

State of the Water in Crosslinked Sulfonated Poly(ether ether ketone)

Abdul G. Al Lafi,^{1,2} James N. Hay¹

¹College of Engineering and Physical Sciences, School of Metallurgy and Materials, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

²Department of Chemistry, Atomic Energy Commission, P. O. Box 6091, Damascus, Syrian Arab Republic
Correspondence to: J. N. Hay (E-mail: j.n.hay@bham.ac.uk)

ABSTRACT: We investigated the material properties of different crosslinked sulfonated poly(aryl ether ketone) membranes, focusing on the effect of the degree of sulfonation and crosslinking density on the water uptake, the physical state of the water, and the pore size distribution within the membranes. We observed that the degree of sulfonation and, in particular, the ion-exchange capacity (IEC) had less effect on the control of the extent of water absorbed than the crosslinking density of the membranes. Crosslinking also enabled the membranes to reach a higher water contents without losing mechanical integrity. Moreover, increasing the crosslinking density resulted in the presence of more bound water, without dissolution of the membrane. The crosslinked membranes had lower methanol permeability and electroosmotic drag values. Only at low IEC values and low water uptake in partially crystalline sulphonated poly(ether ether ketone), SPEEK could the presence of nanometer pores in the water-equilibrated crosslinked membranes be confirmed by thermoporometry and the pore size distributions were then comparable to those reported for Nafion membranes. At higher IEC values, the water uptake was extremely high, up to 300%, and then the structure of the swollen membranes was more analogous to that of a dilute aqueous solution of the sulfonated polymer, and no nanopores were present. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The main reasons for the use of proton-exchange membranes (PEMs) in hydrogen fuel cells are the promotion of proton conductivity and water transport, the inhibition of gas permeation, and the maintenance of their mechanical strength and dimensional stability.^{1,2} All of these properties are strongly dependent on the total water content and the different distribution of water within the hydrated membrane. The state of the water in PEMs, however, has been reported to have more effects than the bulk water content on the electrochemical properties of the membranes.²

The state of water in PEMs has been classified into three types: (1) nonfreezing water, that is, water that is nonfreezing because it is strongly bound to polar groups and so acts to plasticize the polymer; (2) freezable loosely bound water, that is, water that is weakly bound to the polymer chain and displays a relatively broad melting point; and (3) free water, that is water that is not intimately bound to the polymer chain and behaves like bulk water in exhibiting a sharp melting point below 0°C.^{2–5} Knowledge of the different states of water present in the membranes rather than its total water uptake makes the correlation between

the water content and the electrochemical and physical properties of the membrane more interpretable.

It has been reported² that the presence of bound water leads to a depression of the glass-transition temperature of the PEM. This depression affects the temperature of viscoelastic-induced morphological relaxation and, as an indirect result, influences the proton conductivity and reduces the upper limit temperature of use for PEM fuel cells. A larger amount of bound water leads to a lower electroosmotic coefficient; this indicates that the concentration of loosely bound and free water plays a more important role in transport across the membrane than merely the total water uptake. Moreover, it has been suggested that an important reason for the higher methanol permeability for Nafion is its higher fraction of freezable water compared to that of poly(arylene ether)-based copolymers.

An important criteria affecting the transport properties and swelling behavior of PEMs, such as Nafion, is their partially crystalline morphology⁶ and the clustering of water molecules within the membrane. This can be evaluated by techniques such as thermoporometry, which measures the cluster size distribution based on the melting point depression (ΔT) of water.^{7–11} It

has been applied successfully for characterizing the porosity of carbon/polymer composite electrodes¹² and composite PEMs.^{13,14}

In this article, we discuss the material properties of sulfonated poly(ether ether ketone), PEEK, that is, SPEEK, membranes having different degrees of sulfonation and crosslinking densities, focusing on the water uptake, the state of the water within the membranes, and the pore size distribution in the equilibrated membranes. Water sorption experiments were carried out at different temperatures with a gravimetric technique to determine the diffusion coefficients (D_s) of water in the sulfonated membranes. Differential scanning calorimetry (DSC) was used quantitatively to access the different types of water present in the equilibrated membranes by thermoporosity.

EXPERIMENTAL

Materials

Amorphous PEEK was obtained from Goodfellow, Ltd. Cambridge (United Kingdom), as a 100 μm thick film with a density of 1260 kg/m^3 . The crosslinking of the PEEK films was carried out with ion irradiation (H^+ and He^{2+} ions) in the University of Birmingham's Scanditronix MC40 cyclotron, as described elsewhere.^{15,16} The crosslinking degree (X_c) was expressed as the molar fraction of crosslinking units present in the sample and was measured as outlined elsewhere.¹⁷ Sulfonation was carried out on the crosslinked membranes with 96–98% sulfuric acid at room temperature. The degree of sulfonation was determined on the dried membrane by titration with a standard sodium hydroxide solution and was used to measure the ion-exchange capacity (IEC) of the membranes, expressed as milliequivalents of sulfonic acid per gram of dried polymer. Subsequent measurements were made by Fourier transform infrared spectroscopy from the ratio of absorbances at 1470 and 1490 cm^{-1} . The changes in the Fourier transform infrared spectra on sulfonation were consistent with sulfonation and occurred once per repeating unit and not on repeating units involved in crosslink formation. The sulfonation reaction of PEEK films has also been discussed in detail previously.¹⁷

Fenton reagent, 30% H_2O_2 and 15 ppm FeSO_4 , was used to measure the relative oxidative stability of the membranes, and methanol was used to measure their chemical stability.

All reagents were obtained from Sigma-Aldrich Chemical Co., Ltd., Gillingham, United Kingdom.

Water Uptake Analysis

The membranes were immersed in distilled water at the designated temperature, and the weight change (after the removal of surface water) was followed with time. The fractional water uptake (ΔW) was calculated as follows:

$$\Delta W = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 and W_2 are the masses of the dried sample and the sample after immersion in water, respectively.

The hydration number (λ) is the ratio of the moles of water absorbed per mole of sulfonic acid, such that

$$\lambda = \frac{\text{Moles of H}_2\text{O}}{\text{Moles of SO}_3\text{H}} = \frac{(W_2 - W_1)/M_{\text{water}}}{\text{IEC} \times W_1} \quad (2)$$

where M_{water} is the molecular weight of water (18.0 g/mol) and IEC is the ion-exchange capacity of the dry membrane.

The water volume fraction (X_v), defined as^{18,19}

$$X_v = \frac{V_{\text{water}}}{V_{\text{wet membrane}}} \quad (3)$$

where V_{water} and V_{wet} membrane are volume of water and wet membrane is closely related to λ because

$$X_v = \frac{\lambda}{(\bar{V}_M/\bar{V}_W) + \lambda} \quad (4)$$

where $\bar{V}_M \approx \frac{EW}{\rho_0}$, where EW is the equivalent molecular weight of the monomer repeat unit (taken as 368 for all crosslinked samples and assuming that only the repeat units with no crosslinks were sulfonated), ρ_0 is the density of the dry membrane (g/cm^3), and $\bar{V}_W = 18.0 \text{ cm}^3/\text{mol}$.

The acid concentrations [$-\text{SO}_3\text{H}$] in the PEM with different water contents were determined from the following equation.^{5,18,19}

$$[-\text{SO}_3\text{H}] = \frac{\text{Moles of } -\text{SO}_3\text{H}}{V_{\text{wet membrane}}} = \frac{\text{IEC} \times W_1 \times d}{W_2 - W_1} \times X_v \quad (5)$$

This was measured at a lapse of sufficient times to allow the membrane to equilibrate with the water in contact with it. This varied from 400 to 900 h depending on the temperature of the measurements, d is density of polymer.

The D_s of water in the crosslinked polymer membranes were measured from the water sorption kinetics with a solution of Fick's second law for thin films immersed in water.²⁰ The diffusion coefficient of water (D) was expressed by

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left[\frac{-\pi^2 D(2n+1)^2 t}{4l^2}\right] \quad (6)$$

where M_t and M_∞ are the masses of water uptake at time t and at equilibrium, respectively, and l is the thickness of the polymer film, n is 1/2 for Fick Law to be obeyed. In the initial stages of water uptake, that is, for $M_t/M_\infty < 0.5$, the equation simplifies to^{21,22}

$$\frac{M_t}{M_\infty} = 4\sqrt{\frac{Dt}{\pi l^2}} \quad (7)$$

and D was calculated from the initial slope (s) of M_t/M_∞ plotted against \sqrt{t} because

$$D = \frac{\pi}{16}(sl)^2 \quad (8)$$

DSC Analyses

A Perkin–Elmer differential scanning calorimeter (DSC-7), Beaconsfield, United Kingdom calibrated for temperature and enthalpy response with ultrapure metal standards, in particular,

Table I. Numerical Constants Used in Eqs. (10a) and (11)^a

	A (nm)	B (nm K)	C (J g ⁻¹ K ⁻¹)	D (J g ⁻¹ K ⁻¹)
Heating in cylindrical pores	0.68	32.33	11.39	0.0550

^aAfter Brun et al.⁷

indium [mp = 429.78 K, heat of fusion of free water (ΔH_f) = 29.2 J/g], was used for the quantitative determination of the amounts of freezing and nonfreezing water present in the membranes. The fraction of free water in the total water content was calculated from the following equation with the assumption that the heat of fusion of free water in the PEMs was the same as that of ice (332 J/g):

$$w_b(\%) = w_t - (w_f + w_{fb}) = w_t - 100 \times \Delta H_f / \Delta H_{ice} \quad (9)$$

where w_t is the total percentage water content; w_b is the percentage of bound water; w_f and w_{fb} are the percentages of free and freezing bound water, respectively; and ΔH_f and ΔH_{ice} are the heat of fusion of free water and freezing bound water in the sample and that of ice, respectively.

According to Brun et al.,⁷ the pore radius (R_p) and differential pore volume (dV/dR_p) of a liquid droplet can be calculated from the water melting endotherm from the observed ΔT and heat of fusion (q ; W/g) such that for $0 > \Delta T > -40^\circ\text{C}$

$$R_p = A - \frac{B}{\Delta T} \quad (10a)$$

$$\frac{dV}{dR_p} = k \frac{(\Delta T)^2 q}{\Delta H_a(T)} \quad (10b)$$

where k is a calibration constant given by $k = 1/(dT/dt)\rho B$, where dT/dt is the heating or cooling rate, and ρ is the density of water (taken to be 1.000 g/cm³).⁸

The heat of fusion of ice [$\Delta H_a(T)$] is temperature-dependent,^{9–11} such that

$$\Delta H_a(T) = \Delta H_f + C\Delta T + D(\Delta T)^2 \quad (11)$$

ΔH_f , under normal conditions, was taken to be 332 J/g. The numerical values of the constants A – D depend on the measuring conditions (heating or cooling) and pore geometry, but in this study, a cylindrical pore shape was assumed, for which Brun et al.⁷ reported the values that are listed in Table I.

RESULTS AND DISCUSSION

Effect of the IEC, X_c , and Temperature on the Water Uptake by the Membranes

Figure 1 shows typical water uptake plots against time for SPEEK membranes with different IEC values and different X_c . For comparison, the change in the water uptake is expressed as λ ; that is, the number of water molecules per sulfonic acid group present, and normalized to a standard membrane thickness.²¹ A linear dependence on the square root of the exposure

time, as required by Fick's law, was only observed initially, up to about 50% of the equilibrium amount of water absorbed. The amount of water absorbed leveled off, reaching a final constant value; the equilibrium value of λ . D was determined from the initial linear portion of the curves.

In Figure 1(a), the rate of uptake of water and the equilibrium amount at 22°C increased at constant crosslinking density of 0.13 with increasing degree of sulfonation and so increasing IEC values. In Figure 1(b), it can be seen that the crosslinking density had the opposite effect; that is, it decreased the rate of water uptake and the final equilibrium amount at 50°C with increasing crosslinks from 0.13 to 0.23 (the dashed line) at a constant IEC value of 1.84 ± 0.04 mequiv/g.

Figure 2 shows the effect of temperature on the rate of water uptake for membranes with similar IEC and the same crosslink

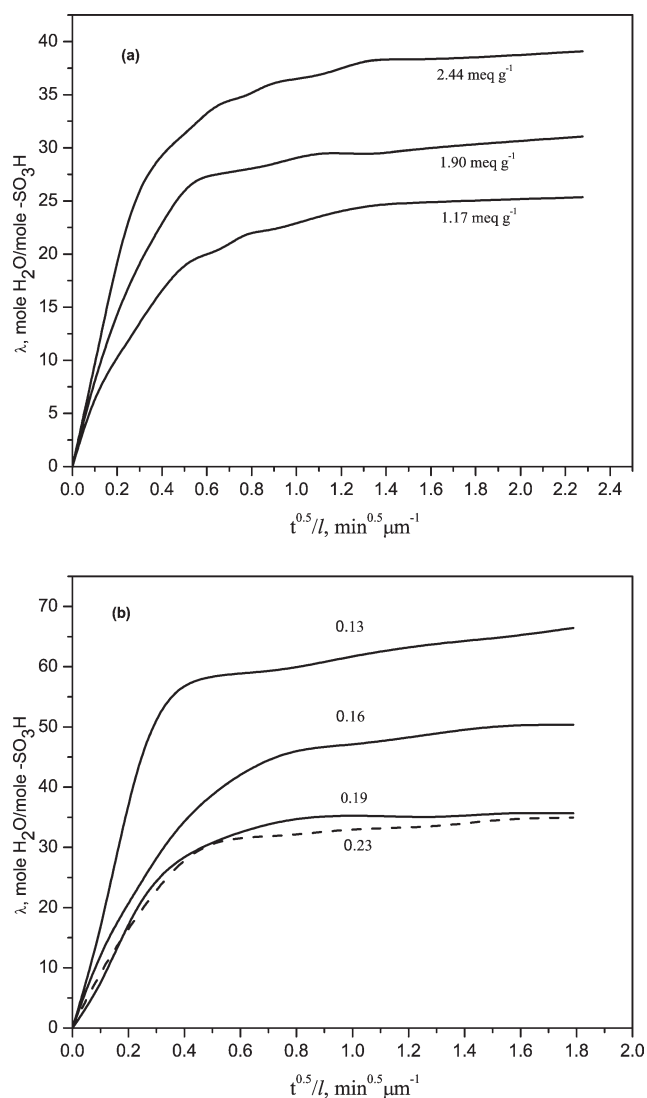


Figure 1. Uptake of water by the crosslinked SPEEK membranes with the square root of exposure time: (a) at a constant crosslinking density of 0.13 and different IEC values at 22°C and (b) at a constant IEC value of 1.84 ± 0.04 and different crosslinks densities at 50°C.

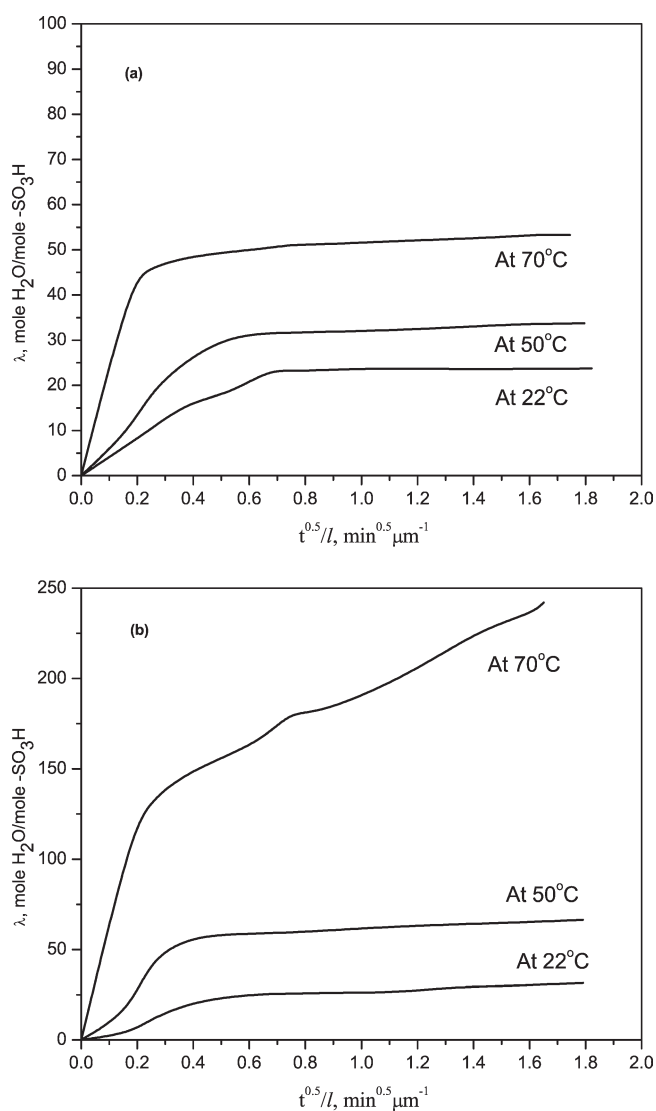


Figure 2. Water uptake kinetics by the crosslinked SPEEK membrane at different temperatures. The crosslink densities were (a) 0.23 and (b) 0.13, respectively. The IEC values were similar at 1.84 ± 0.04 mequiv/g.

densities. A significant decrease in the final water uptake at constant temperature occurred when the crosslinking density increased. Unlike the SPEEK membranes, the crosslinked membranes did not dissolve at high water uptake values and retained structural continuity, such that they returned to their original dimensions when they dried. The effect of crosslinking was more apparent at higher temperatures and with increasing crosslinking density. From 0.13 to 0.23, λ decreased from 150 to 50.

In conclusion, the water sorption increased with increasing IEC values and decreasing crosslinking densities, but the latter had a greater role in controlling the amount of swelling produced by water. In comparison, the water uptake of the SPEEK membranes equilibrated overnight at room temperature were reported to range from 5 to 20. However, with increasing IEC values, the membranes lost structural integrity or dissolved in the water.²³

Effect of the IEC, X_c , and Temperature on the Diffusion of Water throughout the Membranes

D , as defined in eq. (8), was determined from the slopes of the linear plots of M_t/M_∞ against $t^{1/2}$. D increased with the IEC value and temperature but decreased with crosslinking density, as shown in Figures 3(a) and 4(a). The increase with temperature followed an Arrhenius relationship in line with diffusion being a thermally activated process, such that

$$D = D_0 \exp(-\Delta H/RT) \quad (12)$$

where R is the thermodynamic gas constant and D_0 is a pre-exponential factor. The activation enthalpy (ΔH) was observed to decrease with increasing IEC value. The enthalpies were also in line with the value of D s in that the higher D was, the lower the activation enthalpy was. This implied that the hydrophilic sulfonic acid group facilitated the uptake of water by the membrane.

On the other hand, crosslinking had the opposite effect of inhibiting water uptake [see Figure 4(a)]. The overall change in D

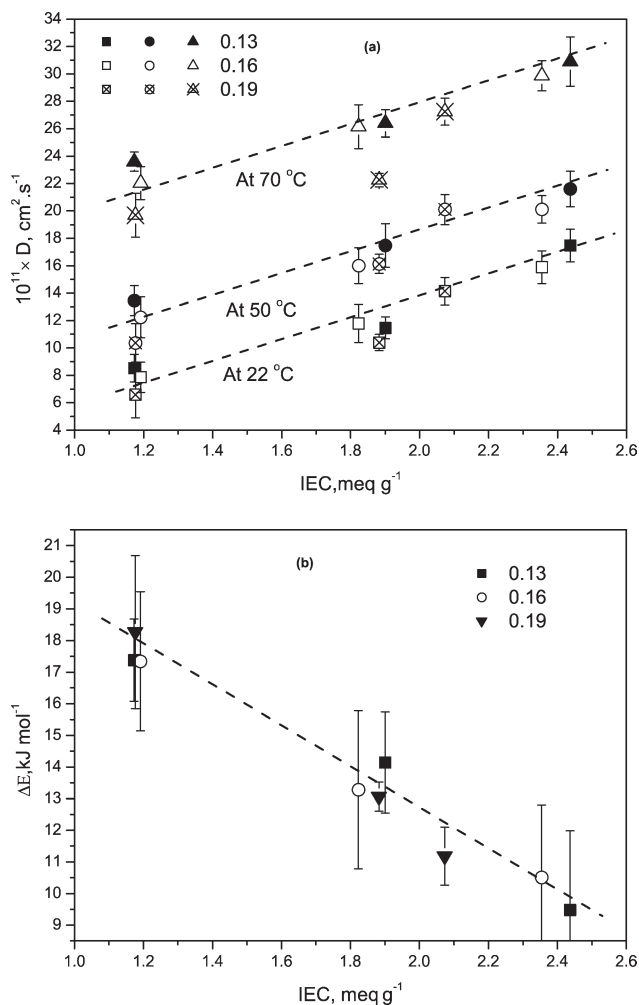


Figure 3. Variation of (a) D at different temperatures as indicated and (b) the corresponding activation energies (ΔE s) with IEC for membranes having similar crosslink densities.

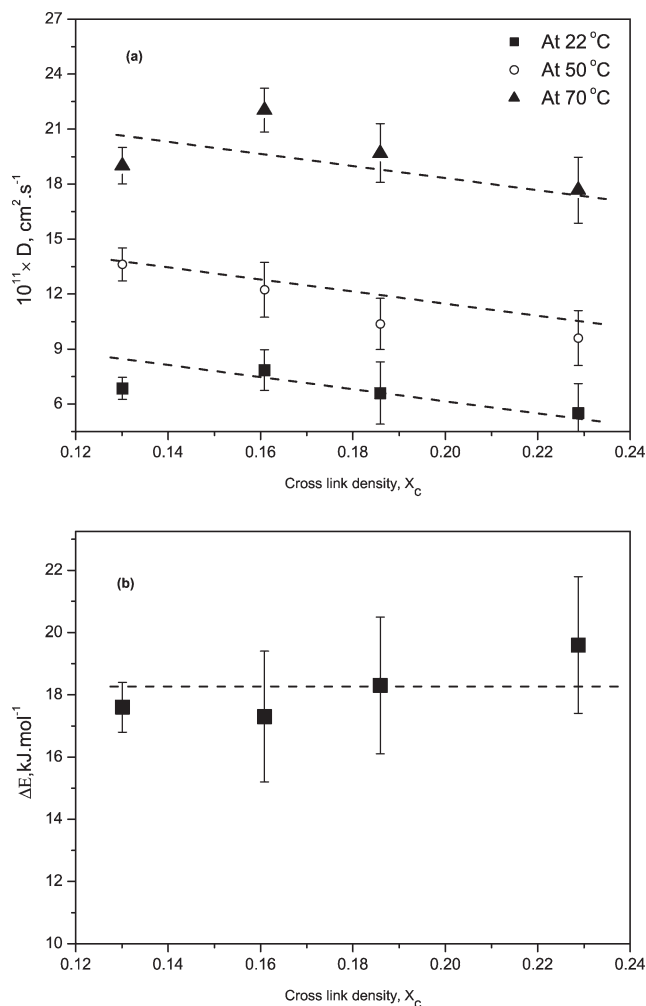


Figure 4. Variation of (a) D and (b) the corresponding activation energies (ΔE s) with crosslinking density for membranes having similar IECs of 1.2 mequiv/g.

was not large, and there was no change in activation enthalpy [see Figure 4(b)] so that crosslinking did not alter the mechanism of the transport of water. The only appreciable effect in limiting the total water uptake at equilibrium was the reduction in the degree of swelling. Because crosslinks were formed before sulfonation they also altered the rate and extent of sulfonation and so restricted the development, extent, and size of the sulfonated regions.

Dilution of Acid Groups

At equilibrium, the crosslinked membranes absorbed much more water than was required to solvate the sulfonic acid groups alone. Figure 5(a) shows how λ changed with the equilibrium water content and X_v for all of the membranes with different IEC and X_c values. Equilibrium λ values up to 400 and a water content of 0.95 were achieved with the crosslinked membranes far in excess of values reported for uncrosslinked materials,²⁴ that is, 5–20 and 0.2–0.4 for λ and X_v , respectively, because increasing the IEC value led to the dissolution and mechanical failure of the membranes. Crosslinking maintained the

continuity of the swollen membrane and allowed it to retain its shape during drying.

The dilution effect of the water on the overall acid concentration within the equilibrated membranes was very pronounced, such that it was reduced by an order of magnitude, from 1.6 to 0.2 M. The dependence of the acid concentration ($[-\text{SO}_3\text{H}]$) in the equilibrated membrane not only depended on the concentration of the sulfonic acid in the dried membrane, that is, its IEC value, but the IEC value in turn also determined the final water content. This, in turn, had a marked effect on the proton ionic conductivity of the membrane and altered the effectiveness of the membrane to act as a PEM.

The decrease in the acid concentration within the equilibrated membranes is shown in Figure 5(b), and the effect was such that the maximum $[-\text{SO}_3\text{H}]$ occurred at $X_v = 0.45$ at an IEC value of 1.2 mequiv/g. The concentration decreased linearly with dilution for all crosslinked membranes, as shown in Figure 5(b).

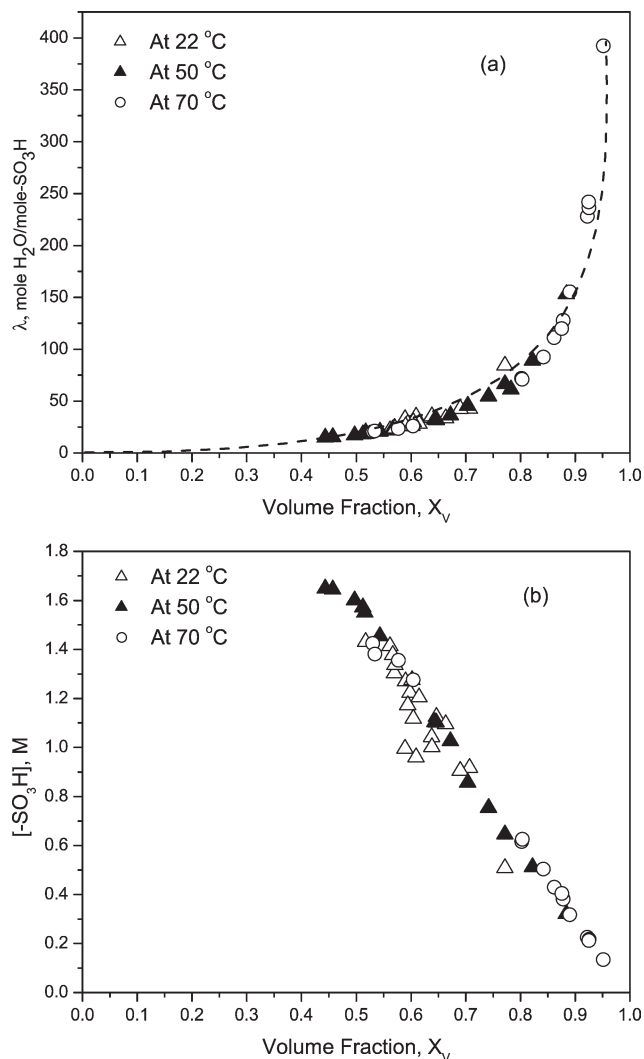


Figure 5. Changes in (a) λ and (b) acid concentration with the equilibrium X_v for different crosslinked SPEEK.

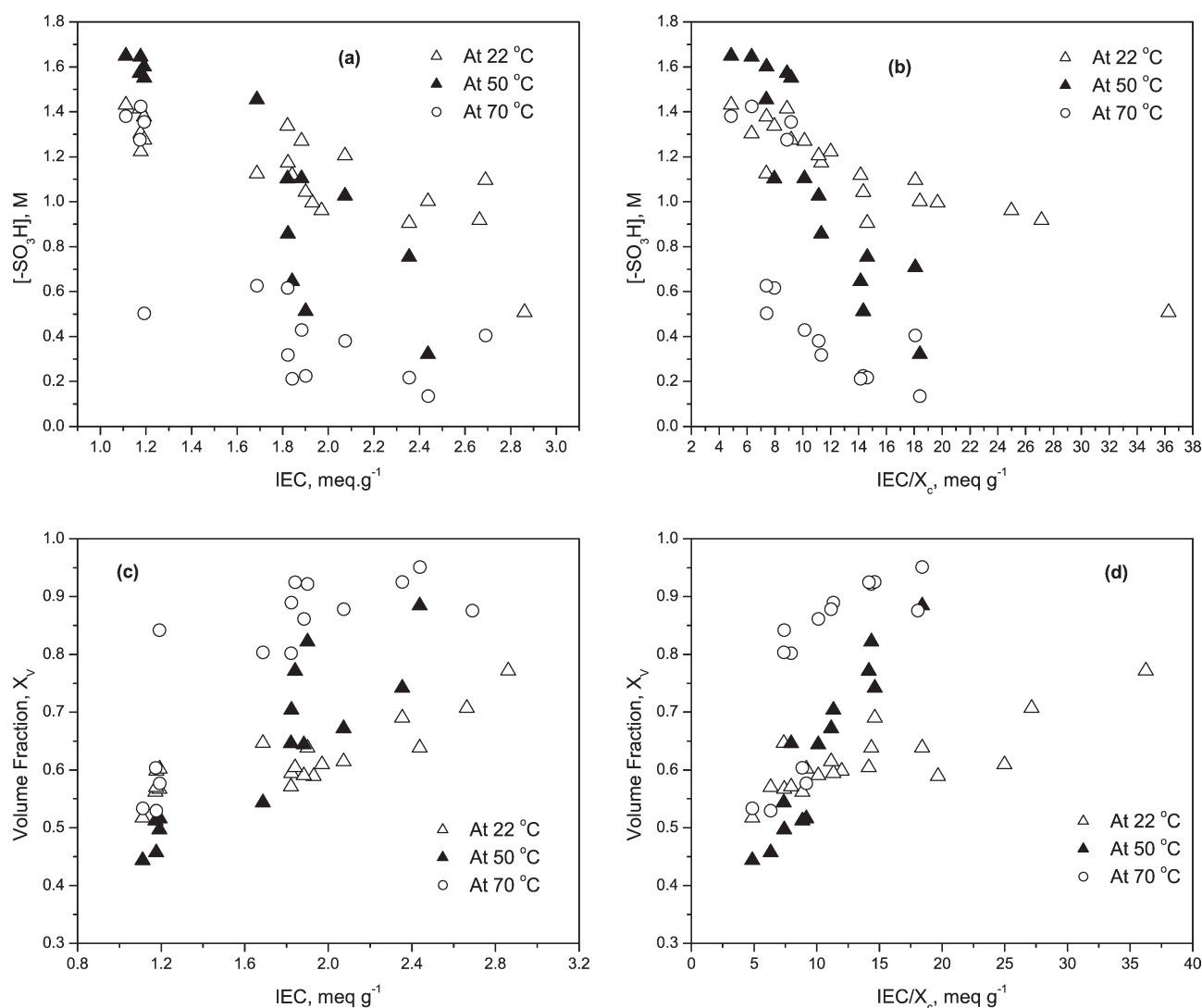


Figure 6. Water uptake at equilibrium: the dependence of $[-SO_3H]$ on (a) IEC and (b) normalized IEC and the dependence of X_v on (c) IEC and the (d) normalized IEC.

The dilution effect on $[-SO_3H]$ and the increase in X_v were not entirely due to increasing IEC; as can be seen in Figure 6(a, b); because there are conflicting effects due to different X_c 's and temperatures. The decrease in concentration and increase in fractional volume of water are more apparent in a plot of $[-SO_3H]$ against normalized IEC values, that is, normalized to take effect of X_c with the ratio IEC/X_c , see Figure 6(b).

Because of the hydrophilic nature of the $-SO_3H$ group, IEC can have a strong influence on the equilibrium water content. This is presented in Figure 6(c, d), and as shown, there was a trend in which X_v increased with increasing IEC. It was also observed that at a low crosslinking density, the data was widely scattered and did not show any simple dependence of X_v or $[-SO_3H]$ on the normalized IEC, that is, IEC/X_c . This may have been due to the fact that crystallization at a low crosslinking density was sufficient to act as physical crosslinking (the crystalline regions did not absorb water); this caused the deviation presented in Figure 6(a–c).

The proton conductivity is determined by the product of proton mobility and acid concentration. It has been reported^{6,25} that the proton mobility in PEM decreases sharply with decreasing W_w . Although a high water content enables greater dissociation of the sulfonic acid and more proton mobility in the PEM, the increase in water content results in a significant dilution of the sulfonic acid groups within the solvated membrane and, thus, a decrease in proton conduction. In other words, the water content must achieve a level at which proton dissociation is sufficiently high for good proton mobility but not too high to dilute the acid significantly.¹⁹

Thermoporometry of the Crosslinked Membranes

The different types of melting endotherms observed for the saturated membranes are shown in Figure 7(a). Membrane A exhibited two well-separated endotherms, which were attributed to the melting of water contained within small pores at low temperatures and to free water at high temperatures. Membranes B and C, however, exhibited progressive overlap of the

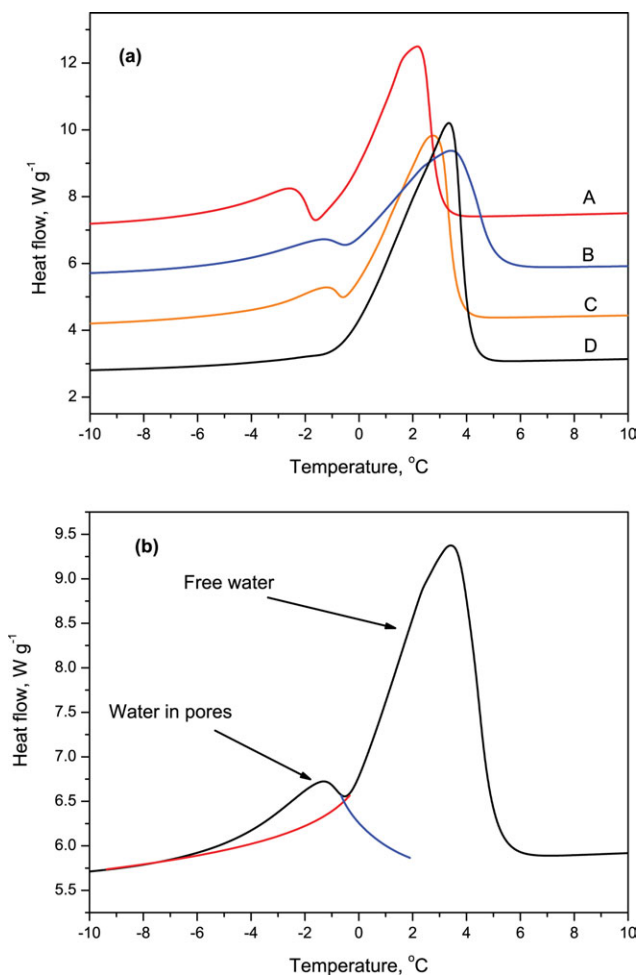


Figure 7. Heat flow versus temperature plots for the saturated crosslinked sulfonated poly(ether ether ketone) SPEEK membranes showing first the pore and the free-water melting endotherms: (a) The different endotherms obtained from various membranes as used to determine the average pore size and distribution and (b) the procedure adopted to separate the overlapping endotherms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

two endotherms as the pore size increased. Eventually, the membranes having large water contents exhibited endotherms of type D, which could not be distinguished from that of free water.

Only the low melting endotherms were used to determine the pore size and distribution, but a curve-fitting procedure was adopted to allow for the overlap with the free water endotherm, as shown in Figure 7(b).

The freezing water content was determined, as outlined in the Experimental section, from the measured heat of fusion on heating from -20 to 10°C^{2-5} after the membrane was cooled to -30°C , and the nonfreezing water was determined from the difference between the total water, determined gravimetrically, and that calculated from the measured enthalpy of fusion. Figure 8 shows the variation of freezing and total water content in the saturated membranes per mole of sulfonic acid and normalized for crosslinking density, that is, IEC/X_c .

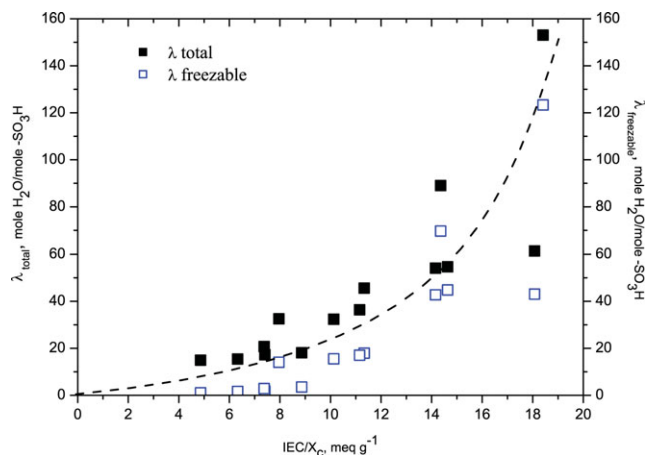


Figure 8. Freezable and equilibrium water content dependence on the IEC and crosslinking density. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For comparison, λ was used because it was the ratio of water molecules to sulfonic acid groups on the polymer. At higher λ s, an increasing proportion of the water crystallized either as free water or within the pores of the membrane, but in every case, about 20–25 mol of water per mole of sulfonic acid group did not freeze. This suggests that this nonfreezing water content was strongly bound to the acid units, perhaps as a hydrogen-bonded structure centered on each sulfonic acid group, which was sufficiently bulky to disrupt the lattice structure of water.

According to Brun et al.,⁷ R_p and size distribution can be calculated from the water melting endotherm and the observed ΔT . The pore size corresponding to the maximum in the distribution curves was considered to represent the average pore size present in the membranes.

Figure 9 shows the pore size distribution determined for the membranes with increasing λ and crosslink densities. As shown, the average pore sizes were similar at about 7 ± 1 nm over a

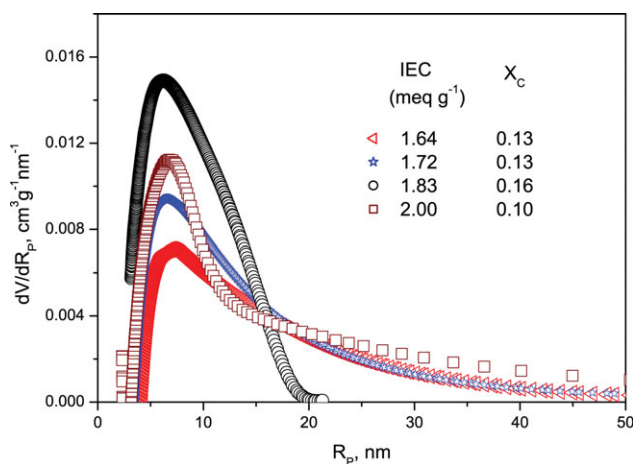


Figure 9. Pore size distribution curves for the crosslinked sulfonated poly(ether ether ketone), SPEEK membranes showing the effects of IEC and crosslinking density, X_c . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

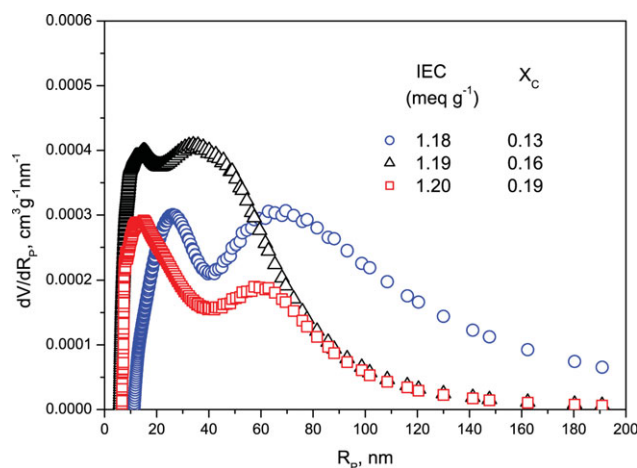


Figure 10. Effects of the crosslinking density on the pore size distribution for sulfonated poly(ether ether ketone), SPEEK membranes at a constant IEC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

wide range of IEC values and crosslink densities. The sizes of pores present were comparable to those reported in Nafion with NMR cryoporometry,²⁶ that is, 1–3 nm.

However, the distribution broadened at the higher IEC values and lowest crosslinking densities; this indicated that more than one distribution was present in these membranes. This was confirmed in Figure 10, in which there was some evidence of the presence of two distributions and a decrease in pore size with increasing crosslinking density. The full results of this analysis are shown in Table II, along with the water content of the membranes before the DSC measurements were carried out. However, the pore size decreased with increasing IEC values and increasing water content. This was not readily understood in terms of the water clusters within pores within the polymer matrix.

Characteristics of the Swollen Crosslinked SPEEK Membranes

The large excess of water over sulfonic acid groups, as implied with water contents as large as 300%, suggested that the incorporation of water within the pores in the swollen polymer matrix was not an appropriate model for this system. It is difficult

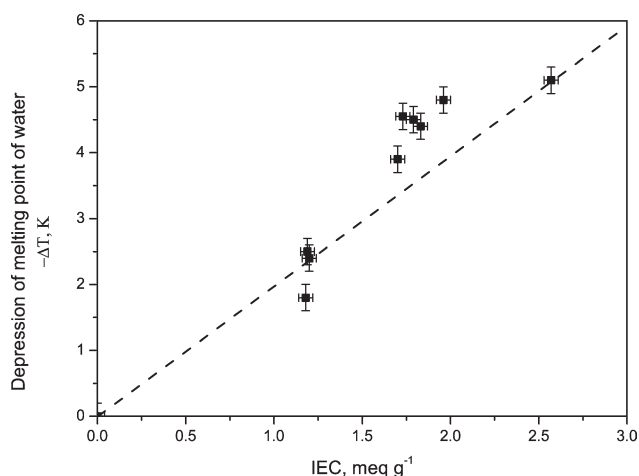


Figure 11. Effects of the IEC value in depressing the melting point of water.

to explain why there was a decrease in water clusters with increasing ratio of water to sulfonic acid groups.

The swollen membranes had some of the characteristics of an aqueous solution, with the polymer conformations limited by X_c and increased with equilibrium water content. Limited solubility was only achieved because X_c was above the gel point. Such aqueous gels will crystallize on cooling and exhibit ΔT s in line with the molar fraction of the impurities present. This is shown in Figure 11, where the depression of the melting point of water, as measured from the maximum in the lower melting endotherm, see Figure 7(a) and (b), are plotted against the moles of sulfonic acid per monomer mole. The dependence was observed consistent with the colligative property being dependent on the molar fraction of sulfonic acid present and nonideal behavior. The line drawn assumes ideal behavior, depression of the melting point of water by the sulfonic acid groups present, and a cryoscopic constant for water of $1.86 \text{ K mol}^{-1} \text{ kg}^{-1}$. The scatter in the results was undoubtedly due to the conflicting effect of crosslinking in reducing the mobility of the polymer segments.

An alternative structure of an aqueous gel for the swollen PEM structure, based on SPEEK and stabilized by crosslinking, is

Table II. Properties of the Crosslinked Membranes and Thermoporometry Analysis

IEC \pm 0.04 (mequiv/g)	X_c (proportion of crosslinked units)	Pore size (nm)	Equilibrium water content EWC (%)	λ (mol of H_2O /mol of HSO_3H)
1.18	0.13	26–71	38	18
1.19	0.16	16–40	37	17
1.20	0.19	15–63	33	15
1.64	0.13	7	316	90
1.72	0.13	6.5	305	89
1.79	0.13	6–7	180	54
1.83	0.16	6	232	55
1.96	0.10	7	205	58
2.57	0.15	6–12	300	61

suggested. This arose from the very large increase in water adsorption, the inhibition of crystallization by the increased concentration of sulfonic acid groups, and the solubilization of the SPEEK molecules.

Stability Tests

The oxidative stability^{27–29} of the crosslinked membranes was examined by measurement of the time taken to break up or dissolve the membranes. We observed that the stability of the membranes, in general, decreased with increasing IEC, but the crosslinked membranes showed higher oxidative stability, and this, in turn, was less dependent on the IEC compared to uncrosslinked SPEEK, which had a similar IEC. The uncrosslinked SPEEK membranes, having IECs in the range 0.8–2.4 mequiv/g, were observed to dissolve completely in Fenton reagent after 12 to 48 h. On the other hand, the breakdown of the crosslinked SPEEK membranes having a high IEC/ X_c ratio occurred after 72 h of treatment. Complete dissolution was not observed, even after 168 h of testing. This was attributed to the presence of an oxidative stable structure in the membranes, which was produced by the crosslinking process. The Nafion membrane and the irradiated membranes with lower IEC/ X_c ratios showed the highest oxidative stability and did not break down during the timescale of the experiment (168 h).

The test in methanol showed that only membranes with low IECs did not break down with increasing exposure time. We observed that most of the irradiated membranes having IECs of 2.0 mequiv/g or greater absorbed up to 50% of their original weight during the first 2 h of immersion in methanol and more than 100% after 20 h and were found to break up after 168 h. On the other hand, irradiated membranes with the highest X_c ($X_c = 0.23$) and IEC = 1.68 and 1.82 mequiv/g showed the lowest equilibrium methanol uptake, that is, 56 and 95%, and did not break up during the experiment. We concluded that the IEC values played a more important role than X_c in dictating the methanol permeability of the membranes.

The hydrolytic stability³⁰ of the crosslinked membranes were examined by measurement of the changes in the IEC values after immersion in liquid water at 70°C and for extended times up to 400 h. No massive decrease in the IEC values was observed (0.2–0.5%); this indicated the stable structure formed on crosslinking and sulfonation of these films.

CONCLUSIONS

We investigated the materials properties of different crosslinked SPEEK membranes, focusing on the extent and rate of water uptake. The main reason for the crosslinking of the PEM was to reduce the swelling in the presence of solvents and to attain high water contents without a loss of dimensional stability. The IEC values had a lesser effect than the crosslinking density on the control of the water content and the diffusion of water through the PEM. Crosslinking enabled the PEMs to reach a very high water content without a loss of mechanical integrity. It has been reported that proton conductivity for different PEMs, including SPEEK, is strongly linked to both the water content and the acid content.¹⁹ In light of the previous results and the findings in this study, we expect that the conductivity

would decrease with increasing crosslinking density, but further detailed analysis is needed to clarify this effect.

Water uptake analysis showed that an increase in crosslinking reduced the rate of uptake of water but improved the oxidative and mechanical stability of the swollen membrane. Increasing the IEC gave rise to more free water at equilibrium. The results indicate that the crosslinked membranes had lower methanol permeability and electroosmotic drag values and improved mechanical stability.²

Both the crosslinking density and IEC had an effect on the pore size in the crosslinked membranes, but IEC had a more marked effect. The presence of a nanostructure in the crosslinked membranes was confirmed, and the sizes of the pores present were comparable to those reported in Nafion. However, the large excess of water over sulfonic acid groups, as implied with water contents as large as 300%, suggested that the incorporation of water within the pores in the swollen polymer matrix was not an appropriate model for this system. An alternative structure for the swollen PEM structure, based on SPEEK and stabilized by crosslinking, of an aqueous gel was suggested. This arose from the very large increase in the water adsorption, the inhibition of crystallization by the increased concentration of sulfonic acid groups, and the solubilization of the SPEEK molecules.

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