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The swelling behaviour of perfluorinated ionomer membranes in ethanol/water mixtures

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Abstract

The microscopic and bulk swelling of "Nafion®" perfluorinated ionomer membranes in mixtures of ethanol and water was studied using small angle X-ray diffraction and optical microscopy. The microscopic swelling decreased with increasing ethanol content, in contrast to the bulk swelling which increased dramatically, reaching a maximum in a mixture containing 75% ethanol and 25% water. Uniaxially oriented membranes swollen with such an optimal mixture were found to relax back to an almost isotropic state, which could not be achieved by using water alone. The conclusion is that the ethanol plasticises the fluorocarbon matrix in Nafion, allowing the ionic material to be redistributed into smaller, more numerous clusters than in membranes swollen with water alone.

Keywords: Nafion; Small angle X-ray diffraction; Bulk swelling

1. Introduction

"Nafion®"[2], a perfluorinated ionomer membrane manufactured by E. I. Du Pont de Nemours and Company, has been the subject of a series of structural studies [1–6] motivated principally by interest in its use as a membrane separator in a variety of commercially important processes. The polymer consists of a polytetrafluoroethylene backbone with sulphonic acid side-groups arranged at intervals along the chain, and these acid groups are known to aggregate into clusters [7]. Three recent papers by James et al. [8,9] and Elliott et al. [10] have shown that when Nafion absorbs water, ionic material is redistributed so that the spacing between clusters increases, but their number density falls. The net result is a bulk swelling which is incommensurate with that inferred from small angle X-ray diffraction data.

In this paper, we report some preliminary results concerning the swelling behaviour of Nafion in ethanol and ethanol/water mixtures. The degree of swelling of Nafion in a pure solvent is related to its polarity for both protic and aprotic solvents. In general, the uptake of polar solvents exceeds that of non-polar for the pure solvent case. However, when water is combined with an adsolvent, the degree of swelling is inversely related to the polarity of the adsolvent. This intriguing fact was the motivation for a systematic study of the microscopic (i.e. inferred from SAXS) and macroscopic (i.e. bulk) swelling of Nafion in ethanol/water mixtures. Ethanol was chosen as the adsolvent because it is less polar than water, but still relatively protic.

2. Experimental

Two-dimensional point collimated SAXS data were collected using nickel-filtered Cu K_α radiation on a flat plate Rigaku-Denki camera, with a typical sample–film distance of 25 cm. The films were digitised for analysis using an Optronics P2000 drum densitometer. The low-angle limit due to beam divergence was approximately 2.6×10^{-3} Å^{-1}, which corresponds to a maximum discernible size for features in real space of around 400 Å. The diffraction patterns were corrected for Lorentz-polarisation effects and sample absorption.

The microscopic swelling of the membranes was determined from an amorphous reflection, the so-called "cluster reflection", which occurs between 0.02–0.03 Å^{-1} depending

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[2] "Nafion" is a registered trademark of E. I. Du Pont de Nemours and Company.

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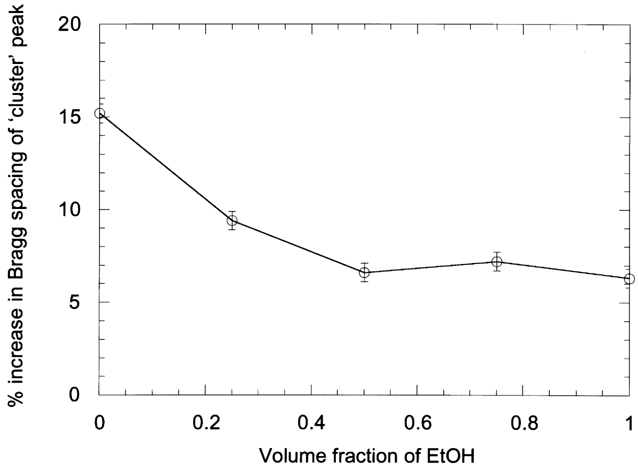

Fig. 1. Percentage increase, compared with ambient conditions, in the equivalent Bragg spacing of the 'cluster' reflection from a Nafion membrane exposed to vapour from ethanol/water mixtures.

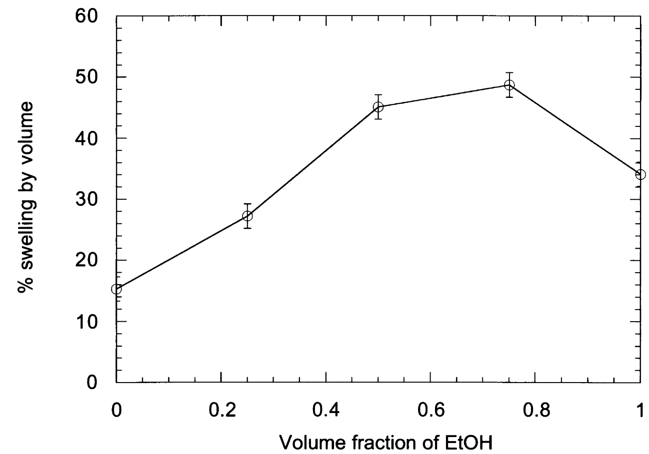

Fig. 3. Bulk volume swelling isotherm of a Nafion membrane exposed to vapour from ethanol/water mixtures.

on the solvent content of the sample. The macroscopic or bulk swelling was measured using an optical microscopy technique described in detail in a previous paper [10].

The solvent content of the samples was controlled by enclosing them in a modified Linkam cell, and circulating air through ethanol/water mixtures of varying concentration around the system in a closed loop. Although the relative proportions of ethanol and water present actually in the membrane could not be measured, the environmental conditions were held constant in both the SAXS and optical microscopy experiments in order to enable meaningful comparison of microscopic and macroscopic swelling results.

3. Results and discussion

The percentage increase in Bragg spacing compared to ambient conditions, of the 'cluster' reflection peak from a Nafion membrane, is shown in Fig. 1 as a function of the

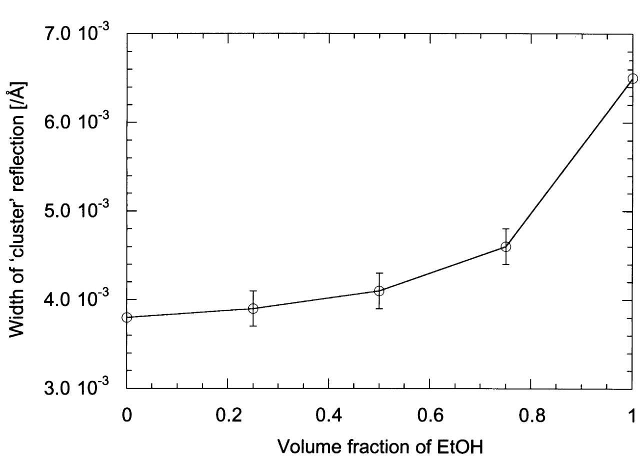

Fig. 2. Width of the 'cluster' reflection from Nafion membrane exposed to vapour from ethanol/water mixtures.

volume fraction of ethanol in the mixture. It can be seen that the microscopic swelling decreased as the proportion of ethanol in the mixture was increased, and was maximal for the pure water control.

In addition to the decrease in microscopic swelling, it was found that the cluster reflection broadened as the ethanol content of the mixture was increased. This is illustrated in Fig. 2, where the full-width-at-half-maximum (FWHM) of the cluster reflection is shown as a function of the volume fraction of ethanol in the mixture. The broadening of the peak suggests a widening of the distribution of intercluster separations. This appears to be greatly increased at high ethanol contents, indicating a relaxation of the positional constraints on the clusters imposed by chain mobility within the fluorocarbon matrix.

It is interesting that the maximum peak width does not correspond with the maximum microscopic swelling, i.e. the point at which the average intercluster separation is greatest. It seems likely, therefore, that the more polar solvent interacts preferentially with the ionic clusters, whereas the less polar solvent mainly affects the behaviour of the fluorocarbon matrix. This observation is consistent with evidence from both neutron scattering [11] and ^{19}F NMR experiments [12,13].

The results from macroscopic swelling experiments performed with ethanol/water vapours are shown in Fig. 3. It is clear that the degree of macroscopic swelling produced was much greater in the presence of ethanol. In particular, there was a peak in macroscopic swelling at 75% ethanol by volume, which indicates that the vapour must contain at least a certain proportion of water in order to achieve the maximum macroscopic swelling.

Most importantly, it can be seen that the degree of macroscopic swelling when ethanol is present exceeds that implied by extrapolation of the microscopic results. This is a reversal of the swelling anomaly found when water alone was used as a swelling agent [9,10,14], where the macroscopic swelling was less than the microscopic

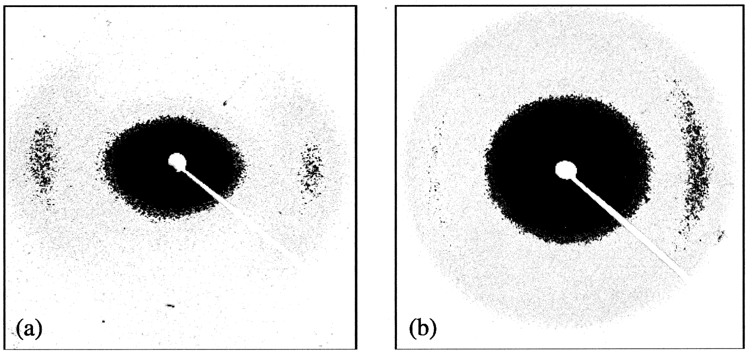

Fig. 4. SAXS patterns from: (a) Nafion membrane drawn uniaxially to 50% strain; (b) the same sample after soaking in a mixture of 75% ethanol and 25% de-ionised water for 1 day. The diffraction patterns were taken at a sample–film distance of 30 cm with the draw direction vertical.

swelling. It seems that the microscopic swelling, which is related to the amount of water absorbed by the ionic clusters, is normally limited by constraints imposed by the fluorocarbon matrix. The result is a structural reorganisation of ionic material and water, which minimises the internal stresses of the membrane. The addition of a less polar solvent such as ethanol, which can penetrate and plasticise the matrix, results in an increase in the number density of clusters and produces an enhanced macroscopic swelling. However, plasticising the matrix in the absence of water causes little microscopic swelling and only moderate bulk swelling, because of the lower affinity of the less polar solvent for the ionic clusters.

To test the hypothesis that ethanol is plasticising the matrix, the relaxation process was investigated microscopically by comparing the degree of arcing of the cluster reflection in SAXS patterns from a uniaxially drawn Nafion membrane and the same sample after immersion in a mixture of 75% ethanol and 25% de-ionised water for 1 day. These are shown in Fig. 4. The cluster reflection appears as arcs in both cases and there is also a low-angle upturn in SAXS intensity which has been associated with the formation of agglomerates of clusters [10]. Calculation of the first two axially symmetric order parameters of the cluster reflection reveals that P_2 and P_4 fall from 0.62 and 0.23 to 0.09 and 0.00, respectively, on swelling in the ethanol/water mixture. This should be compared with a drop to 0.22 and 0.01, respectively, for swelling with pure water. Therefore, although microscopic orientation is lost by hydration alone, it is removed much more effectively when ethanol is also present.

The reason for the partial loss of configurational memory must be related to structural changes in the fluorocarbon matrix, as this is the only part of the membrane which ethanol can permeate to a greater extent than water. We can conclude that chain entanglements in the matrix must restrict the expansion of the ionic clusters, and maintain the anisotropic spatial coherence of these entities in oriented membranes. Only when the matrix is sufficiently plasticised can the clusters reorganise themselves into an isotropically coherent state. This necessarily results in the low-angle upturn in the SAXS data becoming circular in shape.

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