

# Infra-red spectra of perfluorinated cation-exchanged membranes

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Assignment of the i.r. spectrum of Nafion cation exchange membranes was made possible by use of i.r. absorption and reflectance (ATR) spectroscopy. Shifts in the water and sulphonic vibrations occurring upon exchange of various counterions were compared with those occurring in a polyethylene sulphonic acid and polystyrene sulphonic acid membrane. The type of binding of the cations and the possibility of cluster formation are discussed. A dimeric iron unit Fe—O—Fe was identified in the Nafion membrane.

## INTRODUCTION

The exchange membranes are used more and more for industrial purposes. 'Nafion' membranes based on sulphonated fluorocarbons have proved to be particularly suitable for many industrial processes, due to their chemical inertness, high permeability to cations and the different forms in which they are available<sup>1-7</sup>. These membranes belong to the much studied class of ionic polymers, whose structure has been very much studied, in particular by Eisenberg and his group<sup>8</sup>. From these studies, which were made mainly by physical methods (small angle X-ray scattering, dielectric and mechanical measurements and others), it is apparent that the ionic groups are not uniformly distributed in the polymer, but are generally clustered in smaller or larger aggregates. Studies of Nafions by various physical methods<sup>3-5</sup> have also indicated that the exchange sites are clustered and this may have also some influence on the transport properties of the membrane.

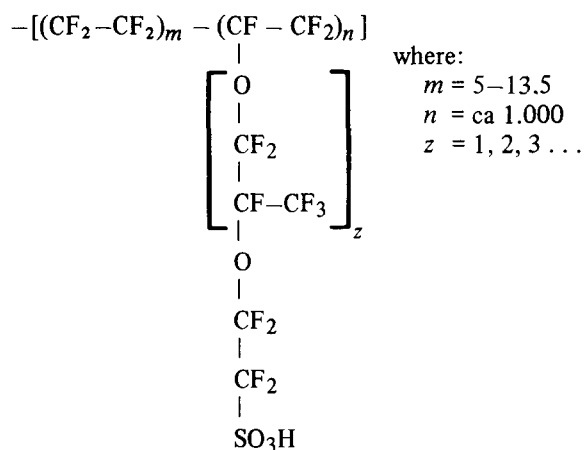
The purpose of the present study was to investigate the properties of these membranes through the changes that occur upon exchange of the counterions. An attempt was made to obtain a more direct proof of clustering and its relation to the transport properties of the membrane. In the present part of this investigation, the structure of two membranes i.e. Nafion and Redcat (polyethylene sulphonic acid) have been studied by infrared spectroscopy. Attempts to study the infrared spectra of Nafions have been made before<sup>6</sup>, because of the very strong absorption bands of the C—F bonds, some spectral regions were completely obscure. In the present work, use of reflectance spectroscopy combined with absorption spectroscopy have enabled the assignment of all relevant vibrations. It was assumed that from these spectra, information on the type of bonding of the cations could be obtained.

## EXPERIMENTAL

The ion exchange membranes studied were Redcat (polyethylene sulphonic acid prepared by the Research and

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Development Authority of the Ben-Gurion University, Beer-Sheba) and Nafion 125 and 152 (Plastics Dept., Dupont and Co., Wilmington, Del., 19898). The Nafions are copolymers of tetrafluoroethylene and monomers such as perfluoro-3,6-dioxo-4-methyl-7-octensulphamic acid:



The value of  $m$  determines the ion exchange capacity which varies from 0.55 to 1.05 meq/g. The thicknesses of these membranes varied between 30 and 125  $\mu$ .

In order to obtain reproducible results, the Nafions were boiled in distilled water for thirty minutes, then dry blotted with filter paper and stored away in stoppered glass bottles. Samples of these membranes (4 x 4 cm) were equilibrated with 0.1N solutions of NaCl, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O for 24 h, then washed quickly with distilled water, dried with filter paper and stored in stoppered bottles. In some cases, these membranes were vacuum dried at room temperature up to 72 h. In order to avoid hydrolysis of the ferric ions in solution (i.e. formation of dimeric or polymeric species), all ferric chloride solutions used were freshly prepared and the pH adjusted to less than one by addition of a few drops of hydrochloric acid.

The infrared spectra of these samples were measured by absorption and reflectance spectroscopy. Absorption spectra were measured on a Perkin Elmer 180 Infrared Spectrophotometer and reflectance measurements were made using the

ATR (attenuated total reflectance) attachment produced by Wilks Scientific Corporation, South Norwalk, Connecticut, USA, on the Perkin Elmer 457 Infrared Spectrophotometer.

**RESULTS**

Table 1 shows the assignment of the vibrational bands of the backbone of the two membranes. These results were ob-

Table 1 I.r. bands of the backbone of Nafion (1) and Redcat (2) membranes (cm<sup>-1</sup>)

1	2
203γ <sub>t</sub> (CF <sub>2</sub> )(E <sub>1</sub> )	
245vwδ(C-C) skeleton bending	
275γ <sub>w</sub> (CF <sub>2</sub> )(E <sub>1</sub> )	
320-345γ <sub>t</sub> (CF <sub>2</sub> )(E <sub>1</sub> )	720 + 730 γ <sub>r</sub> (CH <sub>2</sub> )
530vbr δ(CF <sub>2</sub> )(E <sub>1</sub> ) + νM-O + δS-O	1380w γ <sub>w</sub> (CH <sub>2</sub> )
630vbr γ <sub>w</sub> (CF <sub>2</sub> )(A <sub>2</sub> ) + νC-S and νM-O	1470s δ(CH <sub>2</sub> )
720vw δ(CF <sub>2</sub> )(A <sub>1</sub> )	2860vs
740vw ν(C-C)(A <sub>1</sub> ) skeleton	2915vs ν <sub>a</sub> α ν <sub>s</sub> (CH <sub>2</sub> )
960 + 980s ν(C-O-C)	
1140vs ν <sub>s</sub> (CF <sub>2</sub> )(E <sub>1</sub> )	
1210vs ν <sub>a</sub> (CF <sub>2</sub> )(A <sub>2</sub> )	
1400vw ν <sub>s</sub> (CF <sub>2</sub> )(A <sub>1</sub> )	

tained by the combined use of reflectance (ATR) and absorption spectroscopy (Figures 1 and 2), as even with the thinnest available Nafion membrane, the region of 1400-1100 cm<sup>-1</sup> is completely obscured by the strong C-F symmetric and antisymmetric vibrations. These bands can very well be observed in the reflectance spectrum (Figure 1). The low frequency vibrations are much better observed in the absorption spectrum. The assignments of the C-F vibrations can be made by comparison with polytetrafluoroethylene<sup>9</sup>. Less clear is the assignment of the split band at 980-960 cm<sup>-1</sup>. The polyoxymethylene shows a very strong band at 1090 cm<sup>-1</sup> assigned to ν<sub>a</sub>(COC) and a second one at 932 cm<sup>-1</sup> ascribed to ν<sub>s</sub>(COC). It is possible that replacing of hydrogen by a fluoride in the CH<sub>2</sub> group lowers the ν<sub>a</sub>(COC) vibration to 980 and 960 cm<sup>-1</sup>. This band is slightly shifted when the counter-ion is a transition metal ion, thus implying some coordinative interaction with the oxygen of this group. The vibrations at 630 and 530 cm<sup>-1</sup> are too broad and strong to be assigned only to C-F stretchings. In this region stretchings of C-S, δS-O and M-O (of transition ions in hydrates and oxides) are found<sup>10</sup>. All these vibrations account for the broadness of these bands and their intensity, as a matter of fact when the membranes are in the hydrogen form (especially the Redcat), these bands are sharper and

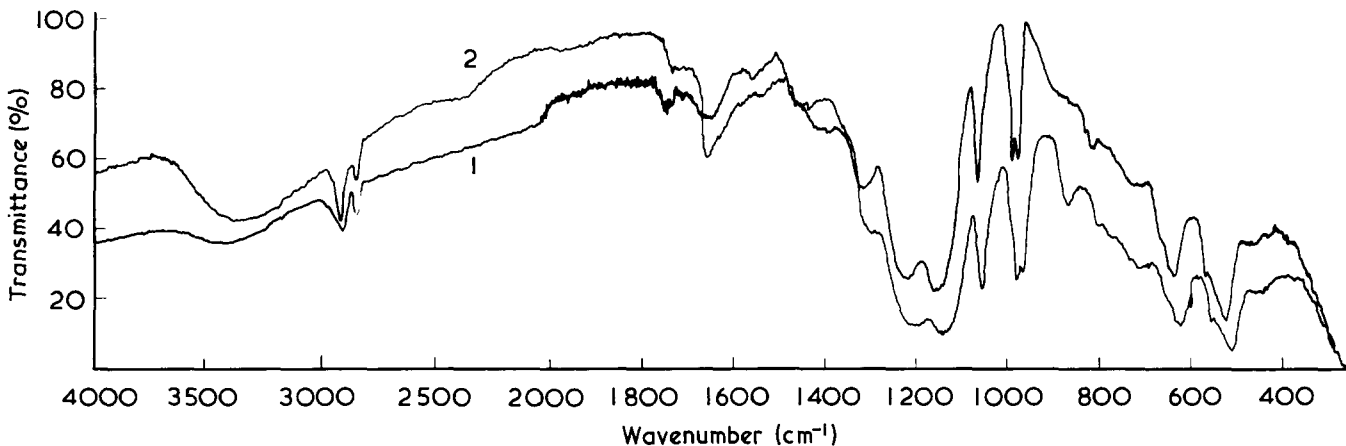


Figure 1 I.r. spectra (ATR) of Nafion membranes, curve 1 (H<sup>+</sup> form) and curve 2 (Fe<sup>3+</sup> form)

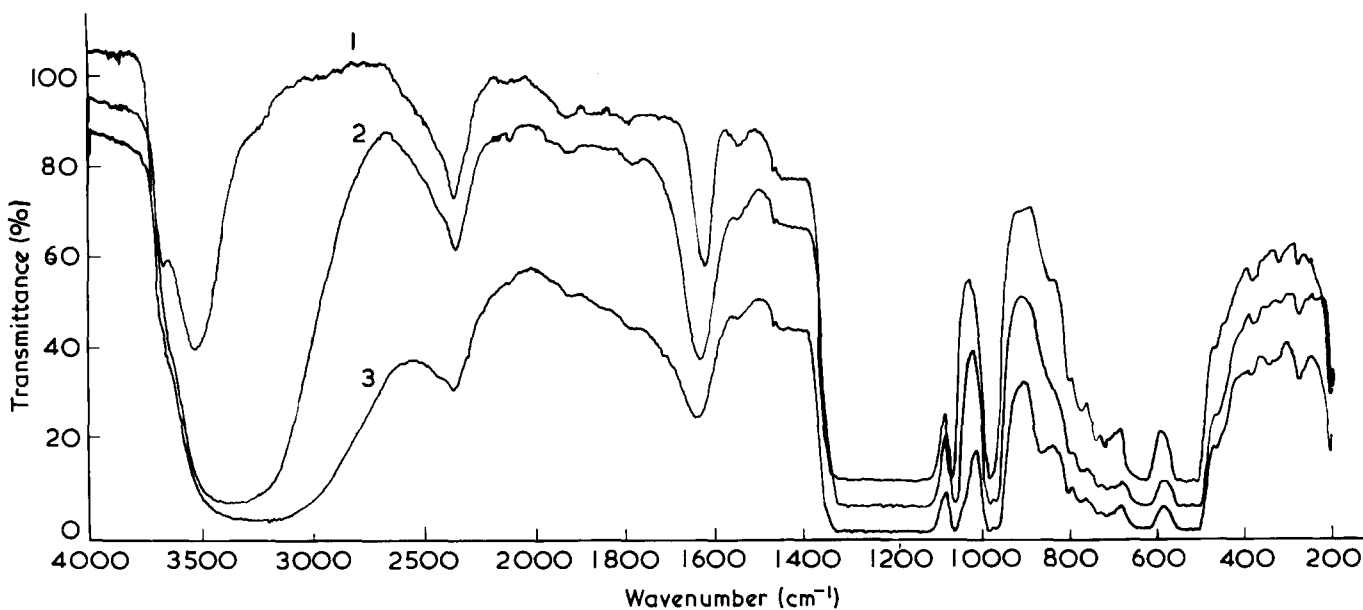


Figure 2 I.r. spectra (absorbance) of Nafion membranes, curve 1 (Na<sup>+</sup> form), curve 2 (Cu<sup>2+</sup> form) and curve 3 (Fe<sup>3+</sup> form)

Table 2 Water and sulphonic bands in Nafion (1) and Redcat (2) membranes in hydrogen forms ( $\text{cm}^{-1}$ )

	1	2
$\nu_1$ free $\text{H}_2\text{O}$	3680	—
$\nu_1$ , $\text{D}_3\text{H}_2\text{O}$	vbr <sup>a</sup>	vbr <sup>a</sup>
$\nu_2$ $\text{H}_2\text{O}$	—	—
$\nu$ hydrolysis and sulphonic bridge	2360brs <sup>b</sup>	~2400vw
$\nu$ $\text{H}_3\text{O}^+$	1700	1700
$\nu_a$ S-O (double bond)	obscured	1350
		1170
$\nu_s$ S-O (double bond)	1060	1050
$\nu$ S-O (single bond)	—	910
$\nu$ (C-S)	630	602
$\delta$ (S-O)	520	520

<sup>a</sup> Proton tunnelling effect

<sup>b</sup> Includes overtone  $\text{CF}_2$  vibrations

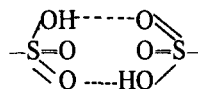
weaker (Figure 1). Figure 2 shows the water and sulphonic acid bands of both types of membranes. The sulphonic acid bands found for the polystyrene sulphonic acid (Zundel<sup>11</sup>) are at 1200 and 1034  $\text{cm}^{-1}$ , the antisymmetric and symmetric vibrations. The  $\nu_a$  at 1200  $\text{cm}^{-1}$  is a doublet and its splitting increases considerably with progressive drying of the membrane (1350 and 1175  $\text{cm}^{-1}$ ). The splitting is also greater the stronger the field of the cation and even greater for the transition ions. In the Nafion membrane the strong  $\text{CF}_2$  vibrations overlap part of the spectrum and part of the sulphonic bands cannot be observed. A strong band at 1060  $\text{cm}^{-1}$  is observed which is assigned to the symmetric stretching vibration of  $\text{SO}_3^-$ . In the reflectance spectrum, more or less pronounced shoulders are found with different cations at about 1300  $\text{cm}^{-1}$ . It seems quite reasonable to assign them to the high energy part of the split antisymmetric vibration of  $\text{SO}_3^-$ , although because of the high intensity of the near  $\text{CF}_2$  vibration it is difficult to locate these shoulders exactly. For the thoroughly dried polystyrene sulphonic acid (PSSA) membrane a band at 907  $\text{cm}^{-1}$  is assigned to the stretching vibration of the single bond of



group. This band is not found in any sample of the Nafion measured and this phenomenon is obviously connected with the large amounts of water present.

This part of the spectrum is much better observed in the Redcat membrane and as the water amount contained in it is small, very strong intensity of the dry sulphonic bands are observed at 1350, 1170 and 910  $\text{cm}^{-1}$  together with a weaker band at 1040  $\text{cm}^{-1}$  attributed to the hydrated sulphonic band (symmetric stretch). The band at about 530  $\text{cm}^{-1}$  contains among others, also the binding of S-O, its exact place being dependent on the cation (different mass effect of hydrogen, sodium or cobalt).

The water bands present in both membranes reflect also the fact that the Redcat membrane is much less hydrated. No band of free water is observed in the Redcat membrane. In the hydrogen form of the membranes apart from the usual water bands, bands of protonated water molecules at about 1700  $\text{cm}^{-1}$  are present. A rather strong band is observed in the Nafions at 2360  $\text{cm}^{-1}$  (in the hydrogen form as well as in all cationic forms). A very very weak band is observed in the Redcat but only in the hydrogen form. According to Zundel, this band may be caused by strong hydrogen bridges of the type



hydrogen ions are exchanged by cations in the membrane, hydrogen ions for these bridges should be made available by hydrolysis. This assignment cannot be transferred directly to the Nafion since if it is the only origin of this band, the type of cation, i.e. its extent of hydrolysis, should determine the intensity of this band. The intensity of this band is not dependent on the cation present. It is reasonable to assume that the band at ~2400  $\text{cm}^{-1}$  is caused by hydrolysis together with an overtone of the very strong  $\text{CF}_2$  vibrations (some combination of  $\nu_a$  and  $\nu_s$  found at about 1200  $\text{cm}^{-1}$ ) and thus the extent of the hydrolysis due to the various cations cannot be evaluated from it.

## DISCUSSION

The essential difference between the two membranes studied is the amount of water and the way it is released. The Nafion membrane contains about 30% water which is only released at high temperatures, while the Redcat membrane contains only 10–15% water and a major part of it is released upon drying in vacuum at room temperature. The difference in water content has its effect on the water bands as well as on the sulphonic bands and gives some information on the type of binding of the cations. As already pointed out before, the band or shoulder of free water (Table 3) exists only in the Nafion membrane. Furthermore, the  $\nu_1$  and  $\nu_3$  of the bonded water are much more strongly redshifted in the Redcat membrane than in the Nafion, indicating a stronger interaction with the water molecules in the Redcat membrane. Some further information on the binding can be obtained considering the sulphonic bands. The anti-symmetric stretching vibration of the S-O band is split completely in the PSSA, while in the Redcat this band is appreciably broadened even to the same wave numbers, but no split may be detected except when the cation is trivalent iron. The symmetric stretching at about 1050  $\text{cm}^{-1}$  is not appreciably changed by various cations in the PSSA and Nafion membranes while there is a pronounced shift in the Redcat membrane. These facts show that the cations, except iron, are essentially symmetrically bonded to the sulphonic group while in the Nafion the cations are bonded asymmetrically as in the case of PSSA. A striking difference between Nafion and Redcat is the strong band at about 2400  $\text{cm}^{-1}$  in the case of Nafion compared to the very weak one in the Redcat membrane (existing only in the hydrogen form) and the absence of the S-O band at about 900  $\text{cm}^{-1}$  in the Nafion. This must certainly be connected to the different amounts of water if hydrolysis is considered, however, such strong hydrogen bridges can only exist if the sulphonic groups are sterically near enough to allow these bridges. The absence of the S-O band at about 900  $\text{cm}^{-1}$  shows also that this group is not free but hydrogen bonded. The position of the sulphonic groups as in the Nafion, hints that clustering is here more probable than in the Redcat. The M-O vibrations which could give some answer to the question of clustering are hidden under the stronger C-F bands. In the Nafion, however, a band of medium strength is found at 870  $\text{cm}^{-1}$  when the counterion is the trivalent iron. This band may be attributed to a bridge  $\text{Fe-O-Fe}^{12}$  and does not exist in the Redcat membrane treated identically (equilibration with ferric solutions at pH lower than

**Table 3** Shifts of vibrations upon exchange of counterions

	H <sup>+</sup>	Na <sup>+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Fe <sup>3+</sup>
Nafion						
$\nu_1$ free H <sub>2</sub> O	3680	3660	3682	3680	sh	—
$\nu_1 \nu_3$ H <sub>2</sub> O	vbr <sup>a</sup>	3460	3460	3450	3380	3250
$\nu$ H <sub>3</sub> O <sup>+</sup>	1700	—	—	—	~1700	~1700
$\nu_2$ H <sub>2</sub> O	—	1620	1632	1630	1632	1640
$\nu_s$ (S-O)	1060	1062	1060	1060	1060	1055
$\nu$ (C-O-C)	980	980	980	980	980	982
	960	—	965	965	965	970
$\nu$ (M-O-M)						870
Redcat						
$\nu_1 \nu_3$ H <sub>2</sub> O	vbr	3440	3340	3340	3230	3200
$\nu$ H <sub>3</sub> O <sup>+</sup>	1700	—	—	—	~1700	~1700
$\nu_2$ H <sub>2</sub> O	1680	1635	1625	1625	1625	1625
$\nu_a$ S-O	1350	1350	1350	1350	1350	1350
	1165	1200 — 1172	1200 — 1140	1190 — 1140	1225 — 1140	1250, 1120
$\nu_s$ S-O	1060	1050	1040	1040	1032	1020
$\nu$ S-O single bone	908	910	910	910	910	905
$\nu$ (C-S) + others	602	620 + 635	615	620	620	615
$\delta$ (C-O)	520	540	540	540	545	530

<sup>a</sup> Proton tunnelling effect

one). The existence of ferric dimers in the Nafion imply some cluster formation. These will be treated in the next part of this study.

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