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Mössbauer investigations of Nafion (*) membranes

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Résumé. — Des expériences d'effet Mössbauer ont été réalisées sur des membranes Nafion neutralisées avec du chlorure de Fer. Le facteur f s'annule à une température qui dépend de la teneur en eau, ce qui montre que la rigidité de l'environnement local de l'ion est fortement influencée par la présence d'eau à l'intérieur de ces membranes. Il est possible de définir deux sites différents de Fer dont les proportions relatives varient avec la concentration en eau. L'un des deux doublets est attribué à un complexe (Fe^{2+} , H_2O) dont les paramètres hyperfins sont à peu près indépendants de la teneur en eau. Le deuxième doublet est attribué à un ion moins hydraté. Les spectres ne révèlent pas la présence d'une structure magnétique hyperfine, même à 4,2 K.

Abstract. — Mössbauer experiments have been performed on Nafion ion exchange membranes neutralized with iron chloride. The recoilless fraction falls to zero at a temperature which depends on the water content, showing that the rigidity of the local ion environment is greatly influenced by the amount of water retained in these membranes. Two different iron sites are defined, whose relative intensities vary with water content. One of the doublets is attributed to a (Fe^{2+} , H_2O) complex whose hyperfine parameters are essentially independent of the quantity of water. The second doublet is attributed to a less hydrated species. No evidence of magnetic hyperfine structure is found, even at 4.2 K.

1. Introduction. — Nafion products have been developed recently by the Du Pont Company. They are perfluorosulfonic acid membranes and are used as separators in electrochemical applications. The backbone of the polymer chains consists of perfluoroethylene units, whereas the side chains are of the form

A large amount of work has been published on their commercial applications, but little work has been done on their molecular structure. Ion clustering has been proposed by Yeo and Eisenberg [1] on the basis of small angle X-ray scattering and dynamic mechanical studies. This clustering has been confirmed by experimental [2] and theoretical [3] studies. Further

support for this model has also been provided by ^{23}Na NMR studies [4]. So far however no information has been reported concerning the environment and interactions of ions in the membrane.

The purpose of this study was to obtain information about these ionic clusters by Mössbauer spectroscopy, a technique which has already given useful results in a study of ionic clusters in styrene methacrylic-vinylpyridine terpolymers [5].

2. Experimental methods. — The acid form of the membrane with an equivalent weight (i.e. the weight of acid polymer per SO_3H group) of 1 200 has been neutralized to about 5 % by immersion of a thin foil ($\approx 300 \mu\text{m}$) in an aqueous solution of 57-ferrous chloride. The samples were dried in vacuum at room temperature and then hydrated at different humidity levels. For a given humidity level, the quantity of absorbed water is largely dependent on the state of the polymer, whether acid or neutralized. As the samples we have studied are neutralized to 5 %, it is not yet possible from the weight increase to estimate the

(*) Registered trademark of E.I. du Pont de Nemours and Co (Inc.) for its perfluorosulfonic acid products.

number of water molecules attached to the iron ions, which are the only ones observable by Mössbauer spectroscopy.

Mössbauer spectra have been recorded in a conventional transmission geometry in the constant acceleration mode. The temperature of the sample could be varied from 4.2 K up to room temperature by means of a liquid helium cryostat, the source (^{57}Co in Rh) being kept at room temperature. Mössbauer experiments have been carried out in the *Laboratoire d'Interactions Hyperfines* at the CEN-Grenoble.

3. **Results.** — Figure 1 shows Mössbauer spectra of a sample dried in vacuum at room temperature. The main features are the following :

- f , factor (i.e. the area of the absorption spectrum) decreases rapidly with increasing temperature and reaches zero at about 300 K.
- there is no evidence of magnetic hyperfine structure at low temperature,
- the mean quadrupolar splitting is of order 3.2 mm/s, which is characteristic of ferrous ion. This mean quadrupolar splitting decreases when the temperature increases,

Fig. 1. — Mössbauer spectra of Nafion sample dried in vacuum at room temperature.

— the shape of the peaks is asymmetric, and this asymmetry increases with increasing temperature. Moreover, the relative intensities of the peaks vary with increasing temperature.

This change with temperature showed us that it would not be possible to fit the experimental spectra by only one doublet. So a theoretical fit was performed using two symmetric quadrupolar doublets. These doublets will be called D I and D II in the rest of this paper. Table I gives the values of the hyperfine parameters corresponding to the spectra of figure 1.

Table I. — Mössbauer parameters corresponding to spectra in figure 1 : δ : isomeric shift (referred to metallic iron), Δ : quadrupolar splitting, Γ : full width at half-maximum, f : area of the absorption peaks.

T_K		δ mm/s	Δ mm/s	Γ mm/s	f a.u.	f_{tot} a.u.
4.2	D I	1.35	3.46	0.33	0.32	0.97
	D II	1.35	3.03	0.47	0.65	
70	D I	1.35	3.40	0.33	0.32	0.72
	D II	1.35	2.98	0.48	0.40	
140	D I	1.31	3.25	0.39	0.24	0.47
	D II	1.30	2.73	0.53	0.23	
210	D I	1.26	2.92	0.49	0.18	0.26
	D II	1.20	2.15	0.52	0.08	
270	D I	1.16	2.70	0.67	0.06	0.09
	D II	1.11	1.78	0.60	0.03	

It should be noted that a better fit was obtained by introducing a supplementary peak for temperatures greater than 70 K. This peak has an isomeric shift of about 0.3 mm/s (referred to metallic iron). At temperatures below 70 K, a slight magnetic contribution appears with a hyperfine field of about 580 kOe. No detailed investigation has yet been made of this small contribution, which could be due to paramagnetic Fe^{3+} ions. Figure 2 represents the variations of intensities and quadrupolar splittings of doublets D I and D II as a function of temperature.

We have also measured the Mössbauer spectra of the same sample rehydrated at a humidity level of 68 %. The general behaviour is similar to that of the dehydrated sample. The main differences concern the f -factor, which falls to zero at about 220 K. The quadrupolar splitting of doublet D II is slightly larger, while that of doublet D I remains practically unchanged. Moreover, the relative intensities of the two doublets are different from the former case.

Preliminary measurements on a sample soaked in water at room temperature for 24 hours show that in this case the relative intensity of doublet D I (= which has the largest quadrupolar splitting) is much larger than that of doublet D II. Table II gives the relative intensities of doublets D I and D II as a function of hydration level.

Fig. 2. — Quadrupolar splittings and relative intensities of doublets D I and D II in spectra of figure 1.

Table II. — *Relative intensities of doublets D I and D II at low temperature in function of hydration level.*

	D I %	D II %
Dried at room temperature	33	67
68 % relative humidity	40	60
Soaked in water	90	10

4. Discussion. — The fit of the experimental spectra with two quadrupolar doublets (we will ignore the small Fe^{3+} contribution mentioned above) shows the existence of two different iron sites in water-containing Nafions membranes. Bearing in mind the width of the elementary peaks, it would be possible to fit the spectra with more than two doublets. We only want to show here the general behaviour of the spectra, and we will not take into account a possible distribution of quadrupolar splittings around the mean values we have determined.

From the changes in the spectra as a function of hydration level, we see that the proportion of one of the two sites (doublet D I) increases when the water content increases, its hyperfine parameters remaining unchanged. If we suppose that there is some water left in samples dried at room temperature (this fact is confirmed by ^1H NMR measurements [6]), it seems reasonable to identify this site with a $(\text{Fe}^{2+}, \text{H}_2\text{O})$ complex, which would be formed as soon as a small quantity of water is present. Additional water molecules would then only increase the number of these complexes by hydration of other sites which did not previously contain water.

Regarding the structure of these complexes, which we are as yet unable to define precisely, we can note that the value of the quadrupolar splitting is not very different from that of frozen solutions of FeCl_2 and FeSO_4 measured by Nozik and Kaplan [7]. They showed that the dissolution of these salts in water led to the formation of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ complexes, and they studied the structural modifications of these complexes as a function of thermal treatment.

In the case of Nafion membranes, ion exchange was accomplished by immersion of the acid membrane in an iron chloride solution. Presumably the hydrated iron ions move through the membrane to neutralize the sulfonic acid groups. Further dehydration of the membrane would then progressively change and destroy these complexes. Nevertheless, the presence of sulfonic groups would certainly lead to a structure different than that proposed by Nozik and Kaplan [7].

In these terms, the second doublet D II would represent a less hydrated ferrous ion; this could explain the fact that its hyperfine parameters vary when water content is changed. If this hypothesis is correct, one would expect that the Mössbauer spectrum of a completely hydrated sample could be fitted by only one doublet, because of the similar local environment of all the iron ions (see Table II).

It will be also interesting to study the Mössbauer spectra of more dehydrated samples, in order to define the mechanism of formation of these complexes. Such studies are now in progress.

5. Conclusion. — These preliminary results of a Mössbauer study of iron-containing Nafion membranes show that :

- iron is present in Nafion in the ferrous form,
- there is no magnetic hyperfine interaction at 4.2 K for the vast majority of the iron ions. This implies that the ion-containing clusters are not saturated with iron,
- water is located inside the clusters and close to the iron ions,
- these water molecules are not randomly distributed in the clusters, but form complexes with cations with well defined structures,
- the rigidity of the ion environment is greatly influenced by the water content. This rigidity vanishes below room temperature. At that temperature the nature of the cluster changes progressively from solid to liquid.

Quantitative measurements are in progress to relate the proportions of doublets D I and D II to the amount of water molecules located around the iron ions. This will give a better understanding of the structure of the ionic clusters in function of water content, and could define more precisely the mechanism of cation and water transfer in such Nafion membranes.

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References

- [1] YEO, S. C. and EISENBERG, A., *J. Appl. Polym. Sci.* **21** (1977) 875.
 - [2] GIERKE, T. D., *Electrochemical Society Fall Meeting*, Oct. 1977, Atlanta, Georgia.
 - [3] HOPFINGER, A. J., MAURITZ, K. A. and HORA, C. J., see ref. [2].
 - [4] KOMOROSKI, R. A., MAURITZ, K. A., *J. Am. Chem. Soc.* **100** (1978) 7487.
 - [5] MEYER, C. T. and PINERI, M., *J. Polym. Sci., Polym. Phys. Ed.* **16** (1978) 569.
 - [6] DUPLESSIX, R., ESCOUBES, M., RODMACQ, B., VOLINO, F., ROCHE, E., EISENBERG, A., PINERI, M., *ACS Symposium Series, Water-Polymers Interactions* (A. Hiltner Editor).
 - [7] NOZIK, A. J. and KAPLAN, M., *J. Chem. Phys.* **47** (1967) 2960.
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