Effect of methanol on plasticization and transport properties of a perfluorosulfonic ion-exchange membrane

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ABSTRACT

The transport properties of a perfluorosulfonic acid membrane swollen in different concentrations of aqueous methanol mixtures are investigated. Solvent uptake, proton conductivity and methanol permeability of a commercial Nafion® 117 membrane are evaluated at different methanol concentrations. Small-angle X-ray scattering analysis is performed to study the morphological effects on the formation of ionic clusters created by aqueous methanol mixtures. It is concluded that the observed decrease in proton conductivity and increase in methanol permeability are associated with morphological transitions as well as with the size of the ion cluster, as determined by the concentration of methanol in the test mixture. Wide-angle X-ray scattering studies indicate that the crystalline region is deformed by absorbed methanol; the size of crystalline domains and the crystallinity change with methanol concentration due to plasticization. Absorbed methanol also degrades the mechanical properties, as witnessed by tensile strength measurements.

1. Introduction

Nafion® is a type of perfluorosulfonated ionomer that is composed of a hydrophobic polytetrafluoroethylene backbone and regularly placed hydrophilic perfluorovinylether side-chains that are terminated by sulfonic acid groups. Nafion® has been widely studied and commercialized because of its remarkable properties such as high water permeability, moderate water sorption, high proton conductivity, and excellent physicochemical stability. In addition, Nafion® has an intriguing morphology that has caught the attention of many research workers [1]. Its applications include electrochemical processes, proton conducting ionomer membranes, catalysis, and pervaporation processes [2–4].

Many structural and morphological studies have been conducted on Nafion® to obtain a detailed understanding of the behaviour of perfluorosulfonated ionomers. Using small- and wide-angle X-ray scattering (SAXS and WAXS, respectively), Gierke et al. [5] developed a widely accepted cluster network model. This model illustrated the influence of solvent-like water on morphological transformations in Nafion®. In addition to the prevalent spherical clusters model at dry state, the same authors proposed that the water swollen morphology was best described by ionic clusters that were spherical in shape and had an inverted micellar structure with a diameter of approximately 4–5 nm. Furthermore,

in consideration of a percolation pathway for ionic transport, it was also claimed that these ionic clusters were interconnected with narrow channels. Moreover, using SAXS, Gebel [6] proposed a structural evolution scheme during hydration and stated that at a water content higher than 50%, the morphology undergoes structure inversion to a connected network of polymer rod-like particles. The WAXS studies of unhydrolyzed membranes showed diffraction peaks that corresponded to crystalline domains within the fluorocarbon matrix [5]. Upon hydration, however, Starkweather [7] observed subtle changes in crystallinity. With increasing water content, the intensity of the crystalline diffraction peak was reduced and was attributed to a relaxation in the oriented crystalline structure.

The modification of morphology due to solvent interaction offers pathways for ions to conduct. This process is known as 'percolation', wherein the ionic clusters are interconnected with narrow channels. This explains the transport of molecules and ions within the interconnected ionic network and is important for fuel cell applications. Zawodzinski et al. [8] reported that the proton conductivity of a hydrated Nafion® membrane in water at 30 °C has a value of 0.1 S cm^{-1}. On the other hand, Hallinan and Elabd [9] observed a dramatic decrease of conductivity (0.017–0.02 S cm^{-1}) in pure methanol. This decline in the proton transport can be attributed to the so-called 'methanol crossover' phenomenon where the methanol fuel diffuses from one side of the polymer membrane to the other through ionic channels and thereby affects the overall fuel cell efficiency. Studies of methanol diffusion through Nafion® membranes have been performed by

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electrochemical techniques [8,10], the IR method [9], and NMR measurements [2,10]. As reported by Hallinan and Elabd [9], the methanol flux increased by three orders of magnitude with increasing methanol concentration from 0.1 to 16 M; the methanol flux was measured by means of Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy. The authors argued that the main contributing factor to the increase in methanol flux arose from methanol sorption in Nafion® and not from the increase in methanol diffusion. Ren et al. [11] found that the methanol and water diffusion coefficients in the membrane were practically constant, regardless of the methanol concentration in the membrane. It is not clear which of these factors largely contributes to the increased methanol flux with increasing methanol solution concentration, i.e., methanol sorption or diffusion, or both.

In order to develop further stable applications, it is essential to understand the detailed characterization of Nafion®, e.g., both the morphological change and transport properties under the high methanol concentration, which is also a way to overcome limits in utilizing methanol fuel, since only low concentrations of methanol are applicable to the direct methanol fuel cell system. In this study, SAXS and WAXS studies are employed to investigate the plasticization effect of methanol on Nafion® and its transport properties under methanol–water conditions.

2. Experimental

2.1. Nafion® 117 membrane

Nafion® 117 membrane (Du Pont, 175 μm thickness, EW = 1100) was used. The membrane was cut into 1×4 cm samples. The samples were pretreated as follows: (i) thermal treatment in an aqueous solution of 3 wt.% H_2O_2 at 80 °C for 2 h; (ii) rinsing with pure water at 80 °C for 1 h; (iii) further treatment in 0.5 M H_2SO_4 at 80 °C for 2 h; (iv) rinsing with pure water at 80 °C for 1 h. For all experiments, the membranes were dried at room temperature for several days, and then placed in a methanol–water mixture of the desired concentration (including pure methanol and water) and allowed to reach equilibrium. Deionized water was used throughout.

2.2. Solvent uptake measurements

The weights of dried and soaked membrane samples were measured during the abovementioned membrane preparation. When the weight of soaked membrane was measured, the upper part of the liquid on the membrane was removed carefully. The liquid uptake of the membrane was calculated as follows:

$$\text{Liquid uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad (1)$$

where W_{dry} is the mass of dried sample and W_{wet} is the mass of wet sample.

2.3. Small-angle X-ray scattering (SAXS)

Synchrotron SAXS measurements were performed at the 4C1 SAXS beamline in the Pohang Accelerator Laboratory (PAL) in Korea. A double-crystal monochromator with an energy resolution ($\Delta E/E$) of about 1% was used to obtain photon numbers with a wavelength of λ = 1.6 Å. The sample-to-detector distance was 0.5 m and the typical beam size was smaller than 1×1 mm. The scattering vector, q is given by:

$$q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \qquad (2)$$

where θ is the scattering angle and the experimental setup covers the range of $0.01 \leq q \leq 0.22$ Å^{-1}. The samples swollen by water, methanol and water–methanol mixtures were prepared by sandwiching them between Kapton windows and then sealing avoid dehydration of membrane.

2.4. Wide-angle X-ray scattering (WAXS)

Wide-angle X-ray diffraction analysis was performed with a PANalytical (X'Pert Pro) system that was equipped with copper radiation (1.54×10^{-10} m) to investigate the transition of the crystalline region of a sample as a function of methanol concentration. Analysis was performed over a scan range of 5–60° at a rate of 2.4° min^{-1} with operating conditions of 40 kV acceleration voltage and 40 mA supply current. Samples were cut into 1×2 cm sizes and covered with polyimide to prevent solvent evaporation from the swollen membrane. The crystallinity, X_{cr}, is defined by rationing the integrated intensities of the separated crystalline diffraction peaks to the sum of the integrated crystalline and amorphous contributions for the decomposed diffractogram [12,13], i.e.,

$$X_{cr}(\%) = \frac{\int_{10}^{22} I_{cr}(s)s^2 \; ds}{\int_{10}^{22}[I_{cr}(s) + I_{am}(s)]s^2 \; ds} \qquad (3)$$

where s is the scattering maximum; I_{cr} and I_{am} are the diffracted intensities of the crystalline and amorphous peaks, respectively.

2.5. Mechanical properties

The tensile strengths of the membranes were measured with a Universal Testing Machine (LF Plus, Lloyd instruments), and the data were edited with Nexygen V4.5 software. The test speed was 4 mm min^{-1}, and the cross-sectional area of dried samples was fixed at 1.75 mm^2. The soaked condition of a given membrane sample was maintained during the tensile strength measurement by adding liquid of the desired concentration.

2.6. Proton conductivity

The proton conductivities of soaked membranes were measured by means of Electrochemical Impedance Spectroscopy (IM6ex, Zahner-Elektrik GmbH) at 25 °C. A frequency range of 5×10^{-1} to 3×10^{6} Hz was used in the galvanostatic mode. The measurements were performed in methanol–water mixtures using a four-probe cell. The specific conductivity σ (S cm^{-1}) of the sample, obtained from the real part of impendence R (Ω) was defined as:

$$\sigma = \frac{L}{R \times d \times w} \qquad (4)$$

where the thickness d (cm), width w (cm) and distance between electrodes L (cm) were measured with a micrometer.

2.7. Methanol permeability

The methanol permeability was determined using a home-made diffusion cell with two compartments labelled A and B. Compartment A ($V_A = 55.4$ ml) was filled with a given concentration of methanol (DC Chemical, Extra Pure grade). Compartment B ($V_B = 48.2$ ml) was filled with deionized water. The membrane (effective diffusion area = 12.76 cm^2) was sandwiched with a Teflon O-ring and clamped between the two compartments. The concentration of methanol diffusing from compartment A to B across the membrane was monitored with a refractive index detector (RI 750F, Younglin). The compartments were stirred continuously during measurements. The methanol permeability was obtained from
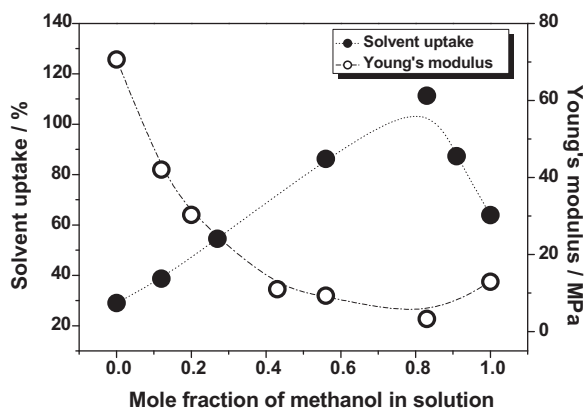
Fig. 1. The solvent uptake and Young's modulus as a function of methanol concentration.

the initial slope of the concentration change with time, i.e.,

$$\text{Permeability} = \text{slope} \times \frac{V_B \times L}{A \times C_A} \tag{5}$$

where A is the area; C_A is the concentration of methanol (wt.%); V_B is the volume of compartment B; L is the thickness of the membrane.

3. Results and discussion

3.1. Sorption and mechanical behaviour of swollen Nafion® by aqueous methanol

The solubility of polymeric membranes is associated with a complex interplay between the properties of the system (including the morphology of the polymer), the mechanical strength as reflected by the crystallinity, and the chemical properties of the solvent and polymer such as hydrophilicity or hydrophobicity. In particular, Nafion® has a unique and amphiphilic chemical nature because it has a hydrophobic fluorinated backbone, which provides a strong chemical stability against solvents, and the sulfonic acid groups at the end of the side chains, which are quite interactive with both water and methanol. It is also known that a peculiar morphology that looks like hydrophilic water clusters of 4–5 nm in diameter are formed as water is absorbed. Thus, it is very important to know how aqueous methanol mixtures can be absorbed in the Nafion® matrix.

In order to investigate the solubility of Nafion® 117, solvent uptake was measured as a function of methanol concentration, as shown in Fig. 1. It is seen that there is an increase in the total solvent uptake from 29 to 63 wt.% when the methanol mole fraction is increased from 0 to 1. The maximum uptake is near a methanol mole fraction of 0.8, i.e., similar to that reported by Skou et al. [2].

The degree of swelling of Nafion in a pure solvent is related to its polarity for both protic and aprotic solvents. The uptake of polar solvents, in general, surpasses that of non-polar solvents, as in the case of pure solvent. When increasing amounts of methanol fractions are mixed with water, the degree of swelling is inversely related to the polarity of methanol since it is less polar than water but is still relatively protic.

In addition, it can be observed that the degree of macroscopic swelling when methanol is present exceeds that implied by extrapolation of microscopic data. This is a turnaround of the swelling anomaly found when the mole fraction of water is 1 [14,15]. Here, the macroscopic swelling is less than the microscopic swelling. The microscopic swelling, which is related to the quantity of water absorbed by the ionic clusters, is normally limited by constrictions inflicted by the fluorocarbon matrix. This phenomenon is due to a structural reorganization of ionic material and water that mini-

mizes the internal stresses of the membrane. The presence of a less polar solvent such as methanol, which can infiltrate and plasticize the matrix, causes an increase in the number of clusters and produces an enhanced macroscopic swelling. By contrast, plasticizing the matrix in the absence of water causes little microscopic swelling and only moderates bulk swelling, because the less polar solvent has a lower affinity for the ionic clusters. As such, the solution with a methanol mole fraction of 0.8 (i.e., where there is maximum uptake) is the point where there is an adequate amount of methanol to enhance macroscopic swelling, and sufficient water to cause microscopic swelling.

An in-depth study of the equilibrium of methanol and water in Nafion® was performed by Gates and Newman [16]. Based on the Gibbs free energy calculation for a ternary system, i.e., a polymer and two solvents, a ternary phase diagram for Nafion® 117-methanol–water at 60 °C was theoretically illustrated. It was found that the solubility of a solute in Nafion® increased in the presence of a second solute and confirmed that a region of phase instability, which was associated with a spinodal line, existed at a methanol mole fraction of 0.749.

Solvent sorption is usually accompanied by membrane swelling, which depends on the mechanical properties of the polymer. Accordingly, the mechanical property as a function of methanol concentration was also investigated in association with solvent uptake. Tensile tests for Nafion® 117 in different methanol–water compositions were conducted in order to compare the behaviour of solvent uptake and the modulus of Nafion® 117. The Young's modulus decreases as the methanol concentration increases, as shown in Fig. 1. For pure water, the Young's modulus is 70.63 MPa [17]. The value decreases to 3.29 MPa with increasing methanol mole fraction up to 0.84, and then slightly increases to 12.95 MPa in pure methanol. It seems that the decrease in Young's modulus coincides with the composition of methanol at which maximum solubility is achieved.

Given the above observations for an ion-exchange membrane such as Nafion® 117, it is concluded that the maximum solubility and lowest modulus occur when water uptake takes place near 0.8 mole fraction of methanol. Thus, it appears that the appropriate portion of methanol can also plasticize the hydrophobically fluorinated domains, as well as swelling the hydrophilic cluster domains. This observation is similar to that of Elliott et al. [18] based on the swelling behaviour of Nafion® in an ethanol–water mixture. Nevertheless, it is still under debate how water, methanol and their mixtures preferentially locate on the nano-sized phase domains and the hydrophobic fluorinated backbones in Nafion® 117, since the solubility of methanol into the polymer is known to be affected not only by hydrophilic sulfonic acid groups but also by the chemistry of the polymer backbone [2].

3.2. Proton conductivity and methanol permeability of swollen Nafion®

Proton conductivity and methanol permeability of Nafion® 117 were measured as a function of methanol concentration. Proton conductivity decreases as the methanol concentration increases, passing through a minimum value near the mole fraction of 0.8, as shown in Fig. 2. Methanol permeability, on the other hand, increases as the concentration of methanol increases, and shows a maximum at a mole fraction of 0.8. It is still under dispute how methanol permeates through ionomer membranes such as Nafion®, and whether methanol moves through the same pathway at that where protons diffuse. As reported earlier [19–21], it is believed that proton conduction and methanol permeation proceed mostly via the same pathway, because the behaviour of both properties shows the same trend. Hallinan and Elabd [9] also investigated the diffusion and sorption of methanol and water in Nafion®
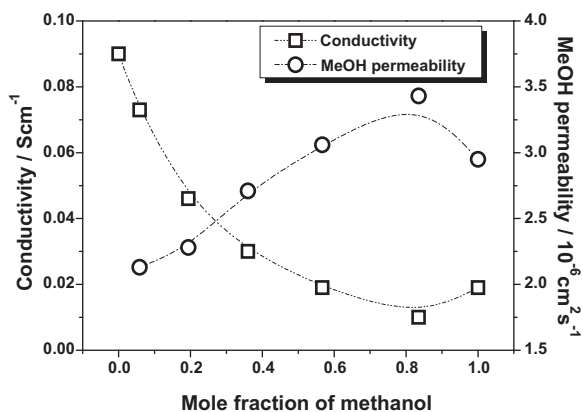
Fig. 2. The conductivity and methanol permeability as a function of methanol concentration.

Fig. 3. SAXS profiles of swollen Nafion® 117 as function of methanol mole fraction: 0 (pure water (○)), 0.46 (□), 0.69 (△), 0.84 (◇), and 1 (pure methanol (▽)).

using time-resolved FT-IR experiments. For Nafion® equilibrated in pure water to 8 M methanol (0.18 mole fraction of methanol), the proton conductivity decreased from 0.031 to 0.019 S cm⁻¹ and then remained at a nearly constant value with increasing methanol concentration (pure methanol: 0.017 S cm⁻¹). It was concluded that a transition from a hydronium (protonated water) to a protonated methanol-based mechanism of proton transport caused the decrease in proton conductivity in membranes swollen by methanol uptake. Protonated methanol is not a form of proton transport and this is why the reduction in proton conductivity is expected to be much larger than that observed. Among the several factors that lessen proton conductivity in methanol-based systems, one factor is that methanol forms a less extensive network of hydrogen bonds in Nafion®, and therefore any Grotthus conduction that may have been present with hydronium conduction may be diminished in protonated methanol conduction. Another factor is that the movement of protonated methanol will be slightly slower than that of hydronium ions, because the hydronium ions made by larger methanol molecules do not make diffusion jumps as large as hydrogen-bound clusters. Furthermore, the hydrocarbon portion of methanol may interact with the hydrophobic backbone of Nafion® as a plasticizer, effectively introducing extra drag at the edges of the ionic channels. In other words, the water would only reside in the hydrophilic domains of the membrane matrix, but the methanol can even swell the hydrophobic fluorinated domain.

Methanol permeability is also associated with the concentration of methanol. The solution–diffusion is the generally accepted mechanism of mass transport through non-porous membranes. The permeation through a homogeneous membrane consists of three fundamental processes: (i) solution of solute molecules in the upstream surface of the membrane; (ii) diffusion of dissolved species across the membrane matrix; (iii) desorption of the dissolved species in the downstream face of the membrane. These three fundamental processes also govern the mass transport across membranes while permeation is taking place. The permeability (P) is described by the product of the diffusivity (D) and the solubility (S), i.e., $P = D \cdot S$.

As mentioned by Ren et al. [11] and Villaluenga et al. [22] from thermo-osmosis analysis of a methanol mixture through a Nafion® membrane, the size of clusters and the channels of proton conduction are both enlarged at a high concentration of methanol so that the mobility of solvents increases. The data in Fig. 2 show that the permeability of methanol increases with methanol concentration. It therefore appears that solubility mainly governs the transport phenomena and strongly affects parasitic methanol crossover in a direct methanol fuel cell.
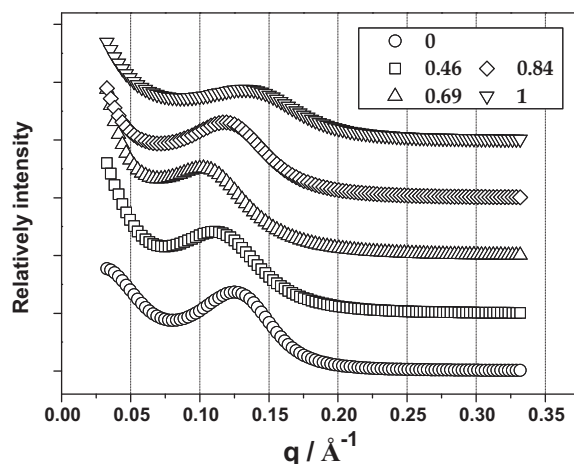
3.3. Nano-structural analysis of Nafion® by small-angle scattering

In order to investigate the effect of methanol on the morphology of Nafion®, SAXS analyses were performed. Profiles for Nafion® membranes equilibrated in different methanol concentrations are presented in Fig. 3. For a pure water system, the scattering maximum peak is located at about 0.12 Å⁻¹ (correlating length = 5.02 nm) and thereby indicates the presence of water clusters [5,6,23]. The peak shape broadens as the methanol concentration in the mixture increases, which means that there is a widening of the distribution of inter-cluster separations.

The correlation length of cluster size with concentration of methanol ($d = 2\pi/q_{max}$) was estimated from the position of the peak, q_{max}, and is illustrated in Fig. 4. The size of solvent clusters increases from 5.01 nm (pure water) to 6.1 nm (methanol mole fraction = 0.69), and then decreases to 4.7 nm (pure methanol).

As pointed out by Urata et al. [24], the methanol absorbed in Nafion® causes the boundary between the aggregations of polymer matrixes and solvents to be ambiguous. Moreover, the hydrophilic clusters formed by solvents become non-spherical and the narrow solvent aggregation region increases with increasing methanol concentration in solution, even though the membrane expands more because of the higher methanol concentration. Another similar analysis between proton conductivity and phase morphology by
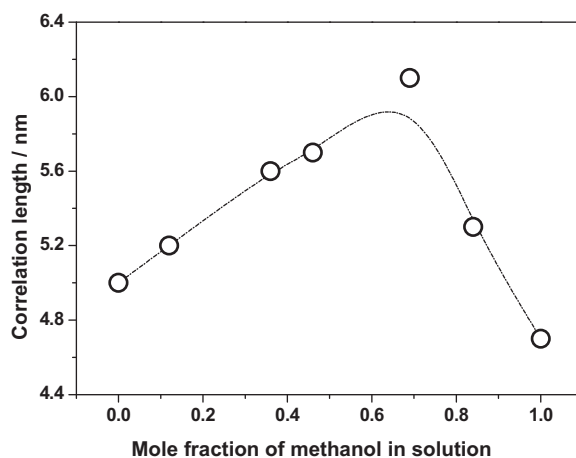

Fig. 4. The correlating length (d) of ionic peaks as a function of methanol concentration.
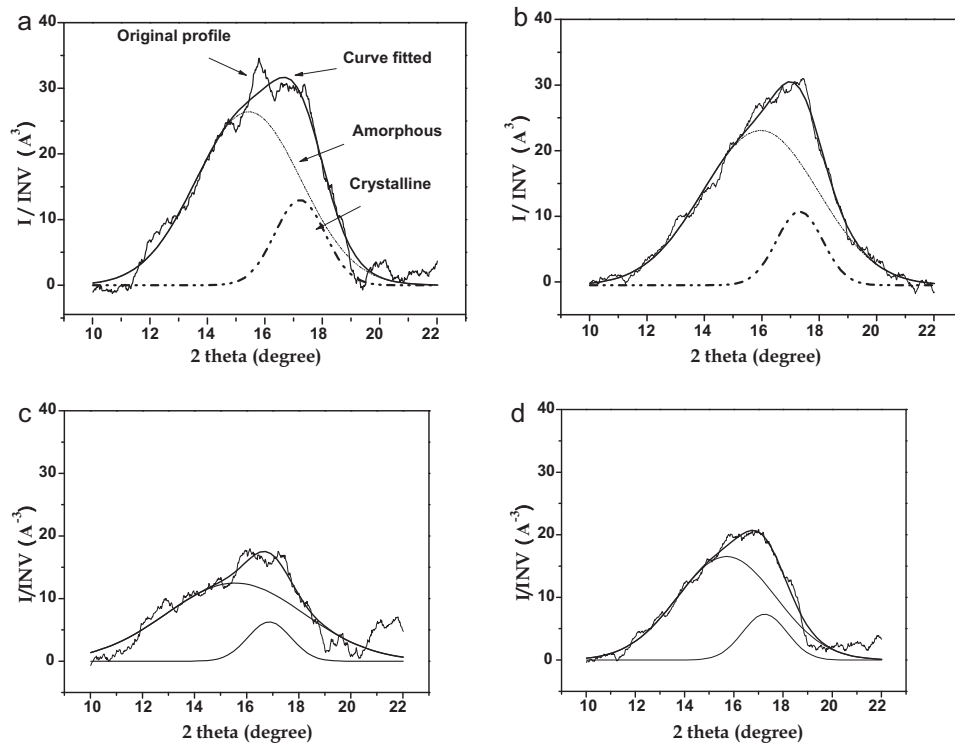
Fig. 5. WAXS pattern of swollen Nafion® 117 as a function of methanol concentration, (A)–(D) is in pure water, 0.12, 0.84 mole fraction of methanol and in pure methanol, respectively.

Affoune et al. [25] showed that the proton conductivity decreased but the diffusion of methanol increased as the methanol concentration increased, because the dielectric constants of mixtures decreased with methanol concentration. Ionic clusters and fluorinated chain domains can be clearly distinguished in the case of the hydrated Nafion®, but the shape of the ionic domains of Nafion® absorbed by methanol is slightly different from that observed in water. Thus, it can be concluded that water interacts more strongly with the sulfonic acid groups, while alcohols preferentially solvate the fluoroether side chain and cause a morphological change. It seems that methanol can alter the morphology from the interfacial region of hydrophilic clusters to the hydrophobic fluorinated domain in Nafion®. In addition, a more polar solvent interacts preferentially with the ionic clusters, whereas a less polar solvent mainly affects the behaviour of the fluorocarbon matrix. Thus, it can be expected that most of the methanol solution distributes into the nearby fluorocarbon backbone side, instead of forming solvent clusters at the methanol mole fraction of 0.84. It should be noted that this observation is consistent with evidence from a study of the swelling behaviour of perfluorinated ionomer membranes in ethanol–water mixtures [18].

3.4. WAXS study on crystalline domains of Nafion® 117

The WAXS profiles of a Nafion® 117 membrane which was equilibrated in methanol mole fractions of 0 (pure water), 0.12, 0.84, and 1 (pure methanol). It is well known that the Nafion® 117 membrane shows a main peak, related to its hexagonal structure, at about $2\theta = 10–22°$ and this is overlapped with X-ray diffraction from the amorphous region of the membrane at lower angles [6,26]. For polyfluorocarbon chains of Nafion® like PTFE, a broad diffraction feature at $2\theta = 10–22°$ has been identified for the convolution of two peaks, $2\theta = 16°$ and $2\theta = 17.5°$, which were related to amorphous and crystalline scattering, respectively [6]. The crystalline

and amorphous peaks were separated through a peak deconvolution process using a Gaussian function, as shown in Fig. 5. It should be noted that the right sharp peak and left broad peak in the decomposed profiles correspond to crystalline and amorphous regions, respectively [26]. It can be observed that the crystalline domains of the polyfluorocarbon chains of Nafion® decrease as the methanol concentration increases from 0 (water) to 0.69, and the scattering peak position of the crystalline domains are broadened and move to smaller angle. Accordingly, these changes of WAXS profiles suggest that some relaxations of the crystalline structure would be possible due to the absorption of methanol. In general, peak broadening has been interpreted in terms of the well-known Scherrer equation, i.e.,

$$t = \frac{0.9 \times \lambda}{\Delta w \times \cos \theta} \tag{6}$$
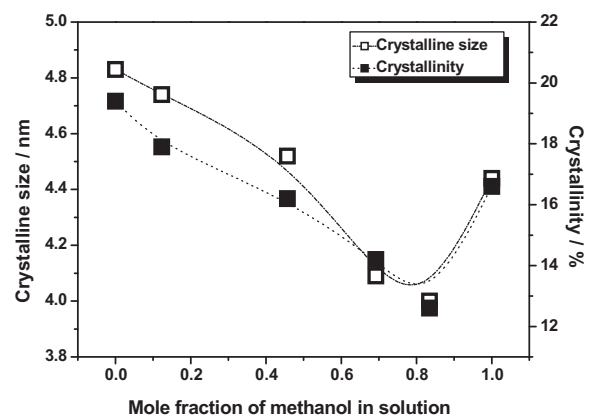

Fig. 6. The size of crystalline and degree of the crystallinity as a function of methanol concentration in solution.

where t is the size of the crystalline domains; 0.9 is a shape factor; Δw is the intrinsic broadness; λ is the X-ray wavelength (0.154 nm); θ is a scattering maximum peak position.

Changes in the degree of crystallinity and crystalline size with methanol content in mixtures are compared in Fig. 6. The crystalline size and degree of crystallinity decreases from 4.83 nm (crystalline size) and 19.4% (crystallinity) to 4 nm and 12.6%, respectively, when the methanol concentration increased from 0 to 0.84 mole fraction. In pure methanol, however, both crystalline size and crystallinity recover to 4.44 nm and 16.6%, respectively. It is to be noted that the crystalline size and crystallinity in a water–methanol mixture with a methanol mole fraction of 0.84 are also minimized, i.e., at the point where the methanol solution is strongly attracted to the hydrophobic backbone side (as discussed above). Accordingly, methanol has a large plasticizing effect on the crystalline domain.

4. Conclusions

The proton conductivity decreases as the methanol concentration increases, and passes through a minimum near the mole fraction of 0.8. The methanol permeability, on the other hand, increases as the concentration of methanol increases, and shows a maximum at the mole fraction of 0.8. From an SAXS analysis of the effect of methanol on the morphology of the ionic clusters, the ionomer peak is found to move to a lower q value, which corresponds to an increase in cluster size with increasing methanol concentration. The consequent change in conductivity suggests an indirect proportionality between the transport properties and the size of the ion cluster. On the other hand, the increase in methanol permeability shows direct proportionality with ion cluster size. A WAXS study of the position of the scattering feature of the crystalline region, suggests a decrease in membrane crystallinity that correlates with a degradation in mechanical strength and amplified swelling in water–methanol mixtures.

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