Clustering of ions in cation exchange membranes: a Mössbauer study

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(Received 22 August 1979; revised 26 November 1979)

A low temperature Mössbauer study of a series of membranes has been made to determine the distribution of ions in them. The presence of three types of iron species has been observed: (1) small units (A) or monomeric species with $d < 30$ Å; (2) ferric dimers (B) bridged by oxygen or hydroxyl ions; (3) clusters (C) of variable sizes. The percentages of the various species as well as the average size of clusters were evaluated from these spectra.

INTRODUCTION

In a previous study[1] infra-red measurements were used to obtain some information about ion binding in cation exchange membranes containing the sulphonic group as the functional group. Although this study gave some information on the particular strength of interaction of the cations studied and their position relative to the sulphonic group, no information about clustering could be drawn from it. Cluster formation in some of these membranes is already indicated in previous studies[2-4], however, more details about the size of clusters and the relative distribution of the ions in them is needed. The knowledge of these structural properties could enable a better understanding of the transport properties of these membranes. It was assumed that the Mössbauer effect could provide the necessary information about the ionic distribution in the membrane. For this study the hydrogen ions of the membrane were replaced by tervalent iron ions. Similar measurements have been carried out on vinylpyridine copolymers, crosslinked by ferric chloride[5]. In this system iron is strongly coordinated by the nitrogen atom while in the present case only electrostatic interaction should be considered between the sulphonic group and the iron ion.

EXPERIMENTAL

The following ion exchange membranes were studied: (a) Nafion (110, 125 and 152)-perfluorosulphonic acid (provided by courtesy of the Plastic Department, Dupont & Co.) of ion exchange capacity of 0.6–1.0 mequiv./g; (b) Redcat-poly(ethylene sulphonic acid) prepared by the Research and Development Authority of the Ben-Gurion University, Beer-Sheba of 0.94 mequiv./g ion exchange capacity; (c) SPS-sulphonated polysulphone was obtained by sulphonation of polysulphone (P-1700, Union Carbide) with chlorosulphonic acid. Films were casted from a 20% polymer solution in dimethylformamide. These membranes were provided by courtesy of the Plastics Department of the Weizman Institute of Science, Rehovot.

All these membranes in hydrogen form (30–200 μm thick) were equilibrated with aqueous or methanol solutions of ferric chloride and adjusted to pH = 1 with a few drops of hydrochloric acid in order to avoid the obtention of hydrolysed iron species. After a period of 24 hours the membranes were taken out of the solutions and quickly washed in a stream of water or methanol respectively. Most of the membranes thus prepared were vacuum dried over P_2O_5 for 24–72 h while some of the membranes were only air-dried i.e. blotted between two pieces of filter paper and kept in well stoppered bottles.

The Mössbauer spectra were measured using a constant acceleration conventional Mössbauer spectrometer, operated in connection with a 256 channel analyser in the time scale mode. The source was kept at room temperature and consisted of 100 mC of ^{57}Co diffused in a rhodium foil. A Harwell proportional counter, running at about 10^5 units per second, was used. The spectra at 4.1 K were recorded by keeping the sample immersed in liquid helium. Temperatures between 1.5 K and 4.1 K were achieved by pumping on the liquid helium. Refrigeration below 1.5 K was attained using a ^{3}He/^{4}He dilution refrigerator[6]. The spectrometer was calibrated against a metallic iron foil (all isomer shifts are given relative to metallic iron).

All spectra were analysed by least-squares computer fits.

RESULTS

Mössbauer spectra were obtained for membrane samples equilibrated with ferric chloride from aqueous and methanol solutions. One sample (Nafion 110 equilibrated in methanol solution) was measured at various temperatures between 0.05K and 85K[7] the other samples were measured at temperatures between 1.5 and 85K. At 85K all the spectra are composed predominantly of two doublets A and B. Doublet A has an isomer shift of $\delta_1 = 0.49 \pm 0.02$

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mm s^{-1} in all samples, and a quadrupole splitting of $\Delta E_1 = 0.45 \pm 0.02$ mm s^{-1} in the Nafion membranes and of $\Delta E_1 = 0.60 \pm 0.03$ mm s^{-1} in the Redcat and SPS samples. Doublet B has an isomer shift of $\delta_2 = 0.58 \pm 0.01$ mm s^{-1} and a quadrupole splitting of 1.68 ± 0.01 mm s^{-1}. In some of the spectra at 85 K, a weak sextuplet, corresponding to a magnetically split spectrum (subspectrum C) could also be discerned. At lower temperatures subspectrum C appears in all samples and its relative intensity grows as the temperature is lowered on account of doublet A, whose relative intensity decreases. Subspectrum C is composed of six broadened and asymmetric lines. These sextuplets have been computer analysed assuming an asymmetric Lorentzian distribution of hyperfine fields given by $N(H) = N_0/\{1 + [(H - H_0)/\Delta H]^2\}$ with ΔH different for $H > H_0$ and $H < H_0$[8,9]. The value of H_0 was found to be 560 ± 20 kOe in all samples. The quadrupole interaction was found to be negligible in these subspectra. The relative intensity and parameters of doublet B do not change with temperature and are characteristic of dimeric iron species[10].

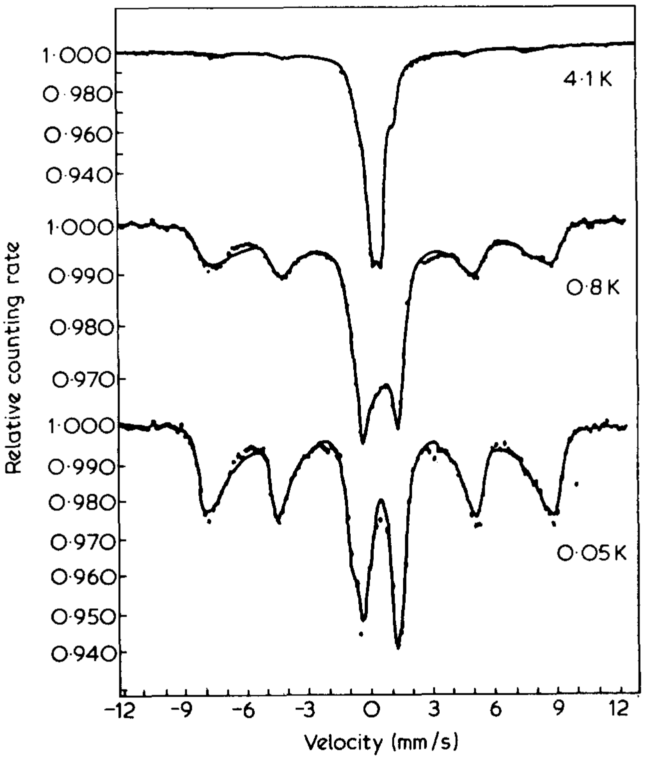

Figure 1 Mössbauer spectra of iron in Nafion equilibrated in methanol solution

Figure 1 shows the spectra obtained at various temperatures in Nafion 110 equilibrated with iron chloride from methanol solution. Each spectrum is composed of subspectra A. B and C. The form of subspectrum C and the temperature dependence of the relative intensities of spectra A and C correspond to clusters with non-uniform sizes containing amorphous iron[8]. At each temperature clusters smaller than a certain critical size show a magnetically unsplit spectrum (A) while clusters above this size give a magnetically split spectrum (C). Using the formula derived by Neel[9], $f = f_0 \exp(-CV/kT)$, for the rate at which the magnetization changes direction, (where V is the volume of the clusters and f_0 and C are constants characteristic for the material) the maximum diameter of the particles which still give unsplit spectra at any temperature can be estimated. Thus, for example, using for the constants f_0 and C the values obtained by Kundig *et al.*[8] for Fe_2O_3, we find that doublet A at 4.1K corresponds to clusters smaller than 30 A in diameter, which may contain also monomeric iron species. Using the constants derived by Coey *et al.*[11], the values obtained for the diameters of the clusters are about 10% smaller.

Table 1 shows the relative intensities of the three subspectra at 4.1K. Spectra A correspond to iron species with diameters smaller than 30 Å, spectra C to clusters with diameters larger than 30 Å, and spectra B to dimeric iron species[10].

A more detailed distribution of the cluster sizes can be obtained from the temperature dependence of the relative intensities of subspectra A and C. Thus *Figure* 2 shows the distribution in cluster sizes in the Nafion 110 sample equilibrated from methanol solution. As can be seen, most

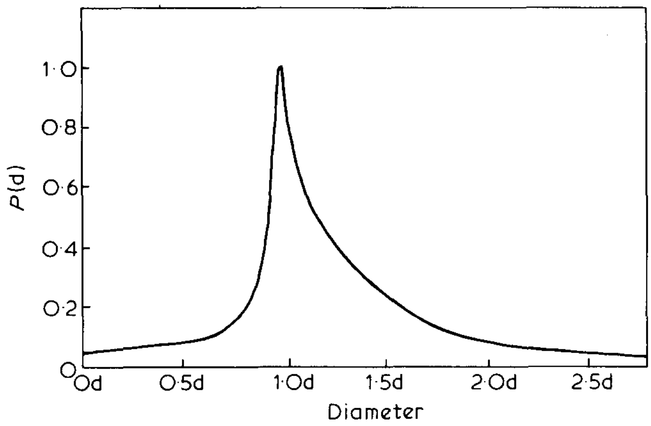

Figure 2 Distribution of cluster diameters in Nafion equilibrated in methanol solution

Table 1 Ion distribution in membranes at 4.1 K

Sample	Capacity (meq/g)	%A (small units)	%B (dimers)	%C (clusters)	%C/ A + C[a]	Mean diam. size d_0 (Å)
Nafion 110(H_2O)	0.91	10	66	24	71	40(41.4)[b]
Nafion 125(H_2O)	0.83	26	16	59	70	40(37.1)
Nafion 152(H_2O)	0.66	27	45	28	51	30(30)
Nafion 110 (methanol)	0.91	67	14	19	22	20
Redcat (air dried)	0.94	54	12	34	38	28
Redcat (vacuum dried)	0.94	71.5	1.5	27	28	25
SPS	1.2	28	36	35	55	34

[a] Percentage of clusters (d >30 Å)

[b] Values in parentheses are those given by Gierke[3]

of the clusters have a diameter of ~20 Å in this sample. In Nafion 152 equilibrated from water it was found that 20% of the clusters had a diameter between 90 and 120 Å, 30% had a diameter between 30 and 90 Å, and about 50% were smaller than 30 Å. The mean diameters d_0 in the various samples are also given in *Table* 1. (50% of the clusters in each sample are larger than d_0 and 50% are smaller than d_0.)

DISCUSSION

As can be seen from *Table* 1, the percentage of clusters with diameter larger than 30 Å (as calculated from total iron except the dimeric species $-C/A+C$ depends on the type of membrane and for the Nafion samples (equilibrated from aqueous solutions), the percentage of clusters increases with increasing ion exchange capacity. The mean diameter of the clusters vary between 20 and 40 Å in the various membranes studied. The smaller clusters are obtained in membrane samples equilibrated from methanol solutions. The differences in sizes of clusters between the samples equilibrated in the two media are probaly due to (a) the much higher swelling of the membrane in methanol[12] which apparently diminishes the possibility of clustering of more ionic groups, and (b) the methanol is less polar and tends to align the polymer chains and thus also decreases the ion clustering tendency.

From *Table* 1 it may also be seen that the amount of dimeric iron species varies appreciably in the various membranes. The concentration of these dimeric species (ferric ion bridged by two hydroxyl or oxygen ions)[13] which is formed by hydrolysis is apparently dependent on the equilibrating solution and drying procedure. Smaller amounts of such dimeric iron species are formed in methanol solutions (less water containing) and when the samples are quickly dried.

The quadrupole splittings obtained for the iron species (spectrum A) are in general consistent with an octahedral iron site (coordinated by six oxygens)[13]. These parameters are, however, essentially lower for Nafion samples (~0.45 mm s^{-1}) than for the Redcat and SPS samples (~0.60 mm s^{-1}) showing a more symmetric environment for the iron in the Nafion samples than in the other membranes. Infrared measurements[1,14] have already shown that while in Nafion membranes the iron is symmetrically bound to the sulphonic group, an asymmetric binding should be considered for the Redcat and SPS membranes[1,14].

Sibashinsky and Tanny[15] have made small angle X-ray scattering measurements on SPS membranes. A small angle peak $2^0 < 2\theta < 3^0$ was observed for samples of SPS in Cs^+, Ca^{2+} and Fe^{3+} form for exchange capacities higher than 0.3 mequiv./g. (No peak is observed for samples in hydrogen form.) The low angle peak shows that in these samples heterogeneities on the colloidal levels exist and thus confirm the presence of clusters. When the capacity of these membranes is higher (< 1 mequiv./g) an additional peak is formed at $2\theta \simeq 1.2^0$. Using a corrected form of the Bragg formula, these authors estimated two kinds of average spacings between the scattering clusters, one of 30–40 Å which corresponds to the distances between the small units and another one at about 70 Å which can be taken as the inter cluster distance. These results are quite consistent with the present Mössbauer measurements. The fact that the small angle peak is the same for the cations, of different charges shows that the structure already existing in the polymer matrix cannot be changed by introduction of a cation of different change.

Gierke[3] has recently developed a phenomenological model for the clustering in Nafion membranes which is consistent with experimental observations such as hydroxyl rejection and current efficiency performance in chlor-alkali cell operation. The average sizes of clusters were estimated from small angle X-ray scattering and water uptake measurements. The sizes of clusters evaluated from Mössbauer measurements are in very good agreement with those evaluated by Gierke[3] (*Table* 1).

The Mössbauer measurements, however, supply additional information concerning all the species present and the percentages of them. The model forwarded by Gierke is consistent with the present measurements if it is assumed that the smaller units (dimeric or monomeric species) are bridging or channelling between the clusters and thus explain the ion transport through the membrane.

ACKNOWLEDGEMENT

The author is indebted to Mrs. Noemi Sibashinsky for her active cooperation during this work.

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