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Ferric Hydrolysis in Water: an Iron-57 Mössbauer Study using Iron-exchanged Nafion

ADRIAN MEAGHER

Laboratory of Applied Physics II, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark

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Abstract

^{57}Fe Mössbauer spectroscopy has been used to study ferric iron exchanged into a cation exchange membrane (Nafion) – a model system for concentrated aqueous solutions. For membranes exchanged from 0.2 M solutions two quadrupole doublets are observed and associated with a μ-oxo bridged ferric dimer (quadrupole splitting, $QS \approx 1.6$ mm s^{-1}) and hydrogen oxide $H_3O_2^-$ bridged aquo Fe^{3+} species ($QS \approx 0.4$ mm s^{-1}). It is proposed that the equilibrium constants of Ropars *et al.* are preferable to those of Hedström for use with low ionic strength ferric solutions. The mono- and di-hydroxo bridges of Ropars *et al.* should, however, be reinterpreted as (mono-) hydrogen oxide- and oxo bridges respectively. It is shown that the μ-oxo dimer is preferred at higher temperatures. For membranes exchanged from 0.02 M solutions (higher pH) an iron hydroxide precipitate can coexist with the other two species.

Introduction

We have, in previous work [1,2], applied the technique of ^{57}Fe Mössbauer spectroscopy to the study of ferric ions contained in the aqueous pores of Nafion (registered trademark of E.I. duPont de Nemours and Company for its perfluorosulfonic acid membrane materials) ion exchange membranes. It became apparent that the polymer matrix had essentially no influence on the cations present in the aqueous phase – these cations and the pore water form a 'single ion solution', to use the terminology of Gupta *et al.* [3]. Nafion offers some advantages over ordinary aqueous solutions for the purposes of Mössbauer (and other spectroscopic) studies:

(i) being macroscopically solid it is easy to handle.

(ii) Mössbauer spectroscopy requires solid samples. Freezing of an aqueous solution can lead to phase segregation and/or precipitation of the hydrated salt. These problems are largely avoided with Nafion.

Here we wish to present results pertaining to the hydrolysis of ferric iron in Nafion. The results, besides being of relevance for aqueous solutions at high iron concentrations, also provide guidance for the interpretation of literature results for ferric ions contained in the interlayer water of montmorillonites.

The hydrolysis of ferric iron in aqueous solution has been extensively studied. The chemical literature (see for example refs. 4, 5) generally accepts the equilibrium constants determined potentiometrically by Hedström [6] for ionic strength 3. These are

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K = 10^{-3.05}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+ \qquad K = 10^{-6.31}$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad K = 10^{-2.91}$$

The dimer may be formulated either as μ-oxo or di-μ-hydroxo bridged. Knudsen *et al.* [7] used Mössbauer spectroscopy to demonstrate that the dimer is oxo bridged. We have previously confirmed this using combined Mössbauer/EXAFS measurements [2]. Greenwood and Earnshaw [5] mistakenly favour the dihydroxo bridged formulation, based on the EXAFS results of Morrison *et al.* [8]. Those results, however, were later criticized by Magini *et al.* [9] and retracted [10].

For interpreting our results we will make use of the concept of the hydrogen oxide ($H_3O_2^-$) bridging ligand. This ligand has been identified by Bino and Gibson in a variety of crystalline complexes [11–13]. Those authors proposed that it could be a general phenomenon in aqueous solutions of many metal ions [12]. Subsequently, vapour tensiometry [14] and Mössbauer spectroscopy [15] experiments provided indirect evidence for $H_3O_2^-$ bridge formation in aqueous solutions of $Cr(bpy)_2$ and Fe EHGS complexes. Differential anomalous X-ray scattering was used to demonstrate the existence of the hydrogen oxide bridge in significant concentration in aqueous solutions of W_3 clusters [16].

Experimental

Nafion 115 was obtained from E.I. duPont de Nemours and Company. The membrane has an

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equivalent weight of 1100 g mol^{-1} SO_3H and a thickness of 127 μm (5 mil). The material as supplied contains a small amount of iron [17], negligible for Mössbauer purposes.

Ferric-exchanged Nafion was obtained by immersing 700 mg of the material for 12 h in 200 ml of freshly prepared 0.2 M or 0.02 M ferric solution. These solutions were prepared by dissolving weighed amounts of reagent grade $FeCl_3$, $Fe(NO_3)_3 \cdot 6H_2O$ and $Fe(ClO_4)_3 \cdot 9H_2O$ in deionized water.

Mössbauer spectra were recorded in transmission geometry in constant acceleration mode. The maximal velocity was around 3 mm s^{-1}. The source, ^{57}Co in Rh, was at room temperature. The sample temperature was 100 or 80 K. At these temperatures for the samples presented here there is essentially no observable signal from the unhydrolyzed Fe^{3+} since it displays paramagnetic hyperfine splitting with very broad lines [1]. There is usually no Mössbauer absorption at room temperature for ions in Nafion because the aqueous phase in which they are located is not solid. Mössbauer spectra were least-squares fitted to Lorentzian peaks. Isomer shifts are quoted relative to metallic iron at room temperature.

Results and Discussion

Influence of Cooling Rate

Figure 1 shows the spectra obtained at 100 K for a Nafion exchanged from a 0.2 M $FeCl_3$ solution. Very similar spectra are obtained for the other iron salts. The top spectrum is for a sample cooled (5 K min^{-1}) to low temperature whereas the bottom spectrum represents a sample quenched in liquid nitrogen ($\geqslant 10^3$ K min^{-1}). Both spectra contain the same two doublets, D1 ($IS = 0.47$ mm s^{-1}, $QS = 0.43$ mm s^{-1}) and D2 ($IS = 0.56$ mm s^{-1}, $QS = 1.67$ mm s^{-1}), but in different proportions, 54% D2 in the quenched sample compared with 42% D2 in the cooled sample.

D2 has been observed previously both in ion exchange resins [1, 2, 18–20] and in frozen aqueous solutions [7, 21–23]. It may be identified with a μ-oxo bridged ferric dimer [7, 2].

Allowing for a range of observed quadrupole splittings (0.37–0.45 mm s^{-1}, say), D1 has also been observed in ion exchange resins [1, 2, 18–20] and concentrated frozen aqueous solutions [7, 22–25] where it has been identified with a range of chemical species. We wish here to propose a novel identification for D1, which is that it is due to aquo Fe^{3+} ions bridged to some extent by $H_3O_2^-$ (hydrogen oxide) ligands. We point out that the quadrupole splitting of D1 (≈ 0.4 mm s^{-1}) is larger than that expected for $Fe(H_2O)_6^{3+}$, (< 0.1 mm s^{-1} [26]) but agrees quite well with that obtained using a very simple point charge calculation for the hydrogen oxide bridged system, where we assume that the major contribution to the electric field gradient at the iron comes from a $-\frac{1}{2}$ e charge located on the oxygen in the $H_3O_2^-$ bridge.

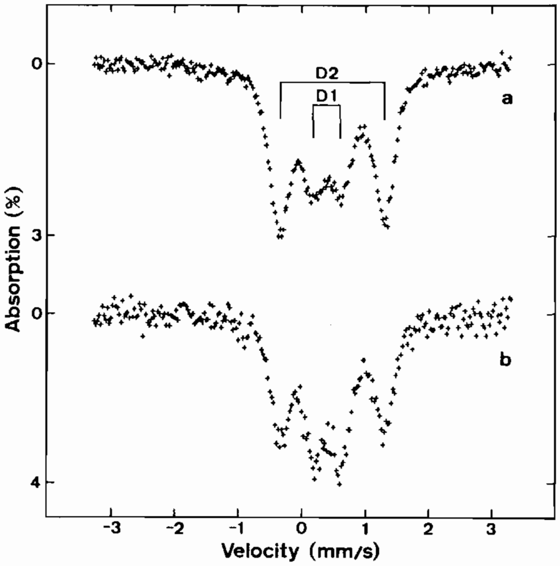

Fig. 1. 100 K Mössbauer spectra of Fe^{3+}-Nafion exchanged from 0.2 M ferric solution cooled at different speeds: (a) quenched at $\approx 10^3$ K min^{-1} and (b) cooled at ≈ 5 K min^{-1}.

Our attribution of D2 (to an oxo bridged ferric dimer) and of D1 (to aquo Fe^{3+} ions bridged by $H_3O_2^-$ ligands) is, if we assume that D1 iron exists as dimers, in excellent agreement with the raw results of Nikol'skii *et al.* [22]. Those authors, however, only considered hydroxo ligands and therefore suggested Fe_2OH^{5+} and $Fe_2(OH)_2^{4+}$ for D1 and D2 respectively. Interpreted literally as mono- and di-hydroxo bridged structures these complexes are not in agreement with our EXAFS results [2]. Moreover, Ropars *et al.* [27] have determined equilibrium constants for ferric iron in aqueous solution at low ionic strength and find that a significant amount of iron is present as a species which they describe as Fe_2OH^{5+}. We reinterpret this as providing evidence for a (mono) hydrogen oxide bridged dimeric species.

Our view, therefore, is that the potentiometric results of Ropars *et al.* [27] are preferable to those of Hedström [6] for low ionic strength solutions. These are

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \qquad K = 10^{-2.97}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+ \qquad K = 10^{-6.98}$$

$$2Fe^{3+} + H_2O \rightleftharpoons Fe_2(OH)^{5+} + H^+ \qquad K = 10^{-0.98}$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+ \qquad K = 10^{-3.00}$$

However, the mono- and dihydroxo bridged dimers of Ropars *et al.* should be reformulated as mono hydrogen oxide and oxo bridged dimers respectively.

We now consider why the oxo bridged species is favoured by quenching as opposed to slow cooling. It is known that water may desorb from Nafion at low temperatures [28]. If this occurs for our cooled sample, we might expect a greater amount of D2, as occurs in room temperature dehydrated (quenched) samples [2]. However, the opposite occurs: D2 is not favoured by cooling. This means that the distribution of iron between oxo bridged dimers and aquo Fe^{3+} groups with $H_3O_2^-$ bridges depends on temperature with the oxo bridged dimers (D2) being favoured at higher temperatures. Confirmation of this comes from an experiment in which Fe^{3+}-Nafion was quenched to 77 K giving 56% D2. After annealing at 220 K for 12 h and requenching, D2 only amounted to 41% of the Mössbauer absorption area. Similar effects have been previously observed in aqueous solution. Chaves and Garg [23] studied frozen solutions of 0.67 M $Fe(NO_3)_3$ and $Fe(ClO_4)_3$. They observe D1 and D2 and find that D2 transforms into D1 if the sample is annealed above 170 K (the glass transition temperature of water). D2 is also found to be favoured by quenching. Although those authors interpret their results in terms of a change of the amorphous structure to a more ordered one, we suggest that D1/D2 transformations may be most easily understood in terms of a temperature dependent equilibrium between the corresponding species (and also the non-hydrolyzed iron) in the liquid state. Indeed, Mulay and Selwood [29] have used magnetometry to show that the (diamagnetic oxo bridged) dimer is preferred at higher temperature (in the range 290–330 K) for ferric perchlorate aqueous solutions.

In view of the fact that the cooling rate affects the Mössbauer spectra obtained we recommend that in future studies of ion exchanged resins/membranes (or indeed clay minerals) that this parameter be reported. This has not been done previously [1, 2, 18–20, 30]. In our previous work [1, 2] the samples were generally quenched in liquid nitrogen, except those measured in the high field cryostat which were cooled fairly rapidly, ≈50 K/min.

Recently Taies and Silver [31] have proposed that the species $Cl(H_2O)_4Fe{-}O{-}Fe(H_2O)_4Cl$ can be formed in aqueous solution when the pyridinium salt of the $Cl_3Fe{-}O{-}FeCl_3$ dimer is dissolved. They associate this species with a Mössbauer doublet having the following parameters at 80 K: $IS \approx 0.47$, $QS \approx 0.70$ mm s^{-1}. Using point charge calculations we find that the reduction in the quadrupole splitting (from 1.67 to 0.70 mm s^{-1}) is too large to be accounted for by the replacement of one water ligand on each iron by a chloride ion.

Influence of pH

Figure 2 shows the 80 K spectra obtained for Nafion exchanged from 0.02 M aqueous solutions of ferric nitrate, chloride and perchlorate. The parameters of a two doublet fit are given in Table I. The dimer (D2) amounts for 15–20% of the absorption area while the remainder is due to a doublet whose quadrupole splitting is larger than that of D1 and is different for each of the three samples. This difference cannot be due to anion coordination so, noting that the *QS* of this unidentified doublet increases with the absorption area, we postulate that there are two unresolved doublets with varying proportions. It seems likely that one of these is D1 while the other, which we denote as D3, is probably due to an iron hydroxide polymer or precipitate. Nikol'skii *et al.* [22] have observed such a species in aqueous solutions with pH ≥ 1.9 where it gave a doublet with $QS = 0.7$ mm s^{-1}. The quadrupole doublet with $QS = 0.67$ mm s^{-1} observed by Knudsen *et al.* [32] in frozen solutions may also be identified with D3. It is unfortunate that Knudsen *et al.* did not notice the separate existence of D1 in their spectra, neither

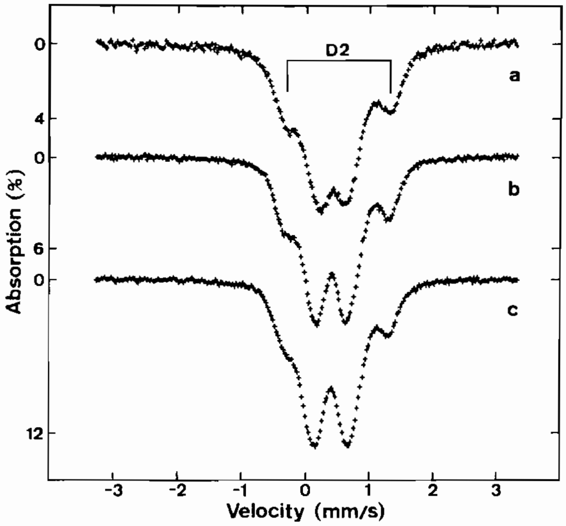

Fig. 2. 80 K Mössbauer spectra for Nafion exchanged from 0.02 M aqueous solutions of different ferric salts: (a) nitrate, (b) perchlorate and (c) chloride.

TABLE I. ^{57}Fe Mössbauer Parameters at 80 K for Nafion Exchanged from 0.02 M Aqueous Solutions of Various Salts

Salt	*IS* ± 0.01 (mm s^{-1})	*HW*^{a} ± 0.02 (mm s^{-1})	*QS* ± 0.02 (mm s^{-1})	%	Absorption area (a.u.)
$Fe(NO_3)_3$	0.48	0.27	0.47	79	2.08
	0.57	0.18	1.67	21	
$Fe(ClO_4)_3$	0.47	0.23	0.53	82	2.38
	0.56	0.15	1.66	18	
$FeCl_3$	0.47	0.23	0.57	86	2.78
	0.57	0.15	1.66	14	

^{a}*HW* = Half width at half maximum.

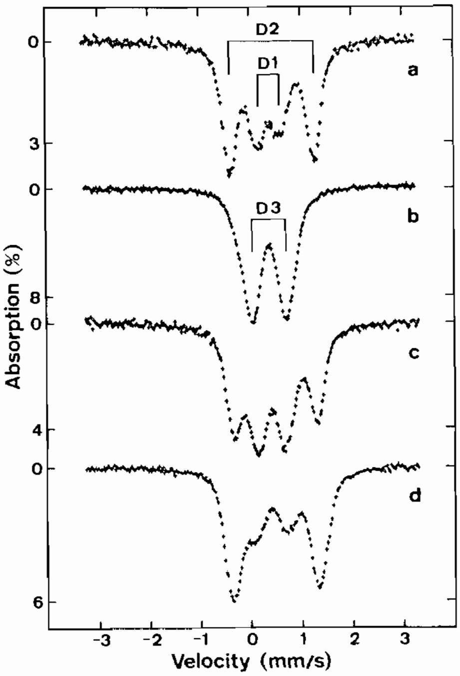

Fig. 3. 80 K Mössbauer spectra (after quenching) for (a) Nafion after exchange from 0.2 M ferric solution, (b) as (a) after reexchange in 0.2 M KNO_3 solution, (c) as (b) after reexchange in 0.2 M ferric solution, (d) as (c) after vacuum pumping at room temperature.

when it coexisted with D3 (pH = 2.1, [32]) nor when it clearly predominated (pH = 1.2, [33]).

Figure 3 illustrates a second method by which D3 may be obtained in Nafion. The top spectrum (a) is for Nafion exchanged from 0.2 M ferric solution and contains D1 and D2. The second spectrum (b) containing only D3 is obtained by reexchanging the previous sample from 0.2 M K^+ solution, a procedure known to cause the formation of iron oxyhydroxide, (giving a hyperfine split sextet with $B_{hf} \approx 48$ T at 4.2 K) [34,35]. On reexchanging again from 0.2 M Fe^{3+} solution we obtain (c) which presumably contains D2, D1 and D3 although the latter two are not resolved. We recall that dehydration of ferric Nafion leads to conversion of D1 to D2 [2]. On dehydration of (c) we obtain spectrum (d) in Fig. 3 in which the proportion of D2 has increased. More importantly, the apparent quadrupole splitting of the inner doublet has increased (from 0.54 to 0.63 mm s^{-1}), just as expected if this doublet is in fact composed of D1 and D3 where the former (with smaller *QS*) decreases on dehydration.

We now turn to the significance of these results for iron exchanged into montmorillonites. Mössbauer spectra have been presented by several authors for ferric ions contained in the interlayer water of montmorillonite [36,37]. These authors observe D2 but do not realize that it is due to an oxo bridged dimeric species, instead associating it with species such as $FeCl^{2+}$ (aq) or $Fe(OH)^{2+}$ (aq). Helsen and Goodman [36] observe that the 77 K Mössbauer spectra of their Fe(III)-montmorillonite contains two doublets (the outer one of which is D2) and that the relative areas of these doublets remain the same for samples prepared at pH values of 1.4 and 1.8. They suggest therefore that the inner doublet is not due to a hydroxide polymer. We wish to point out an alternative possibility which is that the montmorillonite spectra are analogous to those in our Fig. 2 where an increase in average hydrolysis is not reflected by a significant decrease in % D2 but rather merely by an increase in the quadrupole splitting of the inner doublet. Unfortunately Helsen and Goodman do not report both values for the *QS* of the inner doublet. Finally, and in passing, we should mention that comparison with the results of refs. 36 and 38 suggests that some of the isomer shift values reported in ref. 37 may be incorrect.

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