Infrared investigations on perfluorosulphonate (Nafion-117) membranes in the H⁺, Li⁺, Cs⁺ and tetramethyl ammonium [N(CH₃)₄⁺] ionic forms

Deoki Nandan¹, K K Pushpa*, V B Kartha, P K Wahi¹ and R M Iyer*¹
¹Chemistry Division, *Spectroscopy Division, Chemistry Group, Bhabha Atomic Research Centre, Bombay 400 085
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Infrared investigations on H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ ionic forms of the perfluorosulphonate exchanger membrane, Nafion-117, in dry, H2O-wet and D2O-wet conditions have been carried out by transmission and ATR techniques. Correct interpretation of splitting of the 980 cm⁻¹ band and the shift of the 1056 cm⁻¹ band on drying have been given in terms of relative hydration and the electron withdrawal (from -SO₃⁻) by bare cations, respectively. Spectra in the OH and OD stretching regions have been interpreted taking into account the interaction between fluorocarbon network, hydrophobic interaction for N(CH₃)₄ and sulphonate group hydration.

The perfluorosulphonate ion exchange membrane Nafion, is exceptionally stable due to its fluorocarbon backbone. The sulphonic acid head groups attached to the backbone give it water sorption and ion exchange capabilities¹⁻⁵. Some ionic forms of Nafion exhibit large affinity for water⁶⁻¹⁻⁸ and water vapour¹⁻⁸ as compared to many other exchangers including conventional polystyrene-DVB sulphonate (PSS) exchangers such as Dowex 50. A recent thermodynamic study¹⁻³ of the water sorption isotherms of H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ forms of Nafion-117 (Eq. wt., Wₑq ~ 1100, membrane thickness, 70 mils) shows that larger water sorption and related free energy changes in the case of H⁺ and Li⁺ ionic forms could be attributed to the greater cationic hydration (n⁺) and swelling pressures (π). The Cs⁺ form, however, sorbed very little water. An analysis of its sorption isotherm indicated the formation of a solvent shared ion pair of the type -SO₃⁻(H₂O)Cs⁺ in the membrane phase¹. This study, however, could not lead to any conclusions regarding the hydration of the sulphonate anion, and the fluorocarbon matrix-water interactions.

In the present paper we report the infrared investigations carried out on Nafion-117 membrane in the H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ forms with a view to supplement information on the state of water inside Nafion-117 and to resolve controversies such as those relating to absorption bands at ~ 980 cm⁻¹ and 1060 cm⁻¹ etc.

Materials and Methods
The Nafion-117 membrane was first treated with 2M HCl to ensure complete conversion to the H⁺ form. From this stock, Li⁺, Cs⁺ and N(CH₃)₄⁺ ionic forms were generated. The different ionic membranes were characterised by determining their ion exchange capacities in the dry form (vacuum dried at 433 K) and their maximum water and heavy water uptake (Table 1).

The membrane in the above ionic forms was used in the vacuum dried (freshly dried) and partially and fully wetted (with H2O as well as D2O) states. Fully wetted membranes were obtained by soaking them in water (or heavy water) followed by surface drying. Partially wetted membranes were generated by isopiestically equilibrating vacuum dried membranes with vapours of H2O or D2O using electrolyte solutions³⁻⁹ prepared in H2O or D2O (water activity ~ 0.8-0.6). This technique gives precise quantitative uptake of water.

<table>
<thead>
<tr>
<th>Nafion-117 ionic form</th>
<th>Ion exchange capacity (meq/g dry)</th>
<th>n†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂O</td>
<td>D₂O</td>
</tr>
<tr>
<td>H⁺</td>
<td>0.935</td>
<td>13.5</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0.935</td>
<td>13.4</td>
</tr>
<tr>
<td>N(CH₃)₄⁺</td>
<td>0.876</td>
<td>6.5</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>0.865</td>
<td>2.8</td>
</tr>
</tbody>
</table>

†The number of moles of water sorbed per equivalent capacity.

We regret to announce the demise of Dr. P.K. Wahi.
IR spectra were recorded on a Perkin-Elmer model 180 double beam spectrophotometer equipped with a filter grating system. Both transmission and attenuated total reflection (ATR) techniques were employed to obtain spectra in the region of 4000-400 cm⁻¹ at a resolution of 1 cm⁻¹ at 2500 cm⁻¹. As ATR, a surface technique with a penetration depth of about one hundredth of a millimeter, gives effective thickness of the above order, spectra of the very strong C-F and S-O bands could be easily obtained.

**Results and Discussion**

IR spectra obtained for the H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ forms of Nafion-117 in the dry and wet states are shown in Figs 1-3. The assignments of important bands in the various regions of the spectra are given in the following discussions and anomalies in earlier assignments are explained.

**Region 650-500 cm⁻¹**

A strong band is observed around 515 ± 5 cm⁻¹ with a sharp shoulder at 553 ± 3 cm⁻¹ in all spectra (Figs 1 and 2). A band of similar relative intensity is shown by polytetrafluoroethylene (PTFE) and, hence, this can be assigned to CF₂ twisting mode. These bands do not show significant change in frequency, intensity or width as a function of cationic state or water sorption. The CF₂ wagging mode has been assigned to two bands at 625 and 650 cm⁻¹ by Hsu in PTFE. In the sulphonate membranes, these bands are overlapped by the strong −SO₃ bending mode. In the present work also, the bands (629 ± 3 and 653 ± 3 cm⁻¹) in this region do not show much change from sample to sample except that the 653 cm⁻¹ band in the H⁺ and Li⁺ forms is very weak. Hsu has identified this band as corresponding to the more ordered

![Fig. 1](image1.png) ![Fig. 2](image2.png)

Fig. 1—ATR spectra of H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ ionic forms of dry Nafion-117

Fig. 2—ATR spectra of H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ ionic forms of D₂O-wet Nafion-117
NANDAN et al: IR INVESTIGATIONS ON PERFLUOROSULPHONATE MEMBRANES

Fig. 3—Transmission spectra of H⁺, Li⁺, Cs⁺ and N(CH₃)₄⁺ ionic forms of partially H₂O-wet Nafion-117

room temperature form of PTFE, its intensity becoming lesser with the helix reversal causing disorder. It can thus be concluded that the Li⁺ and H⁺ membranes are more disordered than those with large cations like Cs⁺ and N(CH₃)₄⁺, because of the stronger interaction arising from closer spacing with the smaller ions.

Region 980-950 cm⁻¹

Except the N(CH₃)₄⁺ form which yields a third band at 952 ± 1 cm⁻¹, all the other ionic forms show two bands in this region, at 971 ± 2 and 981 ± 3 cm⁻¹, the former with lower intensity in the dry membrane. The band at 952 cm⁻¹ in the [N(CH₃)₄⁺] membrane can be assigned to the C−N stretch of the tetramethyl ammonium group as in N(CH₃)₄Br (ref. 12).

The assignment of the 981 cm⁻¹ band is controversial. Falk⁹ suggested that this band is due to the symmetric C−O−C stretch of the vinyl ether side chain. However, a band of comparable relative intensity is observed in PTFE, which has been assigned to end group CF₃ stretching mode by Levy et al¹². The assignment of this band is rather important as it shows change in intensity and splitting on hydration of the membrane. The splitting of this band has been attributed by Falk¹⁻² to interactions of cation with ether oxygen as a result of exposure of side chain to the electrostatic field of cations like Li⁺, Na⁺, etc. This argument is untenable since the splitting takes place on hydration. On comparing the spectra of the dry and wet forms (Figs 1 and 2) it can be seen that in the Li⁺ membrane the band is well split in the wet form, while it is a single band in the dry form. As it is very difficult to get the H⁺ membrane in the completely dry form, it does not show this effect clearly. Earlier workers¹⁻²,¹² have observed this effect with other alkali substituted membranes also.

It can also be seen that the 981 cm⁻¹ band is split for all hydrated samples. For the Cs⁺ form, cation hydration is quite small¹ and the water uptake by the membrane may be mostly through weak osmotic effects. The splitting of the 980 cm⁻¹ in the Cs⁺ system also indicates that the splitting arises from water uptake and is not due to cation interaction as proposed by Falk. Thus, the splitting has to be attributed to some minor structural changes such as water attached to the main perfluoro-region. This water can be free or bonded to some extent to ether oxygen. If the 981 cm⁻¹ band were due to ether linkage, any water present in the perfluoro region would have bonded to oxygen through hydrogen bonding resulting in the shift and pronounced broadening of the band, but this is not observed. On the other hand, water may sufficiently perturb the terminal CF₃ stretching mode (of the perfluoro group) to cause a change in frequency and consequent splitting. This perturbation is expected to occur because of the presence of ionomers containing terminal CF₃ close to or away from osmotically absorbed water. Any interpretation which involves cationic interaction can not explain the splitting.

Region 1060 cm⁻¹

A moderately strong band in the region 1070-1020 cm⁻¹ has been ascribed to sulphonate symmetric stretch²,⁹. While Zundel¹³ did not find any significant influence of cation on this band in polystyrene sulphonic acid membrane, some more recent work²,⁹,¹² and the present work show this
band to be sensitive to cationic species. The variation of frequency of this band from the dry to the hydrated condition for various ionic forms is given in Table 2. Maximum shift in frequency on dehydration is seen for Li⁺ form. Lowry and Mauritz explain the shift in frequency in terms of induced polarisation of the sulphonate anion group due to the electrostatic field of bare counter ions in the dry membrane. Thus Li⁺, being the smallest amongst alkali metal ions, is assumed to lead to maximum change in frequency as observed. The above explanation does not appear to be very convincing. As the unhydrated proton is even smaller than Li⁺ (also, hydration of proton is more than that of Li⁺), larger frequency shift should have been observed for H⁺ form which is not the case.

Our explanation for the frequency shifts is as follows: The effect of cations is masked due to ion hydration and hydration of sulphonate group. A band at 1056 ± 2 cm⁻¹ present in all the hydrated forms corresponds to the hydrogen bonded sulphonate group. On drying, loss of hydration water from the sulphonate group and consequent absence of hydrogen bonding should result in an increase in S–O stretching frequency. But this effect will be countered by the withdrawal of electrons from sulphonate group by the bare cations. It should be noted that a small ion like Li⁺ would be less effective in electron withdrawal than a large ion like Cs⁺. The Cs⁺ form thus has the frequency closest to hydrated sulphonate. The removal of water from the Li⁺ form leads to no significant opposing effects due to electron withdrawal and on dehydration, frequency increases from 1056 to 1072 cm⁻¹, the frequency of a free sulphonate group. The above reasoning also explains the behaviour of the N(CH₃)₄⁺ form. This cation has a large size and hence behaves like the Cs⁺ ion. The anomalous behaviour of H⁺ cannot be understood at present, though it has to be remembered that the H⁺ form can not be completely dehydrated as discussed later.

It may be mentioned that the total shifts in the frequencies in all the cationic forms between the dry and the wet forms are not large, thereby indicating small, but positive hydration of sulphonate group. This is in conformity with the conclusions arrived at in our earlier study using these Nafion ionic forms⁴.

**Region 3700-2600 cm⁻¹**

This region shows the spectral profile of OH and OD stretching modes of water present in the partially H₂O-wet and D₂O-wet membrane phase. A small residual quantity of H₂O in the dry membranes used for wetting with D₂O (this also contained ~1% H₂O) could be present, leading to OH stretching bands in these systems.

These studies revealed that water in varying proportions are present in the exchanger as hydration water (counter ions), hydration water (sulphonate group) and free liquid water (osmotic water) depending on the ionic form and Wₑq of the exchanger³. Additionally, water could also be attached to the fluorocarbon backbone¹⁴. As all these water molecules would differ in their state of hydrogen bonding, they could be expected to show different absorption bands relating to both symmetric (ν₁) and asymmetric stretching frequencies (ν₃).

(a) Hydrogen form

The wet H⁺ form membrane exhibits strong absorption in this region with a sharp shoulder at

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**Table 2 — Shifts in the symmetric vibration frequency of sulphonate group of Nafions in univalent ionic forms (cm⁻¹)**

<table>
<thead>
<tr>
<th>Ionic form</th>
<th>Dry membrane</th>
<th>H₂O-wet membrane</th>
<th>D₂O-wet membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LM</td>
<td>F</td>
<td>PW</td>
</tr>
<tr>
<td>H</td>
<td>1064</td>
<td>1055</td>
<td>1054</td>
</tr>
<tr>
<td>Li⁺</td>
<td>1073</td>
<td>1071</td>
<td>1072</td>
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<tr>
<td>Na⁺</td>
<td>1059</td>
<td>1065</td>
<td>1060</td>
</tr>
<tr>
<td>K⁺</td>
<td>1057</td>
<td>1057</td>
<td>1057</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>—</td>
<td>1055</td>
<td>1054</td>
</tr>
<tr>
<td>N(CH₃)₄⁺</td>
<td>—</td>
<td>—</td>
<td>1051</td>
</tr>
</tbody>
</table>

LM — Lowry and Mauritz (ref. 2); F — Falk (ref. 9); PW — Present work.

Wₑq for Nafion used by us and LM is ~1100 while F used Nafion of Wₑq ~1200-1400.
3682 cm\(^{-1}\). This band is also present in the spectrum of the dry membrane, thereby showing that H\(^+\) form could not be dried completely. This absorption behaviour in polystyrene sulphonate\textsuperscript{13} and Nafion membranes\textsuperscript{1,9} has been attributed to the presence of species such as H\(_2\)O\(^+\) and H\(_3\)O\(^+\). However, the residual water in dry membranes employed was much less than 1 mol equiv and thus there is little possibility of the formation of the above species. It can however be assumed that statistical distribution of residual water among protons will be such that while some of them will have one water molecule attached, majority will have none. Thus, probably species like H\(_3\)O\(^+\) and D\(_3\)O\(^+\) also show this absorption feature. The shoulder observed in the H\(^+\) form at 3682 cm\(^{-1}\) represents OH asymmetric stretching identified as water attached to the fluorocarbon matrix\textsuperscript{9} (see analysis of bands of other ionic forms).

(b) Li\(^+\), Cs\(^+\) and N(CH\(_3\))\(_4\)\(^+\) forms

The transmission spectra of fully hydrated Li\(^+\), Cs\(^+\) and tetramethyl ammonium forms (with H\(_2\)O) show broad and large bands in the OH stretch region. However, partially dried membranes (Fig. 3) show four bands for Li\(^+\), three for Cs\(^+\) and five for N(CH\(_3\))\(_4\)\(^+\) form, some of which are apparently very weak.

The frequencies observed in the case of Li\(^+\) form of Nafion-117 are: 3255, 3538, 3638 and 3708 cm\(^{-1}\). Falk\textsuperscript{1,9} had observed four analogous bands for Na\(^+\) form of Nafion-142E at 3248 ± 12, 3524 ± 6, 3668 ± 8 and 3714 ± 4 cm\(^{-1}\). The small differences between the two can be attributed to differences in ionic forms and in W\(_{eq}\). The band at 3255 cm\(^{-1}\) corresponds to the H\(_2\)O scissor overtone (\(\sim v_2\)) and is too weak to be observed in the Cs\(^+\) form, though it is seen again in the N(CH\(_3\))\(_4\)\(^+\) form at 3260 cm\(^{-1}\).

Similar to a shoulder seen for the H\(^+\) form at 3682 cm\(^{-1}\), sharp shoulders are also seen for Cs\(^+\) and N(CH\(_3\))\(_4\)\(^+\) forms at 3686 and 3690 cm\(^{-1}\) respectively. These shoulders are close to asymmetric stretching frequency in free H\(_2\)O (3756 cm\(^{-1}\)). Obviously, this water corresponds to water in contact with the fluorocarbon matrix. However, the quantity of this water is small as seen from the band intensity. This shows that though there is no appreciable interaction of pore water with fluorocarbon network, a small amount of water is trapped in the fluorocarbon protrusions in the ionic cluster region of the membrane. The frequency of this band for Li\(^+\) form is slightly higher (3708 cm\(^{-1}\)) thereby showing slightly enhanced interaction of this type. This could be due to greater expansion of the hydrated cluster (Li\(^+\) form takes up much more water) thereby increasing the degree of fluorocarbon protrusions. A rough estimate on the basis of area measurements and sorption isotherms reveals that the total quantity of this form of water is \(\sim 0.1-0.3\) (0.2 ± 0.1) mol equiv for various ionic forms. Falk\textsuperscript{9} estimated that in Nafion, \(\sim 24\%\) of the membrane water containing \(\sim 2\) mol equiv is exposed to fluorocarbon phase, which would yield a value of \(\sim 0.5\) mol for this type of water. Our value of 0.2 mol equiv, however, may be more correct. Since several bands signifying various forms of water have been observed by Falk for the Na\(^+\) form, there is every likelihood of greater amount of water being present in the membrane used by him.

Prominent bands seen for Li\(^+\), Cs\(^+\) and N(CH\(_3\))\(_4\)\(^+\) forms at 3538, 3530 and 3505 cm\(^{-1}\) respectively could originate only from osmotic water. Earlier workers\textsuperscript{9} have assigned this band to hydrogen bonded water without giving any specific evidence. However, the quantity of hydration water (sulphonate hydration or solvent shared ion pair) in Cs\(^+\) and N(CH\(_3\))\(_4\)\(^+\) forms is expected to be small, hence the rest (larger quantity) would be osmotic water (closer to normal hydrogen bonding water). Further, Cs\(^+\) form contains the minimum quantity of osmotic water (\(\sim 1\) mol equiv), therefore, this form would show a shift comparable to Li\(^+\) form. For the N(CH\(_3\))\(_4\)\(^+\) form a greater shift as compared to Li\(^+\) form is due to hydrophobic nature of this counter ion (see later). In the Li\(^+\) form, stronger hydrogen bonded secondary hydration water could also be expected as in the case of dehydration of PSS exchangers\textsuperscript{15}. This should actually yield a band with frequency even lower than 3450 cm\(^{-1}\) (normal liquid water). As this is not seen, we can assume that either the strength of hydrogen bonding of the water is similar to that of osmotic water or there is really no secondary hydration in Nafion (Li\(^+\) form is taken up much more water) thereby increasing the degree of fluorocarbon protrusions. At present, we feel that the osmotic water and the secondary hydration water in Li\(^+\) membrane are spectroscopically unresolved due to limitations because of broadening of the bands. The bands due to osmotic water show this water to be less strongly hydrogen bonded than the normal water. This fact could be explained in terms of swelling pressures accompanying osmotic water uptake\textsuperscript{13,11}.

The next set of bands corresponding to the 3670 cm\(^{-1}\) band of the Na\(^+\) form are seen at
3638, 3625 and 3575 for the Li+, Cs+ and N(CH₃)₄⁺ forms respectively. These can be ascribed to hydration water of the sulphonate anion or the primary hydration water of counter ions as this water is apparently even less hydrogen bonded than osmotic water. Li+ is the only counter ion which shows extensive hydration as compared to the other two. Falk⁹ has assigned this band, as well as the 3715 cm⁻¹ band to OH bonded to the CF₂ backbone, which is unlikely in view of the large difference (45 cm⁻¹) in frequency. The 3715 cm⁻¹ band of Na⁺ form corresponds to the 3708 cm⁻¹ band of Li⁺ form. This can be only due to H₂O attached to the fluorocarbon backbone, since such a band should have similar frequency in the various counter ions. Due to fluorocarbon backbone of Nafion, a lower charge density should result on -SO₃⁻ as compared to that in PSS exchangers⁸. This will lead to reduced strength of hydrogen bonding through which sulphonate ion is hydrated. Again, in the Cs⁺ form, if a water molecule shared ion pair is formed in Nafion⁹, a frequency shift compared to Li⁺ form is expected as observed. A shift towards lower wave number in Cs⁺ form not only shows Cs⁺ to be less hydrated but also as behaving like a hydrophobic ion such as an alkylammonium ion, which tends to strengthen the water structure around it. A large shift in the case of N(CH₃)₄⁺ ion compared to Li⁺ form is also seen as expected¹³. As stated by Zundel¹³, alkylammonium ions have stronger interaction with the -SO₃⁻ ions than alkali metal ions in PSS exchanger. The same thus appears to be true for Nafion phase also.

Two weak OH stretching bands are seen for the N(CH₃)₄⁺ ionic form in the region 3340-3408 cm⁻¹. These probably represent a small quantity of very strongly hydrogen bonded water due to the hydrophobic nature of N(CH₃)₄⁺, which tends to avoid contact with water thereby strengthening the hydrogen bonding in water in its immediate vicinity¹³.

The OD stretching regions of the various forms again show similar bands due to osmotic D₂O (2594 Li⁺, 2585 Cs⁺, 2598 N(CH₃)₄⁺), sulphonate ion hydration (2660 cm⁻¹) and D₂O attached to fluorocarbon backbone (2720-2706 cm⁻¹).

The net lesser hydrogen bonded Nafion phase water compared to normal hydrogen bonded water is confirmed by the present IR study. This study lends very strong support to our observations of protium enrichment in the exchanger phase water¹⁴ when Nafion (and PSS resin) in H⁺, Li⁺ and Cs⁺ form is brought in contact with liquid water containing H₂O and HDO (zero point energy considerations require the lighter isotope to enrich in the phase with weaker hydrogen bonding).

The present infrared investigations of Nafion-117 membranes have revealed (i) a small but positive hydration of the sulphonate anion (ii) involvement of only a small quantity of water (0.2 mol/ equiv) in fluorocarbon-water interactions, and (iii) a less extensive hydrogen bonded structure of pore water compared to normal liquid water.

References