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Casting solvent interactions with sulfonated poly(ether ether ketone) during proton exchange membrane fabrication[☆]

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Abstract

¹H NMR spectroscopy revealed the formation of a strong interaction between sulfonated poly(ether ether ketone) (PEEK) and the casting solvents dimethylformamide (DMF) and dimethylacetamide (DMAc), commonly used in proton exchange membranes (PEM) preparation. The DMF amide function readily forms a hydrogen-bonding complex with sulfonic acid group starting at temperatures as low as 60 °C. DMAc is less susceptible to participate in this reaction and hydrogen-bonding occurs in this case only above 100 °C. Both solvents are prone to thermally activated decomposition possibly accelerated by sulfonic acid functions and the produced dimethylamine (DMA) also forms a strong association with SPEEK. The solvents' decomposition is strongly catalyzed by residual sulfuric acid originating from SPEEK preparation, with the resulting formation of *N,N*-dimethylaminium hydrogensulfate (DMAm). Both DMF and DMAc solvent interaction with SPEEK sulfonic acid groups significantly affect the properties of PEMs, lowering their proton conductivity.

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Keywords: Ion-exchange membranes; Membrane preparation and structure; ¹H NMR spectroscopy; Proton conductivity

1. Introduction

The protogenic properties of the majority of poly-electrolytes used for proton exchange membrane (PEM) preparation are most commonly provided by sulfonic acid functionalities. The PEMs of this kind are usually prepared via wet chemistry whether by post-polymerization sulfonation with sulfuric acid or directly by synthesis involving sulfonated monomers.

In the final stage of PEM preparation, thin uniform films are usually prepared by casting the polymer solutions on a flat surface. So far, judging by the absence of any discussion of the issue in the relevant literature, the choice of a casting solvent did not attract much attention. If it was not completely arbitrary, it still seems to be considered as rather unessential, since the influence of the casting solvent on the PEM properties has never been the subject of any special study. At the same time it should be borne in mind that a sulfonated polymer contains a large number of highly reactive acidic sites and that the cast polymer-solvent blends are often exposed to heating, sometimes up to temperatures well above 100 °C, in order to eliminate the

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Table 1

Proton conductivities of PEMs prepared from SPEEK and SPS using different casting solvents

| Polyelectrolyte | DS | Casting solvent | Conductivity (S/cm) | Reference |
|---|------|-----------------|----------------------|-----------|
| Sulfonated poly(ether ether ketone) (SPEEK) | 0.65 | DMF | 1×10^{-5} | [1] |
| | – | DMF | 7×10^{-4} | [2] |
| | 0.60 | NMP | 6.4×10^{-2} | [3] |
| | 0.60 | NMP, DMAc | 2×10^{-2} | [4] |
| | 0.73 | Not reported | 6.6×10^{-2} | [5,6] |
| Sulfonated polysulfone | High | DMF | 9.4×10^{-4} | [7] |
| | 0.40 | DMAc | 1×10^{-1} | [8] |

high-boiling solvents. Plausible chemical interactions with the various solvents used in the process of PEM preparation may be one of the reasons for the large discrepancies in conductivity data existing in [1–8] for PEMs of similar composition (Table 1). Recently we have indeed found [9] that the solvent can have an important influence on PEM properties, strongly affecting their proton conductivity. It has become evident for instance that dimethylformamide (DMF), which is often used as a casting solvent in membrane preparation [1,2], enters into a strong interaction with sulfonated poly(ether ether ketone) (SPEEK). This interaction appears to have a negative influence on the properties of the SPEEK PEMs by reducing their proton conductivity by more than an order of magnitude. The main objective of the present paper is to study more comprehensively the dimethylacetamide (DMAc) and DMF interactions with sulfonated PEEK by NMR techniques and to give a closer insight into this phenomenon, which affects the proton conducting properties of the polymer films.

2. Experimental

2.1. PEM preparation

The sulfonation of PEEK (PEEK grade 450G was kindly donated by the manufacturer Victrex PLC) was performed using concentrated sulfuric acid according to the procedure described elsewhere [9,10]. The reactions were carried out in the temperature range of 25–80 °C under vigorous mechanical stirring during periods ranging from several hours to a few days. To terminate the sulfonation reactions, the polymer solutions were decanted into a large excess of ice-cold

water under continuous mechanical agitation. The polymer precipitate was filtered and washed until pH = 5. The polymer was then dried under vacuum for 8–10 h at 25–100 °C. The degree of sulfonation (DS) was determined both by ^1H NMR spectroscopy (described below and in more detail elsewhere [9]) and by titration with NaOH following by back titration with HCl. Membranes were prepared from the dry SPEEK dissolved (10–15 wt.%) in a given solvent and cast onto a glass plate. The films were dried under ambient conditions for several days and then under vacuum at 25–140 °C for a few more days.

2.2. Membrane characterization

The ^1H NMR spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz. For each NMR analysis, a solution was prepared by dissolving 35 mg of SPEEK polymer in 1 ml of DMSO- d_6 . Tetramethylsilane (TMS) was used as the internal standard.

The proton conductivity of the polymer membranes was measured by AC impedance spectroscopy as previously described in [9,10]. Thirteen millimeter disc cut from a membrane was placed in an open, temperature-controlled cell, where it was clamped between two stainless steel electrodes. The impedance data were corrected for the contribution from the empty and short-circuited cell.

3. Results and discussion

3.1. SPEEK without solvent

NMR analysis of pure SPEEK directly obtained from the sulfonation reaction was reported in some

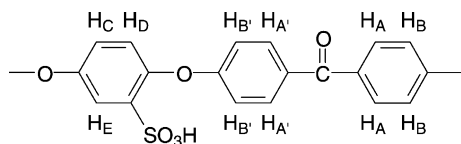


Fig. 1. Nomenclature of the aromatic protons for the SPEEK repeat unit.

details previously [10]. It will be only briefly recalled here that in ^1H NMR spectra of SPEEK the presence of a sulfonic acid group causes a significant 0.25 ppm down-field shift of the hydrogen H_E signal compared with H_C or H_D in the hydroquinone ring (Fig. 1), resulting in a distinct signal for protons at the E position. Typical partial ^1H NMR spectra of pure SPEEK samples (dissolved in DMSO-d_6) with DSs of 0.75 and 1.00 are illustrated in Fig. 2. The H_E signal intensity may be used for estimation of the H_E content which is equivalent to the SO_3H group concentration or the degree of sulfonation per repeat unit. The DS can be derived from the ratio between the peak area of the H_E signal (AH_E), and the integrated peak area of the signals corresponding

to all the other aromatic hydrogens ($\text{AH}_{\text{A,A',B,B',C,D}}$) expressed as:

$$\frac{\text{DS}}{12 - 2\text{DS}} = \frac{\text{AH}_\text{E}}{\sum \text{AH}_{\text{A,A',B,B',C,D}}} \quad (0 \leq \text{DS} \leq 1)$$

In low DS SPEEK, the ^1H NMR spectrum is more complicated because of the high number of signals resulting from a mixture of alternating unsubstituted and substituted repeat units. On the other hand, the spectrum of SPEEK DS 1.00 is simple and signal assignment is straightforward. All four H_A s appear at low field due to the deshielding carbonyl effect. The three-spin system $\text{H}_\text{D}-\text{H}_\text{C}-\text{H}_\text{E}$ is easily recognized from the multiplicity of the peaks involved in spin couplings. H_C is a doublet of doublets at 7.23 ppm because it is interacting with H_E through four-bond coupling (2.5 Hz) as well as with H_D through three-bond coupling (8.8 Hz). The two $\text{H}_{\text{B}'}$ protons are a doublet at 7.03 ppm, shifted upfield by the proximity of the electron-rich SO_3H group. The remaining H_B protons absorb at 7.18 ppm.

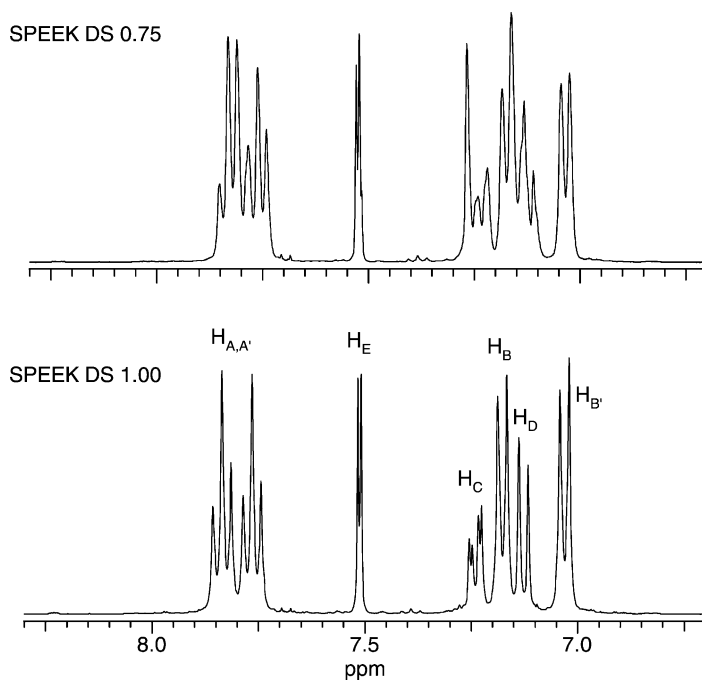


Fig. 2. ^1H NMR spectra of pure SPEEK polymer (dissolved directly in DMSO-d_6) with DSs of 0.75 and 1.00.

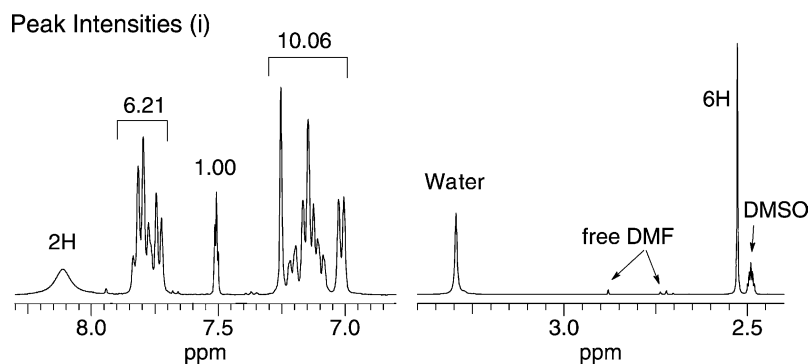


Fig. 3. ^1H NMR spectrum of PEM cast from SPEEK with DS = 0.66 in DMF solution.

3.2. SPEEK interaction with DMF and DMAc

In our experiments, NMR spectroscopy of the SPEEK membranes, cast from solutions in DMF and DMAc, always revealed the presence of residual solvents originating from the film preparation. Furthermore, additional resonances also present in the spectra, suggest that some phenomena occurred during preparation and curing of the SPEEK films. As a typical example the ^1H NMR spectrum of a SPEEK PEM having DS 0.66 cast from DMF solution and dried at 120°C , is shown in Fig. 3. Apart from the quintet at 2.49 ppm assigned to DMSO-d_6 used as NMR solvent, this figure shows two small signals arising from free DMF at 2.74 and 2.88 ppm and in addition, two new resonances: a broad weak signal at 8.11 ppm and a very strong sharp singlet at 2.54 ppm.

In order to obtain more detailed information on solvent–polymer interactions, a special experiment with an excess of solvent was carried out where two 20% (w/v) solutions of SPEEK polymer in DMF and

DMAc were investigated. It must be noted that these control SPEEK samples were very carefully washed to remove residual sulfuric acid. SPEEK with DS of 0.82 was selected because it was not feasible to wash SPEEK DS 1.00 due to its solubility in water, which makes it difficult to remove completely the sulfuric acid. At the same time the DS of 0.82 has a high enough content of $-\text{SO}_3\text{H}$ groups to have an interaction effect with solvents (provided it occurs), but low enough to be washed free of acid.

The freshly prepared SPEEK samples were dissolved in non-deuterated DMF and DMAc, placed in capped vials and heated in an oven at 60°C overnight to ensure that dissolution of the polymers was complete. After ^1H NMR spectra were recorded (one drop of sample solution in DMSO-d_6), both samples were heated further to 140°C for a period of 4 h and NMR spectra were recorded once again (Fig. 4). Finally, NMR spectra were obtained after the samples were further heated at 140°C for 3 days. It is seen from Fig. 4A that signals at 2.54 and 8.15 ppm are also

Table 2

Integrated intensity values of ^1H NMR signals, related to DMF and DMAc interaction with SPEEK

| Time ^a , temperature | DMF | | DMAc | | |
|------------------------------------|---|--|---|--|--|
| | Methyls – $\text{N}(\text{CH}_3)_2$ (2.54 ppm) | $\text{SO}_3\text{H-N}$ and $-\text{CHO}$ (8–8.5 ppm) | Methyls – $\text{N}(\text{CH}_3)_2$ (2.54 ppm) | Methyl – COCH_3 (1.90 ppm) | $\text{SO}_3\text{H-N}$ (8–8.5 ppm) |
| 18 h, 60°C | 6 | 2 | 0 | 0 | 0 |
| 4 h, 140°C | 6 | 2 | 6 | 3 | 1 |
| 3 d, 140°C | 6 | 2 | 6 | 2 | >1 |

The intensity values are referenced to H_E signal at 7.5 ppm, taken to be unity.

^a h: hours; d: days.

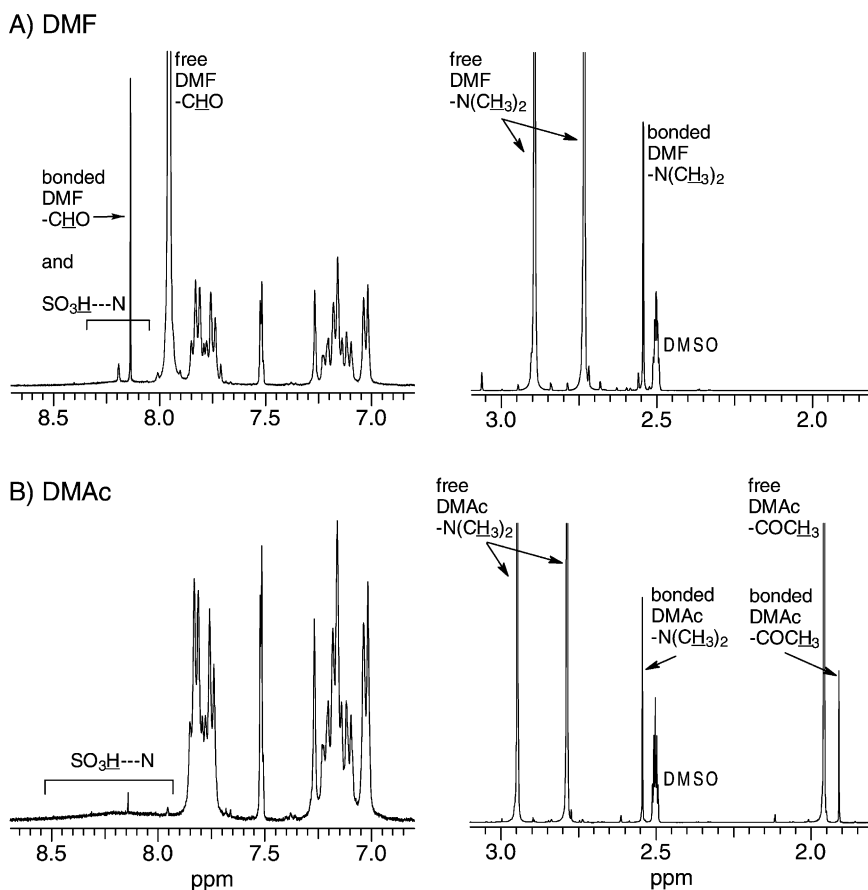


Fig. 4. ^1H NMR spectra of SPEEK polymer samples (DS = 0.82) dissolved in (A) DMF and (B) DMAc (20% (w/v)) both thermally treated at 60°C for 18 h and 140°C for 4 h.

present in the spectra of polymer solutions as seen in the spectrum of SPEEK film in Fig. 3. The integrated intensity values of these signals are given in Table 2. They are referenced to H_E signal at 7.5 ppm (Figs. 1 and 2), which is taken to be unity. To account for these observations the resonance structures of the solvents should be considered.

The electron pair of free DMF occupies a sp^2 orbital of the nitrogen atom and is partly delocalized over the carbonyl group, as illustrated in Fig. 5. Therefore the $N,N\text{-CH}_3$ s are not free to rotate about the C–N bond, causing them to be non-equivalent. Thus, the different electronic environments around the CH_3 groups result in two different ^1H NMR signals at 2.75 and 2.90 ppm. Free unbound DMAc exhibits a similar resonance stabilization (see for instance [11]).

In the presence of SPEEK, however, the nitrogen electron pair of DMF or DMAc is involved in hydrogen-bonding with the sulfonic acid hydrogen atom and is no longer available for delocalization. As a result, free rotation about the C–N bond becomes permitted, which gives rise to a single averaged resonance of methyls at a chemical shift displaced to 2.54 ppm. The N,N -dimethyl of DMAc behaves essentially in a similar manner shifting from 2.95 and

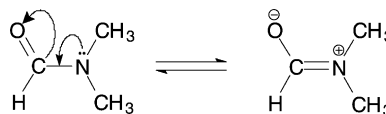


Fig. 5. Resonance stabilization of DMF.

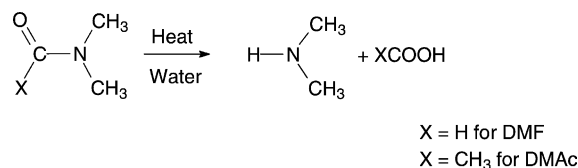


Fig. 6. Thermal decomposition of DMF and DMAc.

2.80 ppm to the same singlet at 2.54 ppm. The sulfonic acid hydrogen atoms involved in this interaction are electron-depleted and therefore believed to be responsible for the resonance at low field (broad peak at 8.15 ppm). In the case of H-bonded DMF, the aldehyde proton is also present and appears at the same low field (sharp peak at 8.15 ppm). The $-\text{COCH}_3$ signal of DMAc is shifted from 1.96 ppm in the free compound to 1.90 ppm for bonded DMAc.

From Table 2 it follows that the integration values of NMR signals produced by DMF–SPEEK bonding in all experiments corresponds to one DMF molecule per $-\text{SO}_3\text{H}$ group of SPEEK. DMAc undergoes polymer-solvent interaction much less readily with SPEEK since it can only be observed at considerably higher reaction temperature (140°C) compared with 60°C for DMF. Table 2 indicates that after this treatment each sulfonic acid group is also H-bonded to one DMAc molecule. However, extended thermal treatment resulted in a decrease of the relative intensity of the $-\text{COCH}_3$ signal at 1.90 ppm. At the same time the integrated intensity of the broad 8.15 ppm signal increased.

Most likely this may be accounted for by partial thermal decomposition of DMAc. It is known that DMAc as well as DMF may decompose at their normal boiling points to give dimethylamine (DMA) and other by-products [12] as illustrated by Fig. 6. The presence of base or acid and water accelerates this degradation. As can be seen from the scheme shown in Fig. 6, DMA produced by partial decomposition of DMAc is free from $-\text{COCH}_3$ group which was converted into acetic acid (CH_3COOH). Thus the evaporation of the volatile acetic acid in the sample heated at 140°C for 3 days results in a reduction of the integration value at 1.90 ppm ($-\text{COCH}_3$ of bonded DMAc). The *N,N*-dimethyl of DMAc (singlet at 2.54 ppm) are also present in DMA and therefore the signal remained unchanged. The newly formed NH from DMA is respon-

sible for the slight increase of the integration value of the broad signal at 8.15 ppm.

Similarly, DMF also appeared to have decomposed into DMA following thermal treatment at 140°C for 3 days. The sharp aldehyde peak at 8.15 ppm, seen previously after only 4 h of high temperature treatment (Fig. 4), had become a broad signal ($-\text{SO}_3\text{H}-\text{HN}(\text{CH}_3)_2$). The aldehydic proton of DMF was replaced by an amine hydrogen and therefore no net change in integration value was observed, despite the change in peakshape. Under these conditions, the by-products of DMF decomposition, DMA and formic acid, cannot be observed by ^1H NMR (Fig. 6). The latter is volatile and the former has the same number of hydrogen atoms as DMF, whose signal at 8.15 ppm caused by NH^+-CHO might be replaced by the NH_2^+ signal of DMA bonded to SPEEK sulfonic acid group.

With the simultaneous presence of acidic SPEEK and basic DMA, an acid-base interaction may be expected. DMA obviously interacts with SPEEK similarly to DMF or DMAc (Fig. 7) also involving two hydrogen atoms into the resonance at 8.15 ppm.

3.3. Interaction of DMF and DMAc with H_2SO_4

In the ^1H NMR spectra of PEM samples prepared from PEEK with a high DS (>0.8), a triplet instead of a singlet at 2.54 ppm was often observed, as illustrated in Fig. 8. It can be inferred that this phenomenon is associated with the presence of residual sulfuric acid. As mentioned above, highly sulfonated PEEK swells or is soluble in water and it is very difficult to wash completely free of H_2SO_4 .

Further experiments without SPEEK were carried out where sulfuric acid was added directly to DMF and DMAc. The experiment was performed in a round bottom flask with a condenser where equal amounts of DMF (or DMAc) and H_2SO_4 were mixed together

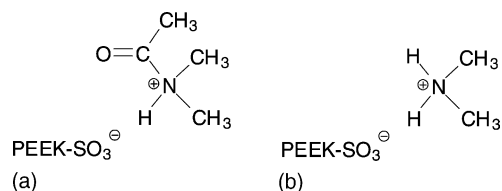


Fig. 7. Interaction of SPEEK with (a) DMAc and (b) DMA.

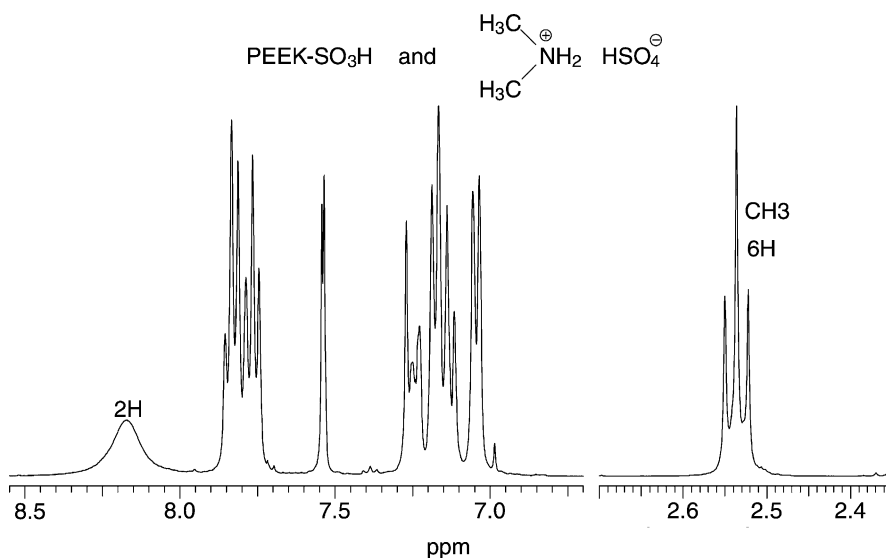


Fig. 8. ^1H NMR spectrum of SPEEK showing the characteristic *N,N*-dimethylaminium hydrogensulfate salt (DMAm) signals.

and heated gradually up to 200°C under atmospheric pressure. Before thermal treatment, no interaction was observed between the acid and DMF/DMAc. However, heating to 200°C brought about a distinct triplet at 2.54 ppm exactly as was observed with high DS SPEEK samples (Fig. 8). Most likely this can be assigned to *N,N*-dimethylaminium hydrogensulfate (DMAm) salt, the structure of which is also shown in Fig. 8. Here the two methyl groups appear to be three-bond spin-coupled to the two amine protons which results in the triplet at 2.54 ppm with a coupling constant (J) of 5.7 Hz. The protons of the aminium group NH_2^+ produce a broad signal at 8.17 ppm. The integrated intensity values of these lines corresponded to 6H (dimethyl) and 2H at low field (8.17 ppm) of the aminium group of DMAm.

Identical NMR patterns emerged when a drop of H_2SO_4 was added to the solutions of carefully washed SPEEK in DMF or DMAc and subsequently heated to 100°C . The decomposition of both solvents was accelerated by sulfuric acid and produced DMAm, identifiable by transformation of the singlet at 2.54 ppm into the triplet. Finally, one last NMR experiment was done using commercial aqueous dimethylamine. The spectrum of dimethylamine in DMSO-d_6 showed the methyls as a singlet at high field (2.2 ppm) due to the high electron density around the nitrogen atom. The

amine-water signal appeared at 3.3 ppm. The sample was acidified with H_2SO_4 and the methyl resonances became a triplet (2.54 ppm, 6H, $J = 5.7$ Hz) while the NH_2^+ hydrogen atom signals appeared at low field (8.15 ppm, 2H). The NMR spectrum of protonated dimethylamine had identical signals to what was seen in numerous SPEEK film samples that had been previously prepared from DMF or DMAc. It is not fully understood what the exact nature of the interactions that are taking place between the PEEK- SO_3H and DMA when sulfuric acid is involved, but it was proved by other experiments that DMAm is created and must surely play a role in this phenomenon.

3.4. Influence of the casting solvent on the SPEEK membrane conductivity

As has been shown above, the sulfonic acid groups of SPEEK, responsible for charge transfer in PEMs prepared from this polymer, are able to form strong hydrogen-bonding with some solvents such as DMF or DMAc. That may significantly affect the conductivity of the membranes as this actually reduces the charge carrier number and/or mobility. In our opinion, this is the main reason for the discrepancies between the properties of different polyelectrolytes which can be found in the literature (see Table 1). Below we

Table 3

Conductivity of PEMs cast from SPEEK solutions in various solvents at 25 and 90 °C

| Pretreatment | σ at 25 °C (S/cm) | | | σ at 90 °C (S/cm) | | |
|---------------------------------|--------------------------|----------------------|----------------------|--------------------------|----------------------|----------------------|
| | DMF | DMAc | NMP | DMF | DMAc | NMP |
| 25 °C, ambient pressure, 5 days | 3.5×10^{-3} | 5.5×10^{-3} | 5.7×10^{-3} | 1.4×10^{-2} | 2.4×10^{-2} | 2.8×10^{-2} |
| 60 °C, vacuum, 1 day | 3.2×10^{-3} | 1.6×10^{-2} | 1.2×10^{-2} | 1.8×10^{-2} | 5.4×10^{-2} | 3.3×10^{-2} |
| 130 °C, vacuum, 1 day | 3.9×10^{-3} | 9.4×10^{-3} | 1.4×10^{-2} | 9.4×10^{-3} | 1.5×10^{-2} | 2.9×10^{-2} |

present the results of an experiment, where three portions of SPEEK from the same batch (DS 0.67) were dissolved in DMF, DMAc and *N*-methyl-2-pyrrolidone (NMP) to the same concentration, cast on glass plates and dried for 5 days at ambient temperature and pressure (Table 3). Conductivities of these samples were measured immediately after preparation, after vacuum treatment at 60 and 130 °C. All samples were fully hydrated by soaking in water overnight immediately prior to the measurements. The table shows the conductivities measured at room temperature and at 90 °C. Drying at atmospheric pressure and room temperature appears not to be sufficient for removing the solvents from PEMs as they were not strong enough after this treatment. It was particularly difficult to dry the NMP cast membrane as this solvent has the highest boiling temperature (202 °C) compared with DMF (153 °C) and DMAc (166 °C). The presence of retained solvents was probably the reason for the low conductivity of these membranes under these conditions. As follows from Table 3, drying under vacuum at 60 °C significantly improved the room temperature conductivity of DMAc and NMP cast membranes, leaving the DMF cast PEM without any conductivity enhancement. As DMF is the lowest boiling point solvent, this anomalously low proton conductivity may be explained by strong hydrogen-bonding of solvent or decomposition product that reduces the number of protons available for proton transport. As discussed above, strong interactions occur during DMF–SPEEK membrane preparation even at 60 °C. In the case of DMAc, heating up to 130 °C reduces the conductivity of SPEEK, which is also consistent with the NMR observations on temperature dependent interaction of DMAc with SPEEK. NMP appears to be the least susceptible solvent to adverse interactions among the ones studied. After high temperature vacuum treatment, NMP cast membranes exhibited the highest conductivity. However, after treatment at 60 °C it was inferior to the conduc-

tivity of DMAc cast PEM due to the presence of residual NMP solvent, which is more difficult to remove than DMAc.

4. Conclusion

It has been demonstrated by NMR spectroscopy that the commonly used casting solvents DMF and DMAc exhibit strong interactions with the sulfonic acid groups of SPEEK. The difference between these two solvents is that DMF readily interacts with the polymer, forming a hydrogen-bonding complex with SPEEK even at 60 °C. DMAc is less susceptible to undergo this interaction and exhibits such bonding only at higher temperature (140 °C). Decomposition of both solvents to DMA and volatile by-products occurs by simple temperature treatment over a period of time, which is possibly catalyzed by sulfonic acid groups. This DMA product also interacts with $-\text{SO}_3\text{H}$. DMF and DMAc are decomposed at room temperature in the presence of sulfuric acid and the reaction is accelerated at higher temperature, resulting in the formation of dimethylammonium hydrogensulfate. The solvent interactions with SPEEK affect the protogenic functions of SPEEK, reducing the number and/or mobility of protons available for proton transport. These interactions dramatically reduce PEM conductivity. This effect is most pronounced for DMF, which makes this solvent inadvisable for PEM casting from polymers containing sulfonic acid functions.

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