH	5	0–0.41	2.73	1.67	0.99826
DMMP	4	0–0.49	2.60	2.05	0.99734

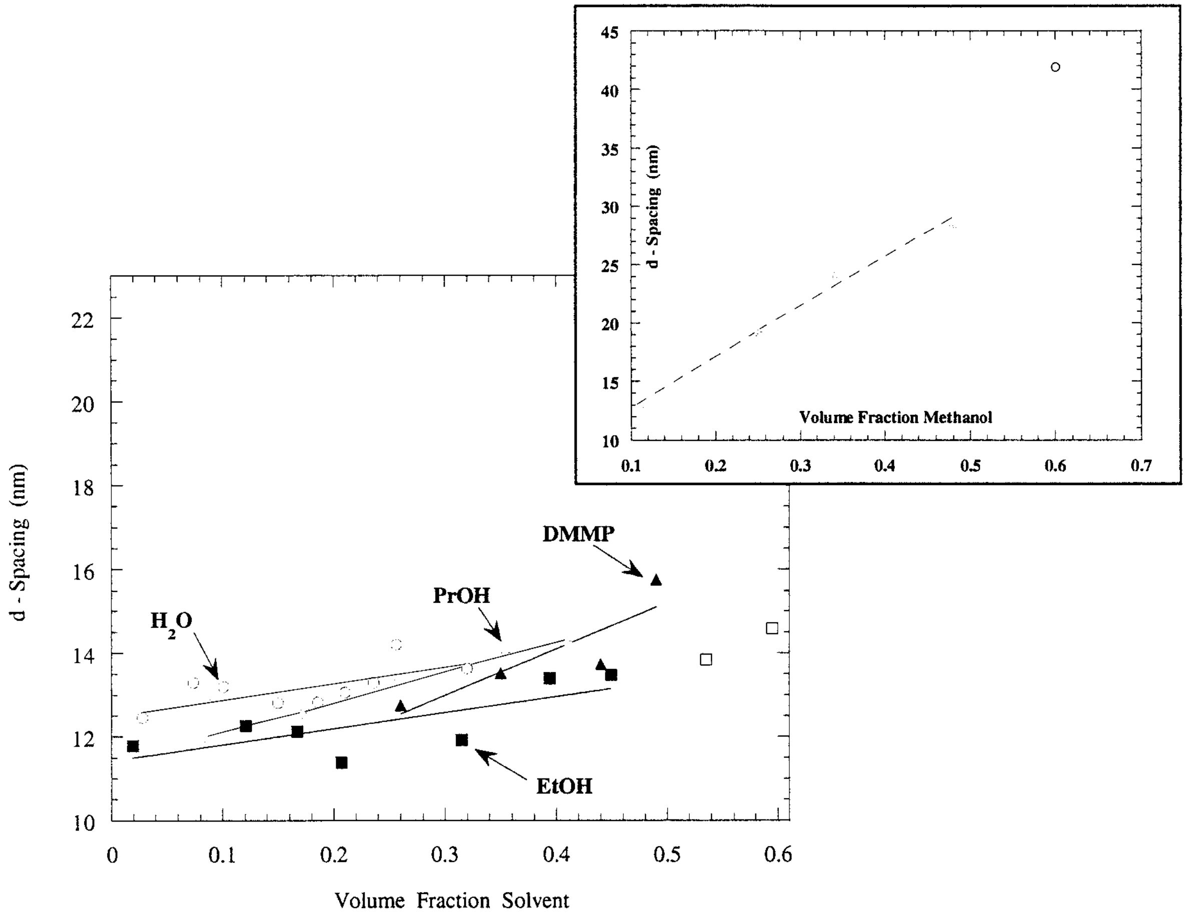


Figure 9. Bragg spacing corresponding to the crystalline-feature peak versus the solvent volume fraction for Nafion membranes swollen with various solvents. The lines represent best fits from linear regression for data up to a 0.50 solvent volume fraction. Associated curve-fitting parameters are listed in Table III.

partitioning into the portion of the structure not represented by the ionic peak, in agreement with the results based on a comparison of the slopes of the curves of the crystalline-feature and ionic-feature spacing versus the solvent volume fraction (Figs. 8 and 9). Evidence for the partitioning of alcohol into nonionic regions of Nafion membranes has also been provided previously by positron annihilation studies.[20]

The nature of the counterion has a significant effect on partitioning in membranes swollen with solvents other than water. For example, for mem-

Table III. Parameters from a Linear Fit of the Curves of Spacing Corresponding to the Crystalline Feature Peaks versus the Volume Fraction of the Solvent in Nafion Membranes Swollen with Water, MeOH, EtOH, PrOH, and DMMP

Solvent	Points Used in Statistics	Volume Fraction	*y* Intercept	*m* (Slope)	*r* (Correlation Coefficient)
Water	9	0–0.32	12.572	3.548	0.654
MeOH	4	0–0.48	8.572	44.446	0.993
EtOH	7	0–0.47	11.416	3.840	0.739
PrOH	5	0–0.41	11.401	7.099	0.995
DMMP	4	0–0.49	9.639	11.137	0.878

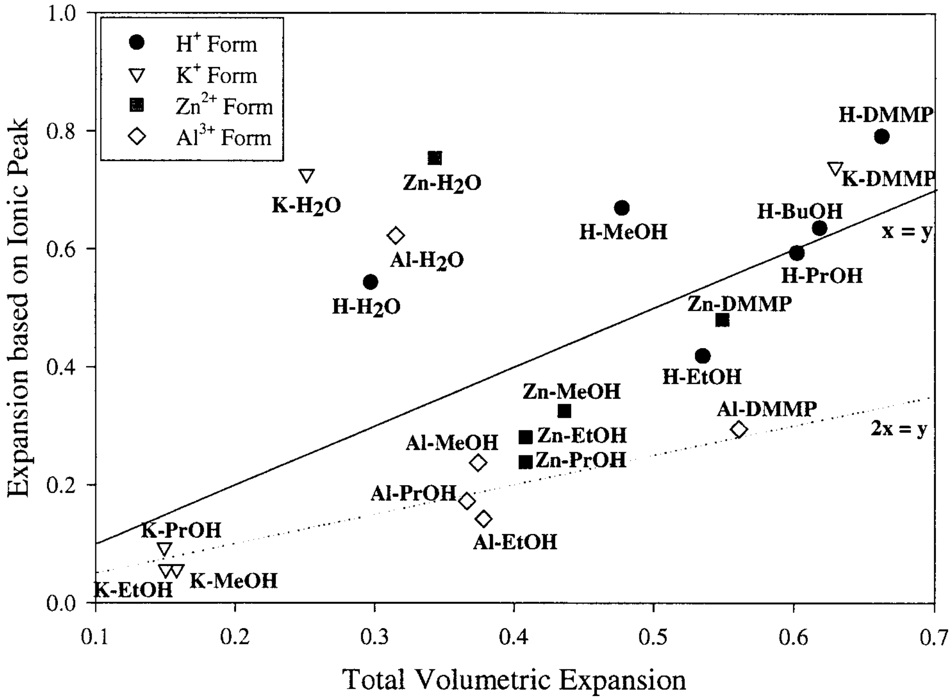


Figure 10. Microscopic volumetric swelling in Nafion membranes calculated from the increase in the ionic-feature spacing versus total volumetric swelling in the membranes calculated from the weight uptake of the solvent. Counterions and solvents are indicated.

branes swollen with EtOH or PrOH, the expansion predicted from the ionic-feature spacing decreases in the order $Zn^{2+} > Al^{3+} > Mg^{2+}$, although the total swelling experienced by the membrane is similar for all three counterions (Fig. 10). This behavior may have implications for the modification of membranes for use with liquid fuels. Although not addressed as part of this investigation, because of partitioning solvent mixtures may perform synergistically within perfluorinated ionomer membranes to enhance swelling. Other researchers have observed that in membranes swollen with water–alcohol mixtures, the alcohol can act to plasticize the Nafion matrix, enhancing macroscopic swelling relative to that achievable in either pure solvent.[21]

As previously noted,[10,11] the slopes of both curves (ionic spacing versus solvent volume fraction and crystal-peak spacing versus solvent volume fraction) would have to match if the structure were to be envisioned as wholly consisting 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 and layered crystalline-type structure (e.g., those suggested by Starkweather,[11] Litt,[16] or Rebrov and coworkers[5,6,17]) 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 is consistent with reports of a networked channel structure in the membranes.[22] For a dispersed layered crystalline-phase model, the disparity in the slopes of the ionic-feature spacing and crystalline-feature spacing 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 MeOH, PrOH, 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 (Fig. 8). Although 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 rodlike 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 capable of swelling the membranes to levels higher than 50%, except EtOH. This discrepancy may be related to the lesser capacity of EtOH for partitioning into, and presumably eventually disrupting, the layered regions of the membrane structure as evidenced by the comparatively small slope in the curve of the ionic feature versus the solvent volume fraction for EtOH (Tables II and III).

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 **q** positions as the membranes swell for all solvents tested. For solvent volume fractions up to approximately 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 approximately 50 vol %. The slopes of the curves of spacing versus the solvent volume fraction differ for the ionic-feature spacing and the crystalline-feature spacing, with the slope of the curve of the crystalline-feature spacing versus the volume fraction exceeding that of the curve of the ionic-feature spacing versus the volume fraction for all solvents except water. This is taken to be indicative of the nonaqueous 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 versus the total volumetric swelling in the system based on total solvent uptake also indicates preferential segregation of nonaqueous solvents into regions of the structure not represented by the ionic feature scattering. For membranes swollen with solvents other than water, regardless of the counterion associated with the acidic group, the total swelling in the membranes exceeds 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 vol %, evidence of significant structural changes has been found that is consistent with recent predictions of phase inversion and the formation of a connected rodlike structure in this solvent regime.[10]

The authors acknowledge their use of the facilities at the National Institute of Standards and Technology Center for Neutron Research in performing all of the 30-m SANS experiments. In addition, S. K. Young acknowledges the financial support of the American Association for Engineering Education Post-Doctoral Research Associate Program and the U.S. Army Natick Soldier Center. Helpful technical discussions with Dr. Donald Rivin of the U.S. Army Natick Soldier Center are gratefully acknowledged.

REFERENCES AND NOTES

1. Roche, E. J.; Pineri, M.; Duplessix, R.; Levelut, A. M. J Polym Sci Polym Phys Ed 1981, 19, 1–11.
2. Gierke, T. D.; Munn, G. E.; Wilson, F. C. J Polym Sci Polym Phys Ed 1981, 19, 1687–1704.
3. Fujimura, M.; Hashimoto, T.; Kawai, H. Macromolecules 1981, 14, 1309–1315.
4. Fujimura, M.; Hashimoto, T.; Kawai, H. Macromolecules 1982, 15, 136–144.
5. Ozerin, A. N.; Rebrov, A. V.; Yakunin, A. N.; Bogovtseva, L. P.; Timashev, S. F.; Bakeyev, N. F. Polym Sci USSR 1986, 28, 275–282.
6. Ozerin, A. N.; Rebrov, A. V.; Yakunin, A. N.; Bessonova, N. P.; Dreiman, N. A.; Sokolov, L. F.; Bakeyev, N. F. Polym Sci USSR 1986, 28, 2559–2565.
7. Kumar, S.; Pineri, M. J Polym Sci Part B: Polym Phys 1986, 24, 1767–1782.
8. Gebel, G.; Lambard, J. Macromolecules 1997, 30, 7914–7920.
9. Gebel, G.; Moore, R. B. Macromolecules 2000, 33, 4850–4855.
10. Gebel, G. Polymer 2000, 41, 5829–5838.
11. Starkweather, H. W. Macromolecules 1982, 15, 320–323.
12. Halim, J.; Scherer, G. G.; Stamm, M. Macromol Chem Phys 1994, 195, 3783–3788.
13. Dreyfus, B.; Gebel, G.; Aldebert, P.; Pineri, M.; Escoubes, M.; Thomas, M. J Phys (Paris) 1990, 51, 1341–1354.
14. Elliott, J. A.; Hanna, S.; Elliott, A. M. S.; Cooley, G. E. Macromolecules 2000, 33, 4161–4171.
15. Marx, C. L.; Caulfield, D. F.; Cooper, S. L. Macromolecules 1974, 6, 344.

16. Litt, M. H. Polym Prepr (Am Chem Soc Div Polym Chem) 1997, 38, 80–81.
17. Rebrov, A. V.; Ozerin, A. N.; Svergun, D. I.; Bobrava, L. P.; Bakeyev, N. F. Polym Sci USSR 1990, 32, 1515–1521.
18. Davis, S. V.; Mauritz, K. A.; Moore, R. B. Polym Prepr (Am Chem Soc Div Polym Chem) 1994, 35, 419.
19. Young, S. K.; Trevino, S. F.; Beck Tan, N. C.; Paul, R. L. J Polym Sci Part B: Polym Phys, submitted for publication, 2001.
20. Sodaye, H. S.; Pujari, P. K.; Goswami, A.; Monohar, S. B. J Polym Sci Part B: Polym Phys 1997, 35, 771–776.
21. Rivin, D.; Kendrick, C. E.; Gibson, P. W.; Schneider, N. S. Polymer 2001, 42, 623–635.
22. Elliott, J. A.; Hanna, S.; Elliott, A. M. S.; Cooley, G. E. Polymer 42, 2001, 2251–2253.