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## Ferric ion (Fe(III)) coordination in concentrated aqueous electrolyte solutions

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**Abstract.** The first-order isotopic difference method of neutron diffraction has been used to study the interatomic coordination of the ferric ion in three concentrated ( $\sim 2\text{M}$ ) heavy water solutions, each prepared under different conditions with differing degrees of acidity: (i)  $1.52\text{M Fe}(\text{NO}_3)_3$ ; (ii)  $1.72\text{M Fe}(\text{NO}_3)_3$  and (iii)  $2\text{M Fe}(\text{ClO}_4)_3$ . In all solutions, a well defined hydration structure was obtained, with nearest neighbour  $\text{Fe}^{3+} \dots \text{O}$  and  $\text{Fe}^{3+} \dots \text{D}$  correlations at  $2.01(2)$  and  $2.68(3)$  Å respectively. A variety of coordination numbers were calculated: in the  $1.52\text{M}$  nitrate solution a complete six-fold hydration shell was found, whereas for the  $1.72\text{M}$  nitrate solution, which was heated prior to preparation, significant hydrolysis was observed. By contrast the  $\text{Fe}^{3+}$  ion in the perchlorate solution showed six-fold coordination but with significant hydrolysis.

### 1. Introduction

Solutions containing iron ions (Fe(II)–Fe(III)) exhibit a rich variety of chemical and biological behaviour (Sylva 1972, Baes and Mesmer 1976, Flynn 1984), and continue to be the subject of theoretical calculations by among others Kneifel *et al* (1989) and Curtiss *et al* (1987). However, despite the widespread interest in such systems, a detailed knowledge of the atomic environment of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  remains incomplete. This is because all investigations, other than the x-ray diffraction studies of Magini and co-workers (1977, 1978, 1981) and EXAFS investigations, such as those of Sham *et al* (1980) only provide a qualitative picture of the manner in which  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are hydrated; even x-ray diffraction studies only provide information of ion–oxygen distances for strongly coordinating cations such as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and the exact nature of the ion–water coordination is always in doubt because of the need to resort to sophisticated modelling procedures. Similarly, the alternative x-ray based technique of EXAFS, which is in principle simpler because it is ‘ion specific’, depends on modelling procedures, and is resolution-limited by the narrow range of momentum

§ While the work described in this paper was being prepared for publication the principal author died from cancer in September 1990 at the age of 28. Many of the details are contained in John’s PhD thesis, which he successfully defended in August 1989. His research studies have included neutron quasielastic scattering studies of triply charged cations, neutron diffraction investigations of ferrous and ferric hydration and in recent years at the Rutherford Appleton Laboratory, critical angle and specular reflection studies of thin films. He always endeavoured to produce state-of-the-art results which would have real impact on the subject under investigation. His doctoral thesis and papers attest to the high standards he set himself.

transfer covered. Moreover, neither of these methods give any quantitative information about the cation-hydrogen correlations. Nevertheless, both methods have been used to provide detailed information of nearest neighbour Fe...O distances,  $r_{\text{FeO}}$  and coordination numbers  $\bar{n}_{\text{Fe}}^{\text{O}}$ , in a number of iron salt solutions: x-ray diffraction studies of Caminiti *et al* (1979) and Caminiti and Magini (1979) show that in most cases for the ferric iron  $r_{\text{FeO}} \simeq 2.0 \text{ \AA}$  and  $\bar{n}_{\text{Fe}}^{\text{O}} = 6$ . (Results of Ohtaki *et al* (1976) and Kalman *et al* (1988) for the ferrous ion also give a hexahydrated structure, but with  $r_{\text{FeO}} = 2.1 \text{ \AA}$ .)

In this paper, results derived from neutron diffraction and isotopic substitution experiments on three aqueous electrolyte iron salt solutions are presented and discussed. It is shown that the use of the iron isotope  $^{54}\text{Fe}$  in these experiments facilitates the direct determination of  $\text{Fe}^{3+}$  structure in solution, in terms of a linear combination of the total  $\text{Fe}^{3+}$  radial distribution factor,  $G_{\text{Fe}}(r)$ . This function can be analysed to give details of iron-water molecule distances and conformation, and the extent of short range order. This information can be used to build up a picture of the relative strengths of other strongly coordinating cations, and to test theoretical calculations or computer simulations of the kind suggested by Kuharski *et al* (1988) which are based on particular ion-water pair potentials. These latter calculations are often directed at an understanding of the classical redox reaction  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ , and a knowledge of local cation geometry is crucial as input to the calculations of rate constants (see Bader *et al* 1990).

The three solutions studied were two ferric nitrate solutions (1.7M and 1.5M) and one ferric perchlorate solution (2M). In order to restrict the number of variables all three solutions were acidic with pHs near zero to ensure the presence of ferric (Fe(III)) rather than ferrous (Fe(II)) ions (Cotton and Wilkinson 1980). The choice of nitrate and perchlorate counterions was originally made to minimize complexation. However, as illustrated below, unexpected results can arise due to particular preparative procedures.

## 2. Theory

The theory of the first-order difference method of neutron diffraction has been discussed in detail elsewhere (see, for example, Soper *et al* 1977). Only a brief outline is presented here.

If neutrons (or x-rays) of wavelength  $\lambda$  are scattered through an angle  $\theta$  by a liquid containing several chemical species then the scattering intensity can, after a number of corrections for absorption, multiple scattering, and incoherent scattering, be related to the normalized structure factor  $F(k)$  of the liquid according to the equation

$$I(k) = N \left[ \sum_{\alpha} c_{\alpha} b_{\alpha}^2 + F(k) \right] \quad (1)$$

where

$$F(k) = \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} (S_{\alpha\beta}(k) - 1) \quad \text{and} \quad k = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}.$$

$c_\alpha$  is the atomic concentration of atom 'α',  $S_{\alpha\beta}(k)$  is the partial structure factor of atoms α and β. Fourier transform atom of  $S_{\alpha\beta}(k)$  gives the pair radial distribution function  $g_{\alpha\beta}$ :

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2\rho r} \int [S_{\alpha\beta}(k) - 1] k \sin kr \, dk$$

where  $\rho$  is the total number density of the solution and is typically of the order of  $0.1 \text{ \AA}^{-3}$ .  $b_\alpha$  is either the mean coherent neutron scattering length, or the atomic form factor (usually written  $f_\alpha(k)$ ) for x-ray scattering. For neutron scattering  $b_\alpha$  is isotropic and the Fourier transform of  $F(k)$  is a linear sum of all pair radial distribution functions.

$$G(r) = \sum_\alpha \sum_\beta c_\alpha c_\beta b_\alpha b_\beta [g_{\alpha\beta}(r) - 1]. \tag{2}$$

For x-ray scattering the form factors are  $k$ -dependent, and consequently  $G(r)$  cannot be written as a simple linear sum of the  $g_{\alpha\beta}(k)$ s. Instead it becomes a convolution of the  $f_\alpha(k)$ s with the corresponding  $S_{\alpha\beta}(k)$ s (Skipper *et al* 1989).

The method of neutron diffraction and isotopic substitution is based on differencing  $F(k)$ s for two chemically identical solutions in which the isotope of the ion, I, of interest is different. In the difference function  $\Delta_I(k)$  only those partial structure factors (and hence partial radial distribution functions) relating to that ion will remain. This method also has the advantage that non-elastic corrections (Placzek corrections) can be eliminated in first order (Soper *et al* 1977). Following the procedure outlined in Soper *et al* (1977) for the particular case of two identical ferric salt solutions with differing isotopic abundances the first order difference  $\Delta_{\text{Fe}}(k)$  between the structure factors of the two solutions can be written as

$$\Delta_{\text{Fe}}(k) = A(S_{\text{FeO}}(k) - 1) + B(S_{\text{FeD}}(k) - 1) + C(S_{\text{FeX}}(k) - 1) + D(S_{\text{FeFe}}(k) - 1) \tag{3}$$

where

$$\begin{aligned} A &= 2c_{\text{O}}c_{\text{Fe}}b_{\text{O}}\Delta b_{\text{Fe}} & B &= 2c_{\text{D}}c_{\text{Fe}}b_{\text{D}}\Delta b_{\text{Fe}} & C &= 2c_{\text{X}}c_{\text{Fe}}b_{\text{X}}\Delta b_{\text{Fe}} \\ D &= c_{\text{Fe}}^2(b_{\text{Fe}}^2 - b_{\text{Fe}}'^2) & \Delta b_{\text{Fe}} &= (b_{\text{Fe}} - b_{\text{Fe}}'). \end{aligned}$$

The isotopic state of iron is characterized by  $b_{\text{Fe}}$  and  $b_{\text{Fe}}'$  in the two chemically identical solutions. The subscript X refers to the nucleus at the centre of the counterion, i.e. Cl or N.

Fourier transformation of equation (1) yields the total  $\text{Fe}^{3+}$  radial distribution function  $G_{\text{Fe}}(r)$ :

$$G_{\text{Fe}}(r) = Ag_{\text{FeO}}(r) + Bg_{\text{FeD}}(r) + Cg_{\text{FeX}}(r) + Dg_{\text{FeFe}}(r) + E \tag{4}$$

where  $E = -(A + B + C + D)$ .

Structural interpretation of the solutions is based on equation (4). As we will see later it is straightforward to assign correlations between  $\text{Fe}^{3+}$  and other atoms based on simple electrostatic arguments. Furthermore, once a correlation has been

identified, if it turns out to be well defined over a range  $r_1 \leq r \leq r_2$ , then a coordination number  $\bar{n}_{\text{Fe}}^\alpha$  can be attributed to the particular interaction Fe- $\alpha$ , which is given by

$$\bar{n}_{\text{Fe}}^\alpha = c_\alpha \rho \int_{r_1}^{r_2} 4\pi r^2 g_{\text{Fe}\alpha}(r) dr. \quad (5)$$

For comparison between results for solutions of different concentrations it is convenient to divide equation (4) by  $A$ , the coefficient of  $g_{\text{FeO}}(r)$ , and reproduce a dimensionless total radial distribution function

$$G_{\text{Fe}}^*(r) = (G_{\text{Fe}}(r) + E)/A. \quad (6)$$

### 3. Experimental procedure

#### 3.1. Sample preparation

All samples were prepared in heavy water ( $\text{D}_2\text{O}$ ) rather than ordinary water ( $\text{H}_2\text{O}$ ), because of the large incoherent neutron scattering by hydrogen. Consequently the use of  $\text{D}_2\text{O}$  as solvent, and the limited amounts of isotopically enriched elements meant that it was not possible to use standard methods of preparation for samples and more laborious alternatives were introduced. Sample preparation was made difficult by the requirement that each pair of isotopically distinct samples was of the same chemical composition and  $\text{D}_2\text{O}:\text{H}_2\text{O}$  purity.

Table 1. Solution details—concentration in  $\text{mol dm}^{-3}$ .

Solution	Fe (Isotope)	$[\text{Fe}^{3+}]$	$[\text{anion}]/[\text{Fe}^{3+}]$	$[\text{D}_2\text{O}]/[\text{Fe}^{3+}]$	Density ( $\text{g cm}^{-3}$ )	$\text{H}_2\text{O}:\text{D}_2\text{O}$ (%)
$\text{Fe}(\text{NO}_3)_3$ (Unheated)	Nat	$1.545 \pm 0.015$	$3.58 \pm 0.04$	$29.9 \pm 0.3$	1.368	99.72
	54	$1.48 \pm 0.04$	$3.78 \pm 0.08$	$31.6 \pm 0.9$	1.366	
$\text{Fe}(\text{NO}_3)_3$ (Heated)	Nat	$1.729 \pm 0.002$	$3.543 \pm 0.005$	$25.45 \pm 0.03$	1.360	99.69
	54	$1.72 \pm 0.01$	$3.58 \pm 0.02$	$25.72 \pm 0.14$	1.364	
$\text{Fe}(\text{ClO}_4)_3$	Nat	$2.01 \pm 0.02$	$3.65 \pm 0.04$	$20.1 \pm 0.2$	1.655	99.50
	54	$1.958 \pm 0.005$	$3.96 \pm 0.03$	$20.2 \pm 0.1$	1.671	

Preparation of iron(III) nitrate solutions (table 1) was carried out in two different ways, the main difference being that in one preparation the solutions were heated and in the other the temperature was restricted to a maximum of  $40^\circ\text{C}$ . In the first preparation iron was dissolved in nitric acid to form an acidified solution and this then deuterated by evaporation. The repeated evaporations were carried out at approximately  $90^\circ\text{C}$  and the solutions rapidly attained a deep yellow/brown colour. For the second preparation the metal was added to deuterated nitric acid. However, because the reaction was exothermic and the nitric acid was concentrated (5.48M), it was necessary to start with the acid in an icebath: this restricted the temperature rise during the subsequent reaction to below  $40^\circ\text{C}$ . Some residue of iron was present after

the reaction but it is uncertain whether it was due to passivation of the iron in the cold conditions (Vogel 1961) or iron oxide impurity. The filtered residue was weighed and corrections made to the concentrations. In both preparations the reactants were contained so that any nitrogen oxides produced were reabsorbed.

The preparation of iron(III) perchlorate solution (table 1) from the metal usually requires extensive recrystallization of the salt and sufficient product to test its composition. However, in the present case only small amounts of 54-isotopic iron were available, and the samples were consequently prepared following the method of Mulay and Selwood (1955) but omitting the final purification steps. Iron was dissolved in nitric acid and the solutions evaporated to a viscous liquid. Concentrated perchloric acid (70%) was then added and the whole reduced until crystals of iron perchlorate appeared. This procedure was repeated twice, until the nitric acid was considered to have been entirely evaporated off. The iron(III) perchlorate crystals were finally filtered from the nascent acid and redissolved in light water. The two solutions (natural and 54-isotopic iron) were prepared in parallel under the same conditions and so were assumed to be similar in concentration. However, after a check was made on their pH a few drops of dilute perchlorate acid were added to one. The weight of iron left in the nascent acid was determined in the standard way (Vogel 1961). After the neutron experiment it was confirmed that no iron had been lost in production of the iron(III) perchlorate, no nitrate or chloride impurities were present in any significant quantity, and most importantly the perchlorate ion concentration in the two solutions was the same.

In all three solutions pH measurements were made and values close to zero were obtained.

### 3.2. Data collection and analysis

The neutron diffraction experiments were carried out on the D4B and D20 diffractometers at the High-Flux Reactor, Institut Laue-Langevin, Grenoble, France. The D4B diffractometer was used to obtain data in the range  $0.3 > Q > 16$  ( $\text{\AA}^{-1}$ ) for  $0.7 \text{ \AA}$  neutrons and the D20 diffractometer  $0.3 > (\text{\AA}^{-1}) > 14Q$  at a wavelength  $0.94 \text{ \AA}$ . The wavelengths and the detector angular zero offsets were determined by calibration with a nickel powder sample.

All samples were contained in the same titanium-zirconium cell for each experiment and loading was carried out inside a glove box containing a dry argon atmosphere. Neutron counts for each sample were collected over 10 to 12 h in several scans in order to check for machine stability and any leakage from the sample cells. Data were collected for each pair of samples for the empty cell, and for the background as well as for a vanadium rod of similar size to the sample cell for absolute calibration.

The data for each pattern were corrected for multiple scattering and attenuation in the normal way (see, for example, Enderby and Neilson (1979)) and put on an absolute scale of barn  $\text{sr}^{-1}$  nucleus $^{-1}$  by reference to the vanadium standard. The relevant parameters for each sample are given in table 2.

For both nitrate cases the data were satisfactory and direct subtraction of the  $F(k)$ s gave the difference functions shown in figures 1 and 2. The full curves in figures 1 and 2 are the back transforms of the  $G_{\text{Fe}}(r)$  results in figures 3 and 4 respectively after the data have been constrained to  $G_{\text{Fe}}(r = 0)0 > r > 1.7$  ( $\text{\AA}$ ) i.e. that region which contains physically unrealistic ripples due to Fourier transformation of a truncated data set.

Table 2. Cross sections and scattering parameters used in the neutron diffraction experiments. The absorption cross section is that for thermal neutrons. The atomic cross sections are taken from Sears (1948) with the exception of the cross section for  $D_2O$  which was taken directly from Hughes and Harvey (1955) at the required wavelength.

Electrolyte	Fe (Isotope)	Scattering ( $10^{-24}$ cm <sup>2</sup> )	Absorption ( $10^{-24}$ cm <sup>2</sup> )	$\lambda$ (Å)	Diam. (mm)	Height (mm)
Fe(NO <sub>3</sub> ) <sub>3</sub> (Unheated)	Nat	4.33 ± 0.04	0.0890 ± 0.0003	0.94	8.0	33.0
	54	4.24 ± 0.03	0.085 ± 0.001			
Fe(NO <sub>3</sub> ) <sub>3</sub> (Heated)	Nat	4.29 ± 0.01	0.1019 ± 0.0004	0.70	8.0	27.2
	54	4.19 ± 0.01	0.0963 ± 0.004			
Fe(ClO <sub>4</sub> ) <sub>3</sub>	Nat	4.65 ± 0.02	1.56 ± 0.02	0.70	12.0	32.7
	54	4.59 ± 0.02	1.64 ± 0.02			

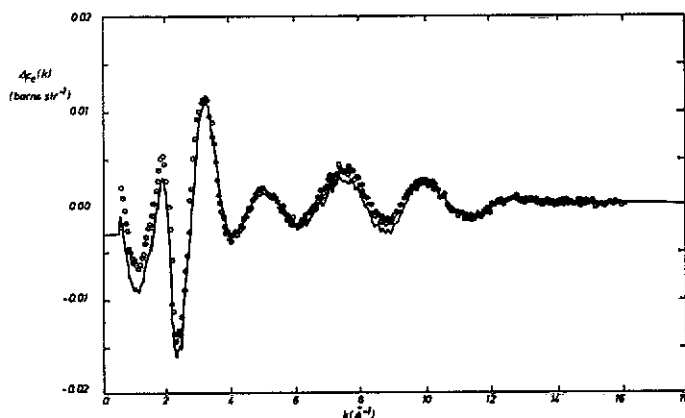


Figure 1. Total Fe<sup>3+</sup> first-order difference function  $\Delta_{Fe}(k)$  in 1.72M Fe(NO<sub>3</sub>)<sub>3</sub> solution in heavy water. The full curve through the data (o) is the back Fourier transform of the result in figure 3.

In the perchlorate case some light water contamination was present in the samples, and this gave rise to a 'Plazcek droop' in the difference function (figure 5). A correction was made by subtraction of a light water spectrum scaled by 0.0045 from the difference function. This did not affect the total distribution function  $G_{Fe}(r)$  in the region of interest above 1.7 Å (figure 7) but a back transform (figure 6) was seen to fit the corrected data better. Following the procedure of Powell *et al* (1989) an additional adjustment for the hydrogen present (0.2% of the total number of atoms) was made by application of the scaling factor applied to the light water pattern.

#### 4. Discussion

It is clear from the difference functions  $\Delta_{Fe}(k)$  (figures 1, 2, 5), that, despite the relatively small difference between the coherent scattering lengths of <sup>NAT</sup>Fe ( $b = 9.5$  fm) and <sup>54</sup>Fe ( $b = 4.20$  fm) the first-order isotopic difference method of neutron diffraction is feasible for systems containing relatively low concentrations of iron. Indeed the  $\Delta_{Fe}(k)$ s show strong oscillations to  $k$  values of approximately 14 Å<sup>-1</sup>,

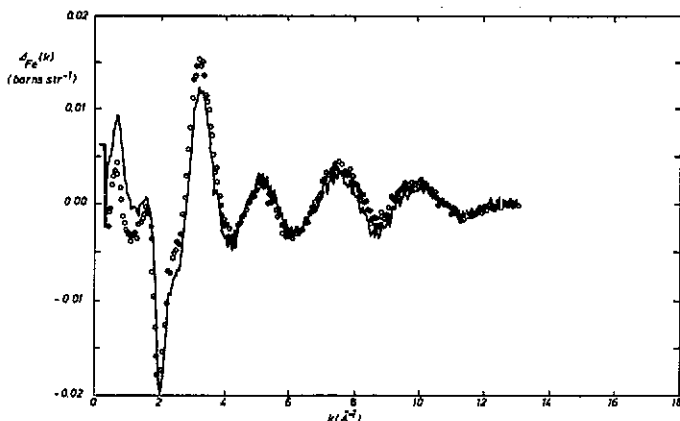


Figure 2. Total  $\text{Fe}^{3+}$  first-order difference function  $\Delta_{\text{Fe}}(k)$  in a 1.5M  $\text{Fe}(\text{NO}_3)_3$  solution in heavy water. The full curve through the data (o) is the back Fourier transform of the result in figure 4.

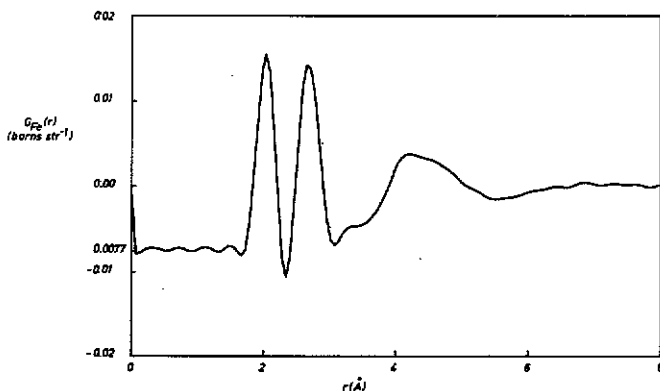


Figure 3. Total  $\text{Fe}^{3+}$  radial distribution function  $G_{\text{Fe}}(r)$  for 1.72M  $\text{Fe}(\text{NO}_3)_3$  in heavy water.

a signature of well defined local order. Of additional interest is the appearance of pronounced peaks in figures 2 and 5 at  $k$ -values less than  $1 \text{ \AA}^{-1}$ . Unfortunately the data in figure 1 are incomplete in this region, stopping at  $k \sim 0.6 \text{ \AA}^{-1}$ . However, the indication is that a peak (or peaks) may well exist at lower  $k$ . Although it is not possible to draw firm conclusions about the exact origins of low 'angle' peaks, detailed work on  $\text{NiCl}_2$  solutions by Neilson and Enderby (1983) suggests that they are due to the presence of relatively strong ion-ion correlations.

Fourier transformation of the  $\Delta_{\text{Fe}}(k)$ s gives the respective  $G_{\text{Fe}}(r)$ s for the three solutions (figures 3, 4 and 7), all of which are dominated by  $\text{Fe}^{3+} \cdots \text{D}_2\text{O}$  correlations, as illustrated by well defined  $\text{Fe}^{3+}$  first hydration shells. Peaks at approximately  $2 \text{ \AA}$  are readily identified with the nearest neighbour  $\text{Fe} \cdots \text{O}$  distance, and those at approximately  $2.68 \text{ \AA}$  arise from  $\text{Fe} \cdots \text{D}$  correlations of the same water molecules (table 3). Integration over these peaks is carried out with equation (5), and provides information of coordination numbers. In contrast to the cases for ions such as  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Cr}^{3+}$ , where the ratio of peaks was 1:2, the values for  $\bar{n}_{\text{Fe}}^{\text{O}}$  and



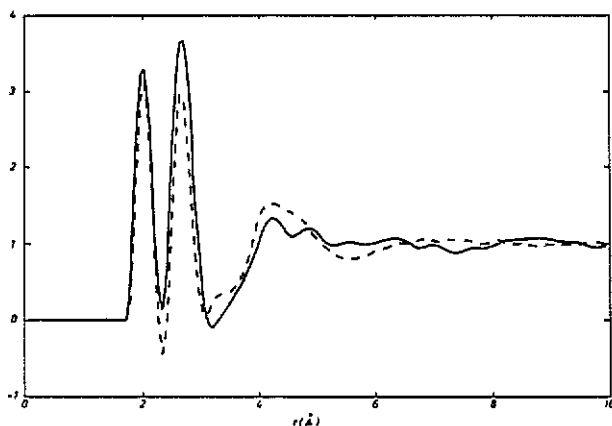


Figure 4 Total normalized  $\text{Fe}^{3+}$  radial distribution functions  $G_{\text{Fe}}^*(r)$  for 1.5M  $\text{Fe}(\text{NO}_3)_3$  in heavy water (broken curve), compared with the equivalent result of figure 3, for the 1.72M iron nitrate heavy water solution (full curve) whose  $G(r)$  is given in figure 3.

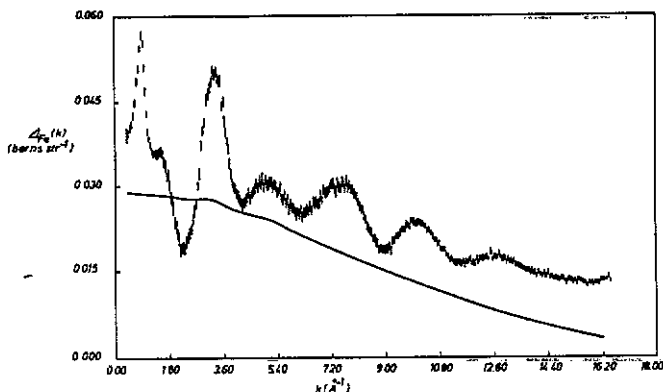


Figure 5 Total  $\text{Fe}^{3+}$  first-order difference function  $\Delta_{\text{Fe}}(k)$  in a 2M solution of  $\text{Fe}(\text{ClO}_4)_3$  in heavy water, which is derived directly from the difference between the structure factors  $F(k)$  for the two isotopically distinct solutions and includes inherent scattering contributions. The monotonic curve shown represents the contribution from the imbalance in light water content between the samples (see text, section 3). Empirical correction for this slope led to the result for  $\Delta_{\text{Fe}}(k)$  in figure 6 (see Powell *et al* (1989)).

$\bar{n}_{\text{Fe}}^{\text{D}}$  are not always in this simple ratio, and form the framework of the rest of the discussion.

Before discussing the results for each sample individually it should be generally noted that the hydrated water molecules are strongly bound to the ion as illustrated by the sharply defined Fe-O and Fe-D peaks in the  $G(r)$  which return to the value of  $F(r=0)$ . Furthermore, a second hydration sphere is clearly defined, although the individual Fe-O and Fe-D peaks are not separated. The strength of the  $\text{Fe}^{3+}$  ion is further illustrated by the relatively long binding times of the various parts of its hydration region. For the first hydration sphere Hertz (1973), found by  $^{17}\text{O}$  NMR a value of  $3 \times 10^{-4}$  s for the oxygen atoms; for protons an estimate of  $3 \times 10^{-3}$  s was obtained by electric field jump relaxation (Hemmes *et al* 1971) and a figure of  $3.6 \times 10^{-7}$  s for dilute acidified  $\text{Fe}(\text{NO}_3)_3$  by proton NMR (Luz and Shulman 1965).

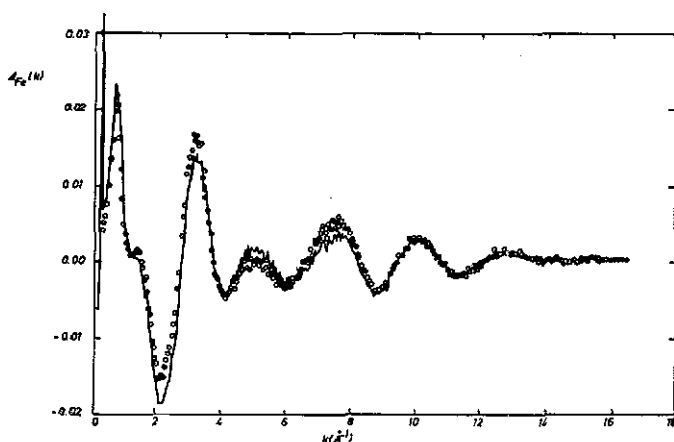


Figure 6. Total  $\text{Fe}^{3+}$  first-order difference function  $\Delta_{\text{Fe}}(k)$  in a 2M solution of  $\text{Fe}(\text{ClO}_4)_3$  in heavy water. The full curve through the data is the back transform of the full curve in figure 7.

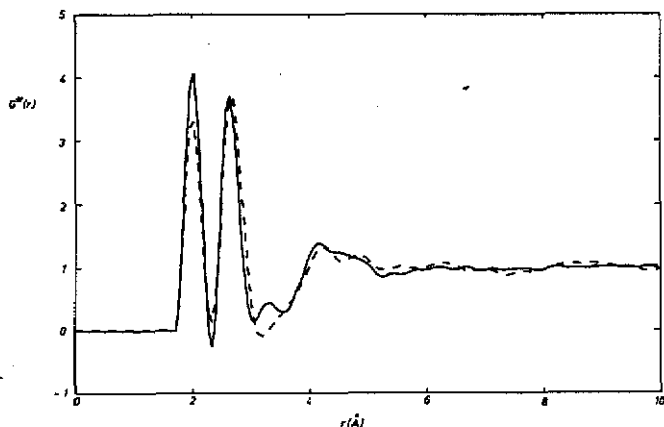


Figure 7. Total normalized  $\text{Fe}^{3+}$  radial distribution function (equation (6))  $G_{\text{Fe}}^*(r)$  for a 2M  $\text{Fe}(\text{ClO}_4)_3$  heavy water solution (broken curve), and for comparison, the equivalent result for 1.72M  $\text{Fe}(\text{NO}_3)_3$  in heavy water (full curve) whose  $G(r)$  is given in figure 3.

The binding time of the second hydration sphere water molecules is appreciably shorter than  $5 \times 10^{-9}$  s and is thought to be  $\leq 10^{-10}$  s (Herdman 1989). Limits were placed on the binding time of the second hydration sphere to the ferric ion of  $10^{-10} > \tau_b > 10^{-11}$  s. By way of comparison, less strongly bound systems such as  $\text{Li}^+$  or anions such as  $\text{ClO}_4^-$  in aqueous solution where the first hydration sphere binding times are  $< 10^{-10}$  s, suggest there is no evidence for a strong second hydration sphere in the static  $G(r)$ .

As mentioned in the introduction the concentration of solutions used here was determined by the conflicting requirements that the solutions be as dilute as possible, in order to see the hydration structure without interference from counterions, but still concentrated enough to give sufficient difference in scattering for an isotopic difference experiment. The scattering length for 54-isotopic iron in the literature is based upon an original measurement by Shull and Wollen (1951) who quote an error of 3–4%. This parameter is crucial for the quantitative interpretation of the data but

**Table 3.** Interatomic distances and coordination numbers for the first hydration sphere around the ferric ion<sup>a</sup>.

Colour	Fe(NO <sub>3</sub> ) <sub>3</sub> unheated Yellow	Fe(NO <sub>3</sub> ) <sub>3</sub> heated Yellow/brown	Fe(ClO <sub>4</sub> ) <sub>3</sub> unheated Pale yellow
$r_{\text{FeO}}/\text{\AA}$ ( $\pm 0.02$ \AA)	2.01(2)	2.02(2)	2.01(2)
$r_{\text{FeD}}/\text{\AA}$ ( $\pm 0.03$ \AA)	2.68(3)	2.68(3)	2.65(3)
$\bar{n}_{\text{Fe}}^{\text{O}}$	6.0(3)	4.9 $\pm$ 0.2	6.3 $\pm$ 0.3
$\bar{n}_{\text{Fe}}^{\text{D}}$	12.0(5)	8.3 $\pm$ 0.3	10.2 $\pm$ 0.5

<sup>a</sup> The errors quoted are from the concentration errors and no allowance has been made for errors arising in the transform of a truncated data set whose errors are estimated to be at most 10%.

as the agreement with x-ray results is so good we may assume that the error quoted in table 3 represents the most pessimistic situation.

The results tabulated in table 3 for the unheated nitrate and the perchlorate solutions confirm the findings of x-ray diffraction, in that the ferric ion in aqueous solution is hexa-aqua-hydrated and that the Fe-O<sub>I</sub> distance is 2.0 \AA for the first hydration sphere, and the mean Fe-O<sub>II</sub> distance is at 4.1 \AA in the second hydration sphere. For similar solutions Magini (1978) and Caminiti and Magini (1979) found the equivalent Fe-O distances to be 2.03 and 4.10–4.15 \AA respectively.

The solution of unheated ferric nitrate may be considered a standard solution, and the results can be used in the interpretation of results derived from other techniques. The power of the neutron difference technique enables one to determine the entire hydration structure. It is clear that for this case the Fe<sup>3+</sup> ion is hexa-aqua-hydrated and that, as the O:D ratio is 1:2, there is no hydrolysis. The protons are, on average, in a cone centred about the Fe-O axis. The most likely configuration is one in which the two deuterium atoms are tilted off the Fe-O axis by 41°: the distance from the oxygen to the proton-proton axis in water is 0.75 \AA, the ferric ion-proton distance is then 2.81 \AA but the mean Fe-D distance was measured as 2.68 \AA. It should be remembered, however, that the static  $G_{\text{Fe}}(r)$  is equivalent to a snapshot photograph of the entire dynamically changing system, which is averaged and then projected onto a one-dimensional display so that precise geometries are not strictly germane.

The second hydration sphere, between  $3.6 > r > 5.2$  \AA shows no evidence of complexes and contains only the O and D peaks from the water. The ratio of Fe<sup>3+</sup>:D<sub>2</sub>O:NO<sub>3</sub><sup>-</sup> is 1:30:3.7 and some nitrate ions must be present. If each nitrate ion is coordinated to two water molecules (Neilson and Enderby 1982) then there is just sufficient water available to form a second hydration sphere if this contains 12 water molecules (Caminiti and Magini 1979).

The results for the heated nitrate solution (figures 2 and 4) and for the perchlorate solution are less straightforward to understand; both exhibit in their first hydration shells a  $\bar{n}_{\text{Fe}}^{\text{O}} : \bar{n}_{\text{Fe}}^{\text{D}}$  ratio significantly different from 1:2, bringing into question the nature of the hydrated species and the preparative methods used to make the samples. For the heated nitrate solution the ratio is 5:8. The solution itself was and, after two years standing in the laboratory, remains coloured yellow/brown which is suggestive of a high degree of dimer or polymerization (Sylva 1972). A detailed structural

study of the species formed would only be possible by means of the second-order difference method of neutron diffraction (Neilson and Enderby 1983) which allows a determination of  $g_{\text{FeFe}}^{(r)}$ .

The results for the perchlorate solution are also unexpected, showing a  $n_{\text{Fe}}^{\text{O}} : n_{\text{Fe}}^{\text{D}}$  ratio of 6.3:10.2. Even allowing for errors in solution concentration and light water contamination the results suggest that the hydration shell of  $\text{Fe}^{3+}$  exhibits a significant degree of hydrolysis and could indicate the presence of species such as  $[(\text{H}_2\text{O})_4\text{Fe}(\text{OH})_2\text{Fe}(\text{H}_2\text{O})_4]^{4+}$  or  $[(\text{H}_2\text{O})_5\text{Fe}-\text{O}-\text{Fe}(\text{H}_2\text{O})_5]^{4+}$  inferred from spectroscopic studies of Knudsen *et al* (1975) and EXAFS studies of Morrison *et al* (1978). However, the question of complete equilibrium of the species must also be raised; Magini *et al* (1981) observed that in concentrated ferric perchlorate solutions it is necessary to work with supersaturated solutions to guarantee that equilibrium has been established. Unfortunately in neutron diffraction based on isotopic substitution there is an overriding need to use two deuterated samples prepared under identical conditions, although in recent years there is a possibility of using light water samples of nickel salts (Powell *et al* 1989).

## 5. Conclusions

It has been shown that the difference in scattering lengths of the natural and 54-isotopic iron is large enough to examine the hydration structure around iron ions in aqueous solution. The accuracy of the results suggests that even more dilute solutions ( $\sim 0.5\text{M}$ ) may be examined. The increased resolution of the neutron isotope difference method allows the proton structure to be examined in detail. For example in the case of an unheated ferric nitrate solution the hexa-aqua-ion was found, and in the case of a perchlorate solution a significant degree of distortion in the  $\text{Fe}\cdots\text{D}$  correlation was observed. Results of this study open up a large field of investigation for ferric and ferrous ions in solution. As the more rapid count rates planned on instruments such D20 at the ILL, Grenoble and SANDALS at ISIS, Rutherford Appleton Laboratory, Chilton, Oxon become available, when a run on one solution will take only 30 min, then it will be possible to follow structural changes which accompany the slow oxidation reactions expected in iron solutions.

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