Dynamics of hydrated iron(II) cations in nafion polymer membranes

E. R. Bauminger, I. Nowik and S. Ofer*
Racah Institute of Physics, The Hebrew University of Jerusalem, 91904, Israel

and C. Heitner-Wirguin
Department of Inorganic & Analytical Chemistry, The Hebrew University of Jerusalem, 91904, Israel

Mössbauer studies of Fe^{2+} in water-soaked nafion polymer membranes in the temperature range between 90 K and 250 K have been performed. Above a critical temperature (~ 180 K) the spectra exhibit both elastic narrow absorption lines and quasielastic broad lines. These spectra are typical of bounded diffusion phenomena observed by Mössbauer spectroscopy in macromolecular systems like haemoglobin, myoglobin and ferritin. Similar spectral shapes have been observed by quasielastic neutron scattering from water in nafion membranes. Within 50 K above the critical temperature the total Mössbauer absorption area decreases by an order of magnitude whereas the narrow absorption line decreases by two orders of magnitude. The results are interpreted in terms of bounded diffusive motion of the iron. Using a model based on overdamped harmonically bound Brownian motion, the essential parameters of the iron motion can be derived as a function of temperature. The iron motion most probably reflects the motion of a large Fe^{2+} complex, e.g. $Fe(H_2O)_6^{2+}$, which is attached to the polymer side chains via the sulphonic group.

(Keywords: nafion; Mössbauer spectroscopy; iron; bounded diffusion; glass transition)

INTRODUCTION

The properties of nafion membranes have been studied by a wide variety of spectroscopic techniques: ^1H and ^{19}F n.m.r., ^{57}Fe and ^{151}Eu Mössbauer spectroscopy[3-5], inelastic neutron scattering[6], EXAFS[7] and electron microprobe studies[8]. All these studies dealt with the location and dynamics of the water and various ions in the nafion membrane. It is evident from all the studies that the absorbed water behaves differently than water in frozen aqueous solutions, undergoing a glass transition (T_g) at temperatures between 180 and 220 K, depending on the exchanged ions present. The neutron scattering studies indicate that the water is trapped in cages, 10 Å in diameter[6].

The dynamic properties of the lattice in which the iron atoms are bound can be studied by the Mössbauer effect through the recoilless fraction, the f-factor, which is proportional to the area of the absorption spectrum. Recently, Mössbauer spectra of a particular shape, composed of elastic narrow absorption lines and quasielastic broad absorption lines, have been observed for iron in several biological systems[9,10]. These spectra were attributed to bounded diffusion phenomena, characterizing a special phase of matter, which is neither solid nor liquid. Mössbauer studies performed previously in nafion over a wide temperature range, showed a sharp decrease of the f-factor above 180 K, consistent with ^1H n.m.r. studies[1], which showed the onset of general motions above this temperature. In the present study detailed

Mössbauer studies at temperatures above T_g were performed, with the intention of learning more about the dynamics of the Fe nuclei in these polymers. Since the iron is trapped in the membrane, it was hoped to observe bounded diffusion phenomena similar to those found in biological systems. Indeed spectra composed of both narrow and broad lines were observed. The results are interpreted in terms of several kinds of thermal fluctuations that occur above T_g – a fast fluctuation associated with the steep temperature dependence of the recoilless fraction and a slower fluctuation associated with bounded diffusive motion and the appearance of a broad component in the Mössbauer spectrum.

Ferric and ferrous ions can exchange with the hydrogen ion of the sulphonic acid group in the nafion membranes. Ferric iron is found in three different environments inside the nafion[4,5]: (1) Fe^{3+} ions far from each other (> 12 Å); (2) Fe^{2+} dimers and (3) small clusters of Fe^{3+} ions. Mössbauer studies of ferrous iron in nafion with 6% or more of water, show that all Fe^{2+} ions are in equivalent sites. The present studies were performed therefore on Fe^{2+} exchanged nafions. The Mössbauer parameters of the ferrous iron in nafion are very similar to those of ferrous iron in aqueous solution[3,4]. EXAFS results also suggest that the water molecules are strongly coordinated to the ferrous ion in octahedral coordination – indistinguishable from Fe^{2+} in aqueous solution[7]. These measurements suggest therefore that the chemical iron species in the hydrated samples are $Fe(H_2O)_6^{2+}$. The ionic phase is different from a simple ionic solution due to the interaction between the ions and the sulphonic terminated side chains of the polymer. The dynamics of

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the iron ion in the membrane probably reflect therefore the dynamics of the $Fe(H_2O)_6^{2+}$ complex attached to the polymer side chains.

EXPERIMENTAL

Nafion 125–perfluorosulphonic acid (provided by courtesy of the Plastics Department, Dupont & Co.) was equilibrated with aqueous solutions of ferrous chloride (^{57}Fe) and adjusted to pH = 1 with a few drops of HCl to avoid formation of the hydrolysed iron species and oxidation to the tervalent iron. After 24 h, the membrane was quickly washed and vacuum dried over P_2O_5 for 24–72 h. The membrane was transferred into lucite cells which were placed in a cryostat in which specified temperatures could be maintained in the range between 90 and 320 K. A conventional Mössbauer apparatus, with a 100 mCi Co^{57} (Rh) source was used.

RESULTS AND DISCUSSION

Two typical absorption spectra in nafion membranes equilibrated with aqueous solutions of ferrous chloride are shown in *Figure 1*. The spectrum at 150 K, similar to all spectra below 180 K (T_c), is a normal Mössbauer spectrum typical for Fe^{2+} in a solid environment. This spectrum consists of a hyperfine doublet with relatively sharp lines, corresponding to the 'elastic' or recoilless absorption which is the essential and familiar characteristic of the Mössbauer effect in solids.

Above T_c, the spectral shape changes dramatically. The spectrum obtained at 210 K shown in *Figure 1*, is characteristic for all spectra obtained above $T_c = 180$ K. In these spectra, in addition to a relatively narrow part showing a similar structure to that at lower temperature, there is a very broad line with wings extending to velocities of ± 15 mm s^{-1}. The wide component can be fitted quite well to a Lorentzian shape with temperature
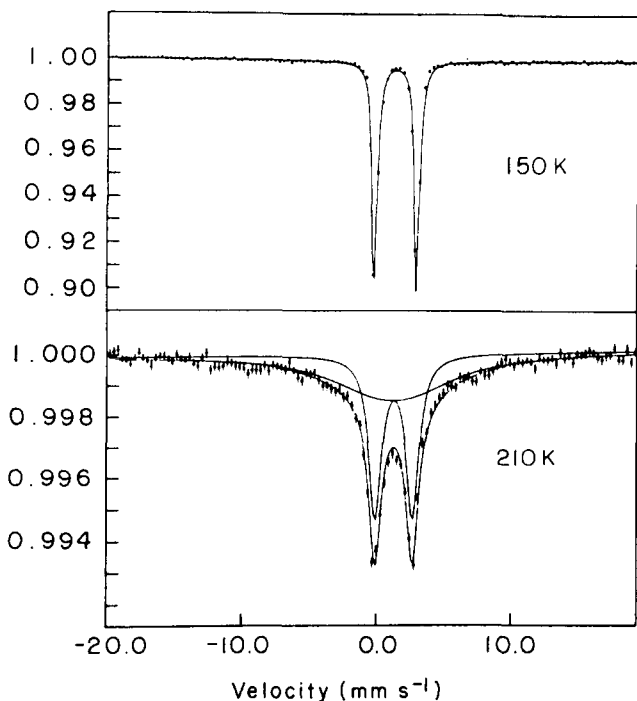

Figure 1 Mössbauer spectra of the 14.4 keV transition of ^{57}Fe in nafion polymer membranes
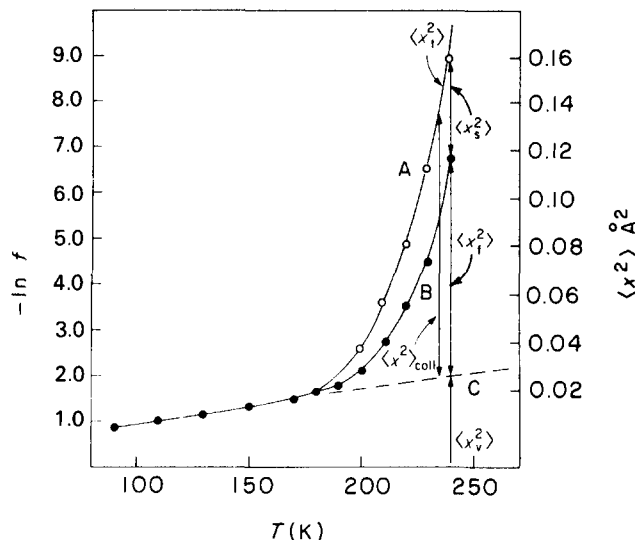

Figure 2 Temperature dependence of the spectral area of the total Mössbauer spectrum (full circles), and of the narrow absorption line (open circles). The recoil-free fraction f is proportional to the spectral area and $\langle x^2 \rangle$ is proportional to $\ln f$ (see text). The various contributions to $\langle x_t^2 \rangle$ are indicated. The values of $\langle x^2 \rangle$ are given on the right hand scale

dependent linewidth. The decomposition into the narrow and wide components is shown in *Figure 1*.

The spectra above T_c, that show both 'elastic' narrow lines and 'quasi-elastic' wide lines of comparable intensity must be ascribed to the dynamics of the iron ions in the membrane. The spectra obtained above T_c are characteristic of Mössbauer absorption in atoms diffusing within a cage[11] or participating in overdamped, harmonically bound Brownian motion[9,10,12].

Figure 2 shows the temperature dependence of $-\ln f$, where f is the recoilless fraction, which is proportional to the area under the Mössbauer spectrum. The curve is normalized to give $f = 1$ at 0 K. Curve (A) in *Figure 2* is derived from the area of the narrow doublet, while curve (B) is derived from the area of the total spectrum. Below 180 K only the solid-like narrow spectrum is observed. The change of the f factor with temperature between 90 K and 180 K points to a Debye temperature of about 130 K, in agreement with previous measurements reported by Rodmacq *et al.*[4]. At $T_c = 180$ K, together with the appearance of the quasielastic broad line, there is a sharp change in the temperature dependence of the recoil-free fraction. Both the area of the narrow component and the total area under the resonance absorption spectrum decrease rapidly with increasing temperature. The observed spectral shapes are interpreted as arising from a relatively slow bounded diffusive motion of the iron ion, with characteristic times of 10^{-8} s. Additional fast fluctuations, of characteristic times $\tau \ll \tau_N$ – the nuclear excited state lifetime ($\tau_N = 1.4 \times 10^{-7}$ s for Fe^{57}) – are reponsible for the fast decrease of the total area under the absorption curve. In the harmonic approximation, the recoilless fraction f is simply related to the mean square displacement (msd) $\langle x^2 \rangle$ of the Mössbauer nucleus in the direction of the γ-rays by $\langle x^2 \rangle = -\lambda^2 \ln f$, where λ is the reduced wavelength of the γ-ray (0.137 Å). This relationship can be used to calculate the partial msds, corresponding to the slow and fast fluctuations, from the measured f values.

In *Figure 3* the temperature dependence of the quadrupole splitting ($\frac{1}{2}eqQ$), of the isomer shift (δ) and of
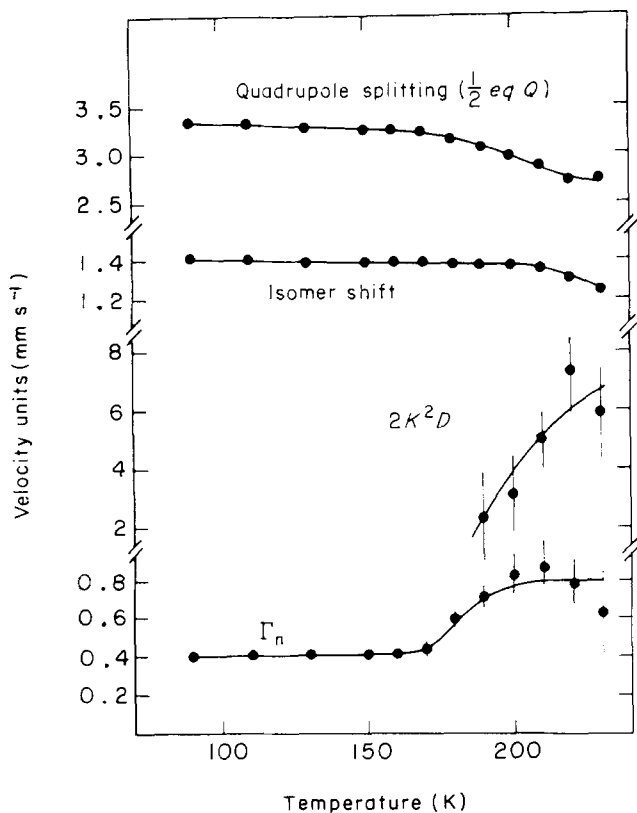
Figure 3 Temperature dependence of the various parameters obtained in the analysis of the Mössbauer spectra. The quadrupole splitting, the isomer shift and the widths of the wide and narrow lines ($\Gamma_w = \Gamma + 2k^2D$)

the widths of the narrow and broad lines of the ^{57}Fe Mössbauer spectra in the nafion membranes are shown. The Mössbauer parameters found at 90 K are almost identical to those obtained in ferrous aqueous solutions. ($\delta = 1.43$ mm s^{-1} relative to metallic iron and $eqQ/2 = 3.33$ mm s^{-1}). This indicates that the immediate environment of the Fe^{2+} ion is the same in both media, forming a Fe(H$_2$O)$_6^{2+}$ complex[4]. Neutron diffraction measurements on water in nafion membranes indicate that the water occupies isolated pockets of up to 10 Å in diameter[6]. Each such volume can contain only one Fe^{2+} complex[7]. In the analysis of the neutron diffraction measurement the water molecules were assumed to diffuse freely within a restricted volume. The Fe(H$_2$O)$_6^{2+}$ complex is of dimensions comparable in size to the dimensions of the water pocket in which it is located and is attached to the side chains of the polymer[4]. Therefore, it is preferable to treat the present results of the motion of the iron ions within a model in which the particles are taking part in overdamped, harmonically bound Brownian motion[9,10,12]. Within this approach, the shape of the Mössbauer spectrum is analysed in terms of a sum of Lorentzian lines from which two parameters are derived: one parameter is $\langle x_s^2 \rangle$, the *msd* from equilibrium due to the bounded slow diffusive motion; the other is α, which is the ratio between the harmonic and damping force constants and is also equal to the average relaxation rate of the Fe^{2+} deviation from its equilibrium position ($x_s = x_0 \exp(-\alpha t)$). D, the diffusion constant, is given in this case by $\alpha \langle x_s^2 \rangle$. The experimental results also yield the total spectral area and its temperature dependence. This yields, within the harmonic approximation, through $\langle x^2 \rangle = -\lambda^2 \ln f$, the mean square deviation of the fast fluctuations, which are reponsible for the loss in the

spectral area. This $\langle x^2 \rangle$ contains $\langle x_v^2 \rangle$, the *msd* of the vibrational local motion of the Fe nuclei, present also below T_c in the frozen complex, and $\langle x_f^2 \rangle$, the *msd* of the fast collective motions of the complex. $\langle x_f^2 \rangle$ corresponds to α values, very large compared with Γ, where $\Gamma = 1/\tau_N$. The total *msd*, $\langle x_t^2 \rangle$, is thus given by $\langle x_t^2 \rangle = \langle x_s^2 \rangle + \langle x_f^2 \rangle + \langle x_v^2 \rangle$. $\langle x_t^2 \rangle$ can also be derived from the area of the narrow component of the absorption spectrum. The recoil-free fraction obtained from the area of the narrow component is given by $f_n = \exp(-k^2 \langle x_t^2 \rangle) = \exp[-k^2(\langle x_s^2 \rangle + \langle x_f^2 \rangle + \langle x_v^2 \rangle)]$ [9].

The values of $\langle x^2 \rangle$ below the critical temperature T_c are associated with the local thermal vibrations of the individual iron ions relative to their neighbours, $\langle x_v^2 \rangle$ defined above. In *Figures 2* and *4*, the total mean square displacements $\langle x_t^2 \rangle$ of the iron ions above T_c (derived from the areas of the narrow subspectra) are resolved into three components, associated with the different modes of thermal motions: $\langle x_v^2 \rangle$ is obtained from the linear extrapolation of $-\ln f(T)$ from lower temperatures (curve C in *Figure 2*). The difference between $\langle x_t^2 \rangle$ and $\langle x_v^2 \rangle$ gives the mean square collective displacements $\langle x^2 \rangle_{coll}$, associated with large scale motions of the iron ion together with its surroundings. This may be the Fe(H$_2$O)$_6^{2+}$ complex and probably reflects the motion of even a larger unit, taking into account that the Fe^{2+} complex is attached to the acid terminated side chains of the polymer. $\langle x^2 \rangle_{coll}$ is resolved into its two parts $\langle x_s^2 \rangle$ and $\langle x_f^2 \rangle$. The values of $\langle x_s^2 \rangle$, which correspond to slow collective motions responsible for the existence of the broad lines, are obtained from the differences between the values of $\langle x^2 \rangle$ in curves (A) and (B) of *Figure 2*. $\langle x_f^2 \rangle$, responsible for the loss of the spectral area, is obtained from the differences between $\langle x^2 \rangle_{coll}$ and $\langle x_s^2 \rangle$. The values of $\langle x_f^2 \rangle$ are thus given by the differences between the corresponding values of $\langle x^2 \rangle$ of curves (B) and (C) in *Figure 2*. The values obtained for $\langle x^2 \rangle_{coll}, \langle x_s^2 \rangle$ and $\langle x_f^2 \rangle$ are shown in *Figure 4*.

The values of α and $\langle x_s^2 \rangle$ obtained experimentally, yield the diffusion constant D ($D = \alpha \langle x_s^2 \rangle$). D can also be obtained approximately from the width Γ_w of the wide line in the spectrum. ($\Gamma_w = \Gamma + 2k^2D$, where k is the wave vector of the γ-ray). The temperature dependence of the diffusion constant D is shown in *Figure 3*. At 210 K, α has the value 1.9×10^8 s^{-1} and $D = 3.4 \times 10^{-10}$ cm^2 s^{-1}.
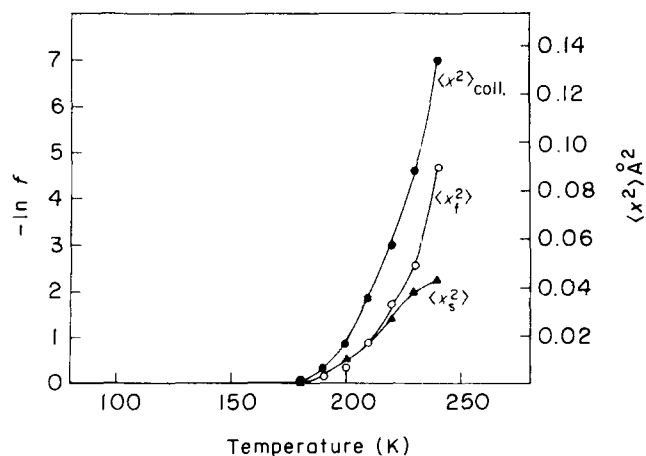

Figure 4 Temperature dependence of the mean square deviations of the collective motions of the ferrous iron complex in water equilibrated nafion membranes.

As shown in *Figure 3*, the narrow line also broadens above 180 K. This phenomena has been interpreted in other cases as being due to slow diffusive motions. However, if many modes of motion for the iron ion are assumed, then the general motion is described in terms of many $\langle x^2 \rangle$ and α values. The low values of $\alpha(\alpha \sim \Gamma)$ contribute to the broadening of the narrow line[13]. The widths of both the broad and narrow lines are proportional to an average of $\langle x^2 \rangle$ where the broad line correspond to an average over α values in the range $\Gamma \ll \alpha < 100\Gamma$ whereas the width of the narrow line corresponds to values $\alpha \sim \Gamma$, and the lost area corresponds to $\alpha \gg \Gamma$ and $\langle x_f^2 \rangle$. It is clear that the width of both lines should increase with temperature, due to the increase in the mean square displacements.

CONCLUSIONS

The major conclusion of the present study is that, although at low temperatures the Mössbauer spectra of iron in a water equilibrated nafion membrane are identical to those in a frozen aqueous solution, the dynamics in the two cases at higher temperatures are completely different. At 180 K there is an onset of bounded diffusional motion of the iron ions together with a marked softening of the membrane associated with large *msds*. The phase transition which takes place at 180 K is believed to be connected with the glass transition in the ionic phase. The glass transition temperature T_g is very different from that observed in a free aqueous solution, probably due to the bonding of the iron complexes to the polymer side chains. Bounded diffusion phenomena observed in the membrane above T_g, are not observed in free aqueous solutions. The bounded diffusion leads to the appearance of an inelastic line in the Mössbauer spectra. Although spectra characteristic for bounded diffusion have been anticipated by Litterst *et al.*[14] for polymers based on vinyl ferrocene, nafion is the first polymer where these spectra have actually been observed. The phase transition at 180 K has been previously observed in nafion–Eu^{3+} by Boyle *et al.*[3] and in nafion–Fe^{2+} and nafion–Fe^{3+} by Rodmacq *et al.*[4]. The observed spectra indicate that the iron is bound to some parts of the polymer, most probably to the sulphonic groups and water molecules and the movements of the iron ions are associated with movements of larger parts of the polymer. The similarity of the Mössbauer spectra in various proteins and in nafion suggests that the occurrence of bounded diffusion is a universal feature of macromolecules.

The temperature dependent changes are closely connected with the state of water in the membrane. This is consistent with ^1H n.m.r. measurements, which show the onset of general motions in the aqueous phase at 182 K. Measurements of methanol equilibrated membranes are now under way.

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