

Local and Long-Range Structure of Water in a Perfluorinated Ionomer Membrane

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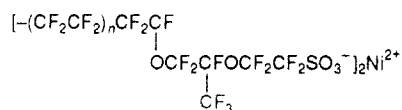
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ABSTRACT: We have measured the H-H and O-H correlations within nickel-substituted amorphous Nafion membrane using a novel combination of small- and wide-angle neutron scattering. Diffraction patterns were measured over a momentum transfer range of 0.03–20 Å⁻¹ for three isotopic water mixtures. From the partial structure factors atom-atom radial distribution functions for H-H and O-H from 1 to 100 Å were obtained by Fourier inversion. The local water structure is similar to that of bulk water. On a larger scale atom-atom correlations show that the average radius of aqueous domains is 18.5 Å with a mean separation of 70 Å. The shapes of the atom-atom radial distribution functions are consistent with the water being located in a continuous network.

Introduction

Perfluorinated sulfonate Nafion ionomer membranes were developed by Du Pont as solid polymer electrolytes for fuel cells but have subsequently found a wide variety of applications in electrochemistry. Their main use is in the chlor-alkali industry where they are a major component of the composite membrane used to separate the concentrated brine anolyte from the caustic soda catholyte.

The ionomer membrane used in this study was the nickel form of Nafion 117, which is a copolymer of tetrafluoroethylene and perfluorovinyl ether sulfone. Treating the copolymer with alkali hydroxide converts the sulfone to the sulfonate. The general formula for these ionomers is



The equivalent weight of Nafion 117 is approximately 1100 g/equiv, which gives an average value of 6.6 for n .

The ion transport properties of Nafion membranes are greatly influenced by the water uptake characteristics. Both the chemical and physical structure can affect the total amount of water absorbed within the membrane. In dry air, the nickel-substituted membrane takes up 5–15% water by volume, but when soaked in water, this rises to 40%. The water inside the membrane is believed to be associated with the matrix-bound sulfonate anions and nickel counterions (see, for example, Falk¹). The fundamental ion transport properties are thought to be affected not only by the total amount of water but also by the way this water is distributed within the hydrophobic polymer matrix and its local ionic structure.

Most of the effort in trying to elucidate the membrane structure has been centered on the neutron and X-ray scattering.^{2–4} Two types of features occur: Bragg peaks

from crystalline domains with a spacing corresponding to crystalline PTFE and small-angle scattering originating from amorphous domains containing the polymer matrix and water and, if present, crystalline domains. Although many scattering experiments have been performed on Nafion type materials, their conclusions are unclear. It is now established that there are two features in the small-angle scattering from the amorphous region, an "ionomer" peak and a low-angle upturn. The ionomer peak at 0.11 Å⁻¹ has been attributed to the hydrophilic clusters and the low-angle upturn ascribed to large domains within the amorphous structure, macroscopic voids, or the nature of the cluster-cluster interaction. Apart from experimental work aimed at understanding the nature of these clusters and their distribution, there have been many attempts to devise models for the cluster structure consistent with the many observations. These have recently been reviewed by Mauritz.⁵

Small-angle scattering experiments generally probe only a relatively small range of reciprocal space, and direct Fourier inversion methods of data analysis cannot therefore be used. The data analysis must then involve comparison of the measured intensity with that calculated from a structural model. However, it is only possible to write an analytical form for the scattering for a few simple models. If the structure of the material studied is complicated, as in this case (judging by the failure of simple model fitting), the conclusions which may be drawn from small-angle scattering experiments are limited.

There is particular interest in the role of the counterion in determining the structure of the hydrophilic clusters. There is evidence from infrared spectroscopy^{1,6,7} that the local water structure differs from that in bulk water. Monitoring the O-H combination band suggests that some of the water is bound to the terminal sulfonate group. In this paper we describe the use of neutron wide-angle

diffraction to investigate the local water structure. In this technique, which has been widely used to study the binding of water to ions,^{8,9} the quantities of interest extracted are the atom-atom radial distribution functions for the atom pairs H-H, O-H, and X-X. It is possible, using more elaborate isotopic substitution, also to determine radial distribution functions involving the counterion. Nickel is an element for which this is possible, and since we hope at a future date to extend measurements to the counterion, we used the nickel version of Nafion 117. Register and Cooper⁴ have also studied systems with the nickel counterion because of its special X-ray scattering features.

Atom-atom correlations, for example, between hydrogen atoms, will show features due to correlations between atoms within the same cluster. However, if such measurements could be extended to sufficiently small values of momentum transfer, then correlations between atoms in adjacent clusters should also be observed, especially given the absence of protons from the polymer matrix. We have therefore combined small-angle and wide-angle scattering measurements from the same samples. Measurements over this wide range of momentum transfer may be Fourier inverted to give the correlation function in real space.

Experimental Details

Nafion 117 was obtained from Aldrich Chemical Co. A single large sheet was placed in a preheated oven at 300 °C in dry-nitrogen gas for 1 h and then rapidly quenched in liquid nitrogen. It was then boiled in pure water for 1 h. The crystalline content of this annealed-quenched material was too low to observe using wide-angle X-ray diffraction, and therefore all observed scattering must originate from the amorphous structure. Strips of membrane 1 × 2 cm² were cut from this annealed and quenched membrane. Conversion to the nickel salt was carried out by boiling the membrane for 1 h in 0.5 M NiCl₂ solution, and conversion between water isotopes was achieved by soaking in the appropriate isotope for a minimum of 24 h. The mean water content of the fully soaked membrane was measured as 34.2% by mass or 41% by volume, its mean wet thickness as 240 μm, and its dry thickness as 210 μm.

Small-angle neutron scattering was measured using the D17 instrument at ILL, Grenoble, France.¹⁰ The fully soaked membranes were placed in 1-mm-path-length quartz cells. Because the SANS patterns of ionomer membranes are extremely sensitive to the water content, great care was taken to ensure that the water content of all the membranes measured was identical. This was done by completely surrounding the membrane with water of the appropriate scattering length density. The cell was sealed to prevent evaporation and isotopic exchange. Measurements with sample to detector distances of 2.80 and 0.8 m (using neutrons of wavelength 12 Å) were combined to give momentum transfer range of 0.01–0.25 Å⁻¹. Experiments were performed using H₂O, D₂O, and 50:50 H/D mixture as soaking solutions.

The wide-angle neutron scattering was measured using the LAD spectrometer on ISIS at the Rutherford Appleton Laboratory.¹¹ In this instrument there are detector banks located on either side of the sample covering the angular range 5–135°. In this experiment only the banks in the range 5–35° were used because of the difficulty of making accurate recoil corrections for the higher angle banks for samples containing predominantly light nuclei.¹¹ The samples were sealed into a rectangular cross-sectional can made of a null-scattering alloy. As many pieces as possible of fully soaked membrane compatible with obtaining a reasonable diffracted signal were used. It was not possible to surround the membranes with solution, but a few drops of solution was added to maintain them in a wet state. In principle, this should be no different from surrounding them completely with solution, and this was confirmed by the exact overlap of the low- and wide-angle patterns. The can was vacuum-sealed with indium to allow evacuation of the flight path. The wavelength range available on LAD yielded a momentum transfer range of

0.05–20 Å⁻¹, therefore providing a good overlap with the data from the small-angle scattering experiment.

Data Analysis

The small-angle scattering was placed on an absolute scale by reference to the incoherent scattering from 1 mm of pure H₂O, taking into account the small correction necessary for the scattering from the empty quartz cell.¹² The scattering intensity from a cell containing membrane and water has two origins: incoherent scattering from both the water surrounding and inside the membrane and small-angle coherent scattering from the membrane itself. The scattering intensity from 240 μm of wet membrane is given by the scattering intensity of the cell contents minus the incoherent scattering from the water both inside and surrounding the membrane

$$S_{\text{memb}}(Q) = S_{\text{cell}}(Q) - fS_{\text{solution}}(Q) \quad (1)$$

where f is the fraction of the cell path length containing solution. This was taken to be equal to $1 - t_{\text{dry}}$ where t_{dry} is the thickness of the dry membrane, 0.210 mm. The resulting scattering intensity was then scaled by $1/t_{\text{wet}}$ to convert it into the form of a differential cross section, $F(Q)$. Thus

$$F(Q) = (1/t_{\text{wet}})[S_{\text{cell}}(Q) - fS_{\text{solution}}(Q)] \quad (2)$$

The wide-angle scattering was made absolute by reference to the scattering from a vanadium sheet. The quantity measured was the total differential scattering cross section, $T(Q)$, which is the sum of the total coherent structure factor, $F(Q)$, and the self-scattering or incoherent scattering term, $S(Q)$.

$$T(Q) = S(Q) + F(Q) \quad (3)$$

The total coherent structure factor, $F(Q)$, is a sum over all the partial structure factors

$$F(Q) = \sum_{\alpha, \beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(Q) \quad (4)$$

where c_{α} and c_{β} are the atomic fractions of species α and β , b_{α} and b_{β} are their coherent scattering lengths, and $S_{\alpha\beta}(Q)$ is the partial structure factor for the two species. In this experiment the above may be written as

$$F(Q) = c_{\text{H}}^2 b_{\text{H}}^2 S_{\text{HH}}(Q) + c_{\text{O}} c_{\text{H}} b_{\text{O}} b_{\text{H}} S_{\text{OH}}(Q) + \sum_x \sum_y c_x c_y b_x b_y S_{xy}(Q) \quad (5)$$

where x and y refer to all atom-atom correlations excluding the first two terms. Provided that the self-scattering can be successfully subtracted, three measurements with H₂O, D₂O, and a 50:50 H/D mixture are sufficient to allow the calculation of individual partial structure factors. The subtraction of the isotope-dependent self-scattering is carried out using a polynomial fitting procedure as described in ref 13. This is done for each group of detectors, and one of the criteria for a successful subtraction is that the subtracted total structure factors for adjacent detector banks should overlap correctly because they depend only on Q and not on the detector angle. The three combined $F(Q)$ functions were then analyzed to extract the partial structure factors according to eq 5. The partial structure factors from small- and wide-angle experiments were combined and found to overlap satisfactorily in the Q range 0.05–0.25 Å⁻¹.

The structure factor for the protons in the system is shown in Figure 1 with the small κ range in the inset. The ionomer peak is at a value of κ just above 0.1 Å⁻¹, and the

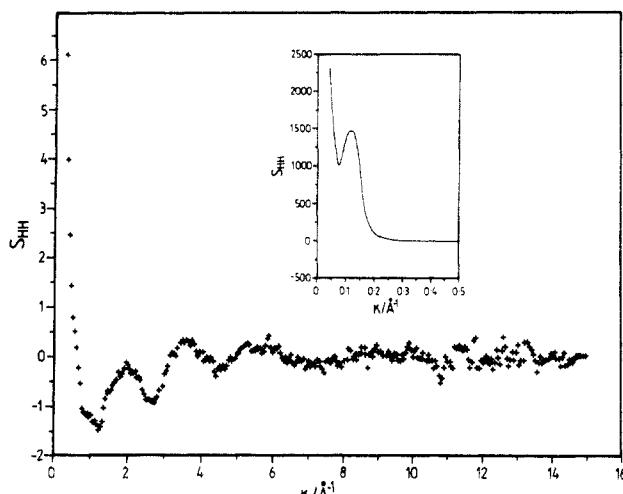


Figure 1. Hydrogen/hydrogen partial structure factor for the fully saturated membrane. The expanded small-angle scattering range is in the inset and shows the ionomer peak and the small-angle upturn.

small-angle upturn, also observed by others, is clearly seen. Above Q of about 9 Å^{-1} the quality of the signal is less good, and this contributes to errors in the short-range part of the radial distribution functions to be described below.

The partial structure factors are related to the atom-atom correlation functions, $g_{\alpha\beta}(r)$, by the following expression:

$$S_{\alpha\beta}(Q) = 4\pi\rho \int r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin(Qr)}{Qr} dr \quad (6)$$

The inversion of $S_{\alpha\beta}(Q)$ to give the correlation functions used the principle of maximum entropy to determine that distribution function most likely to be consistent with the data. This procedure has been described in detail elsewhere.¹⁴

Results and Discussion

Figure 2 shows the H-H and O-H correlation functions for water in the clusters compared with those for bulk water. The distribution functions have been normalized to the mean atomic concentrations in the membrane. This gives the short-range correlations the rather peculiar appearance of not reaching the appropriate limit of unity even at a distance of 10 Å . This is because the mean density has not been reached at this distance, owing to the cluster structure. The approach to the correct limit can be seen in Figure 3. The radial distribution functions for water have been arbitrarily scaled to optimize the overlap at short range. Since the atom density of hydrogen in the membrane is almost exactly half that in bulk water, the scale factor is 2 and $g_{HH}(r)$ (water) has a limit of 2 (Figure 3b).

The intramolecular correlations at a distance of 1.56 Å (H-H) and 1.0 Å (O-H)¹⁵ are identical, as one would expect. The first intermolecular peaks are also similar, but the second ones show small differences. This may be due to a contribution from interaction of the water with the polymer-bound sulfonate groups.¹ We can therefore draw the preliminary conclusion that when the water content is high, the structure of the water in the clusters is predominantly that of bulk water. This situation may change at lower water contents where the water structure is likely to be more strongly influenced by $\text{H}_2\text{O} \cdots \text{SO}_3^-$ interactions, and this we intend to investigate further. The present water content corresponds to an average of 21 water molecules per sulfonate group. However, only

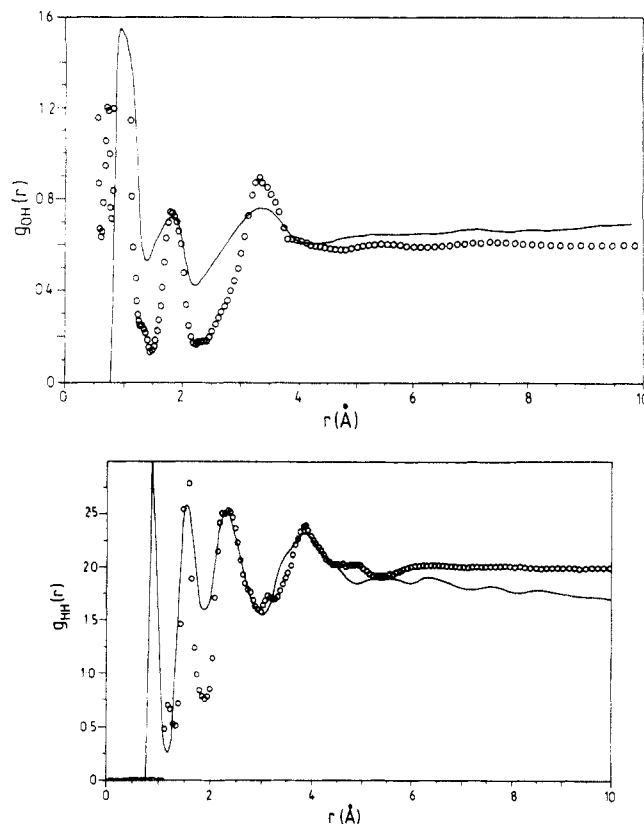


Figure 2. (a) O-H and (b) H-H radial distribution functions for a fully soaked nickel-substituted amorphous Nafion membrane (continuous line) compared with that for bulk water (circles). The membrane distribution functions have been normalized to the mean density of water in the membrane, but the water distribution functions have been scaled by a factor of 2 so that they can be compared with those of the membrane. There are significant errors at distances of 1 Å which rapidly increase as r decreases.

one or two water molecules will be directly associated with each sulfonate.

The H-H correlation function over the entire distance range of the experiment is shown in Figure 3. The medium-range correlations are between hydrogen atoms within a cluster, and the long-range correlations are between H atoms in different clusters. These longer range correlations are shown more clearly in an expanded radial plot in Figure 3b. The H-H correlation function therefore holds information about both the shape of the clusters and their distribution. The H-H partial structure factor can be written as the product of the cluster shape function, $S_{\text{shape}}(Q)$, and the structure function, $S_{\text{structure}}(Q)$:

$$S_{HH}(Q) = S_{\text{shape}}(Q) S_{\text{structure}}(Q) \quad (7)$$

From eq 7 it follows that the H-H correlation function may be written as

$$g_{HH}(r) = g_{ic}(r) * g_{cc}(r) \quad (8)$$

where $*$ indicates convolution, $g_{ic}(r)$ is an intracenter distribution function, and $g_{cc}(r)$ is the cluster center to center distribution function. Knowledge of either of the functions on the right-hand side of eq 7 or eq 8 is sufficient to determine the other.

$g_{HH}(r)$ is most sensitive to the cluster shape and size in the intermediate distance range, $10\text{--}25 \text{ Å}$. If, as has been done by many previous investigators, the shape of the cluster is assumed to be spherical, the distribution function is consistent with a cluster radius of 18.5 Å as shown in Figure 4. From the long-range behavior of $g_{HH}(r)$ the mean periodicity of the structure is 70 Å , and in a simple model

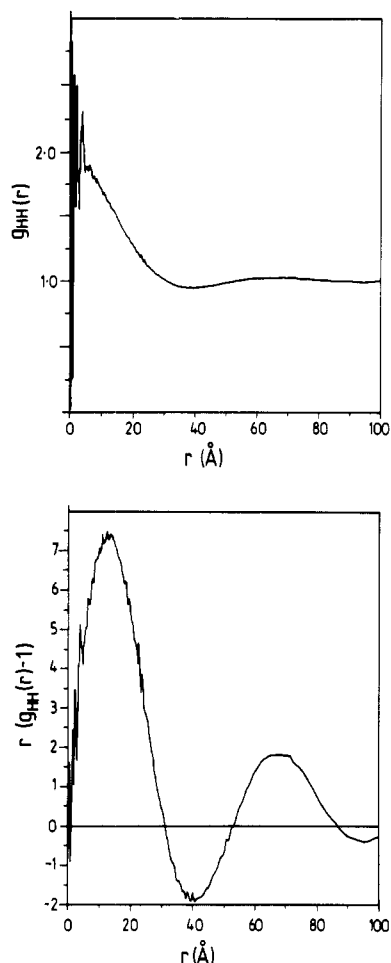


Figure 3. H-H radial distribution function shown (a) on an expanded distance scale and (b) on an expanded radial scale as $r\{g(r) - 1\}$.

consisting of a distribution of spheres this would be their mean center to center distance.

Until now it has not been established by experiment whether or not the structure is a series of isolated aqueous clusters or a continuous network. Our data can be consistent only with a continuous network for two reasons. First, the measured water content of the membrane is 41% by volume, which is approximately two-thirds of that possible for close-packed spheres. A structure of unconnected 18.5-Å-radius spheres with a mean center to center separation of 70 Å can only accommodate a maximum of 8% water. Second, given that the center to center separation is much larger than the cluster diameter, $g_{HH}(r)$ should drop to approximately zero at a distance of about 40 Å before reaching its limiting value of unity at large distances. Figure 3 shows that this is not the case, and, moreover, the value at 40 Å (approximately the minimum in the curve) is shown by Figure 4 to be 90% of the mean water content of the membrane. Thus, just outside the aqueous "sphere" there is on average only a

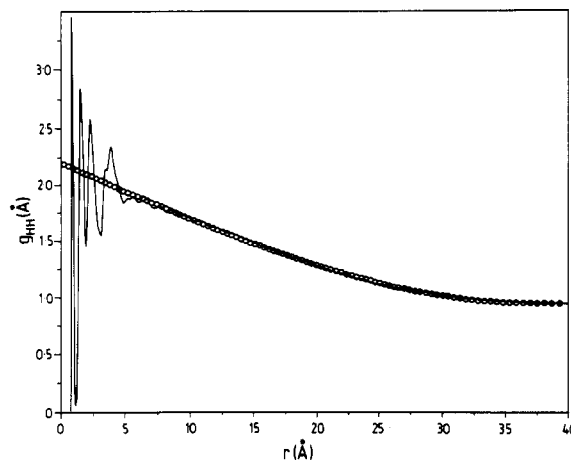


Figure 4. Comparison of calculated and observed H-H radial distribution functions. The calculation is for uncorrelated hydrogen atoms in an isolated sphere of radius 18.5 Å embedded in a medium corresponding to 90% of the mean hydrogen composition of the membrane.

slight excess of polymer over the mean value. It might be thought that the polydispersity in the sphere size might affect this conclusion, but the degree of polydispersity required would probably be associated with the loss of the well-defined interparticle separation. In any case polydispersity cannot account for the discrepancy in the water content. Only a network, consisting, for example, of rodlike aqueous regions intersecting at nodes to form a continuous structure, can be consistent with our experimental data. Attempts to model different network structures are in progress.

References and Notes

- (1) Falk, M. *Can. J. Chem.* **1980**, *58*, 1495.
 - (2) Dreyfus, B.; Gebel, G.; Aldeberi, P.; Pineri, M.; Escoubes, M.; Thomas, M. *J. Phys. (Paris)* **1990**, *51*, 1341.
 - (3) Ding, Y. s.; Hubbard, E. S.; Hodgson, K. O.; Register, R. A.; Cooper, S. L. *Macromolecules* **1988**, *21*, 1698.
 - (4) Register, R. A.; Cooper, S. L. *Macromolecules* **1990**, *23*, 310.
 - (5) Mauritz, K. A. *Rev. Macromol. Chem. Phys.* **1988**, *C28*, 65.
 - (6) Mauritz, K. A.; Gray, C. L. *Macromolecules* **1983**, *16*, 1279.
 - (7) Barnes, D. J. *Structure and Properties of Ionomers*; Pineri, M., Eisenberg, A., Eds.; NATO Series 198; Reidel: Dordrecht, The Netherlands, p 501.
 - (8) Enderby, J. E.; Nielson, G. W. In *Water, A Comprehensive Treatise*, Franks, F., Ed.; Plenum Press: New York, 1979; p 2.
 - (9) Skipper, N. T.; Soper, A. K.; McConnell, J. D. C.; Refson, K. *Chem. Phys. Lett.* **1990**, *166*, 141.
 - (10) *Neutron Facilities at the High Flux Reactor*; Institut Laue-Langevin: Grenoble, France, 1986.
 - (11) *Experimental Facilities at ISIS*; Boland, B. C., Ed.; Rutherford-Appleton Laboratory: Didcot, U.K., 1990.
 - (12) Ghosh, R. E. A. *Computing Guide to Small Angle Scattering*; Institut Laue-Langevin: Grenoble, France, 1988.
 - (13) Andreani, C.; Merlo, V.; Ricci, M. A.; Soper, A. K. *Mol. Phys.*, in press.
 - (14) Soper, A. K. In *Neutron Scattering Data Analysis*; Johnson, M. W. Ed.; IOP Conference Series 97; IOP Publishing Ltd.: Bristol, 1990; p 57.
 - (15) Walford, G.; Clarke, J. H.; Dore, J. C. *Mol. Phys.* **1977**, *33*, 25.
- Registry No.** H₂O, 7732-18-5; D₂O, 7789-20-0; Nafion 117-nickel, 66796-30-3.