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Ferrous Fe(II) hydration in a 1 molal heavy water solution of iron chloride

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Abstract. The first-order isotopic difference method of neutron diffraction was applied to the iron ions of an acidic 1 molal solution of iron chloride in heavy water. Results were obtained for the Fe^{2+} hydration; these show that this ion is hexahydrated with nearest neighbour Fe . . . O and Fe . . . D distances of 2.12(2) Å and 2.75(5) Å, respectively. There is also evidence of a weak second hydration shell.

The aim of this communication is to present and discuss results of a recent neutron diffraction isotopic substitution study (NDIS) of 1 molal iron chloride in heavy water under ambient conditions. Two identical samples of isotopically labelled ferrous ($^{\text{N}}\text{Fe}$, ^{54}Fe) chloride in heavy water were prepared as referred to in the classic text by Vogel (1961): metallic iron was dissolved directly in 3.1 Molar deuterated hydrochloric acid. Because the reaction was exothermic, a relatively dilute solution (1 molal in Fe) was prepared in order to maintain the temperature at less than 40 °C. The resulting ferrous chloride solutions were initially colourless but became faintly yellow after a few hours. There was no subsequent change in colour either before or after the neutron diffraction experiments, which took place four days after the preparation.

Neutron diffraction experiments were carried out under ambient conditions on the D20 diffractometer of the ILL. Neutrons of wavelength 0.943 Å were scattered by each sample which was contained in a titanium/zirconium null-alloy sample container. The container itself was situated in an evacuated bell jar. The data were gathered on a 128 channel multidetector which was incremented across an angular range from $1.5^\circ \leq \theta \leq 140^\circ$, which corresponded to a momentum transfer range (in units of Å^{-1}) of $0.4 \leq k \leq 12$. The data for the two samples were analysed by standard correction procedures and normalized to give structure factors, $F(k)$, in units of barns per steradian, by reference to a standard vanadium bar (Enderby and Neilson 1979). Additional corrections for slight imbalance in light-water content were introduced according to the method described by Powell *et al* (1989) and subsequently a difference, $\Delta_{\text{Fe}}(k)$, was

§ Deceased.

Table 1. Concentrations and ratios of species in 1 molal iron chloride heavy water solution.

Isotopic label	Mean neutron coherent scattering length (fm)	Iron molal concentration	Anion/Cation (Cl ⁻ /Fe ²⁺)	D ₂ O/Iron	D ₂ O/H ₂ O	Density (g cm ⁻³)
⁵⁷ Fe	9.54(4)	0.96(1)	3.13(4)	52.2(5)	99.76(5)	1.232(5)
⁵⁴ Fe	4.20(1)	0.95(1)	3.14(4)	52.4(5)	99.78(5)	1.228(5)

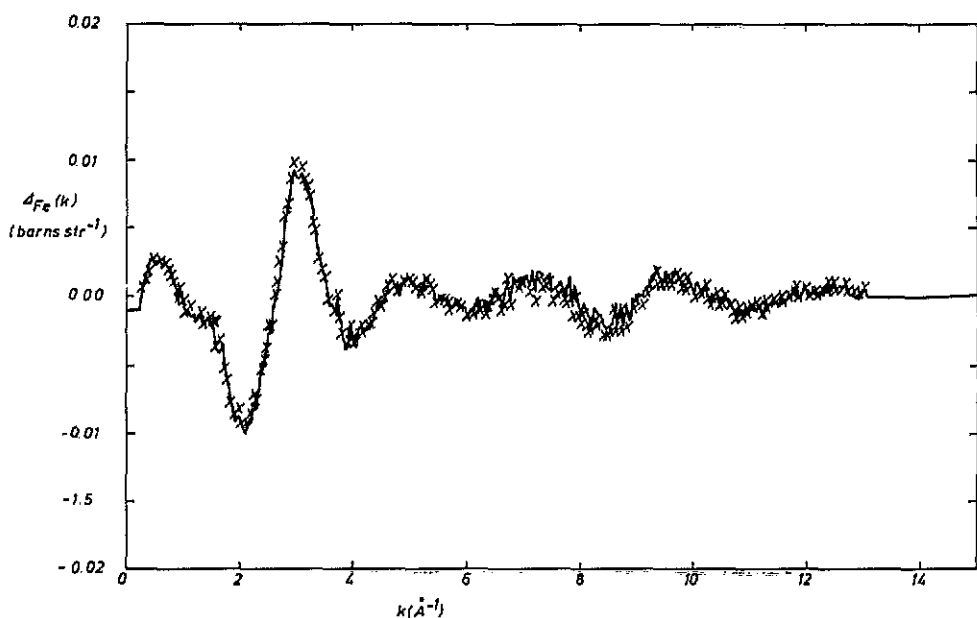


Figure 1. Total Fe²⁺ difference function, $\Delta_{\text{Fe}}(k)$, for 1 molal iron chloride in heavy water. The cross represents the data calculated directly from the experiment, and the full curve is the back transformation of the full curve in figure 2.

calculated from the two renormalized structure factors. This function can be written in units of 10^{-3} b as:

$$\Delta_{\text{Fe}}(k) = 1.2[S_{\text{FeO}}(k) - 1] + 2.7[S_{\text{FeD}}(k) - 1] + 0.1[S_{\text{FeCl}}(k) - 1] + 0.03[S_{\text{FeFe}}(k) - 1]. \quad (1)$$

The coefficients were calculated from a knowledge of the concentrations and coherent neutron scattering lengths of the species in the solution (table 1). $S_{\alpha\beta}(k)$ is the partial structure factor of atoms α and β and is related to the pair radial distribution function by the following equation:

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

where ρ is the total number density of the solution and is typically $\sim 0.1 \text{ \AA}^{-3}$. The Fourier transformation of (1) gives the total iron ion radial distribution function

$$G_{\text{Fe}}(r) = 1.2g_{\text{FeO}}(r) + 2.7g_{\text{FeD}}(r) + 0.1g_{\text{FeCl}}(r) + 0.03g_{\text{FeFe}}(r) - 4. \quad (3)$$

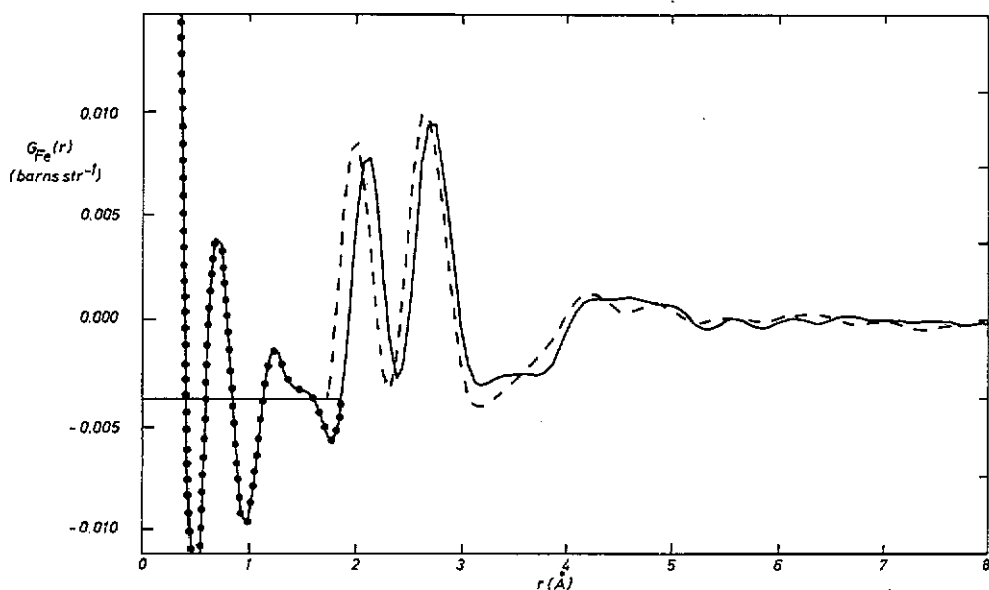


Figure 2. Total Fe^{2+} radial distribution function, $G_{\text{Fe}}(r)$, for 1 molar iron chloride in heavy water. The dotted curve at $r < 1.9 \text{ \AA}$ represents the type of unphysical noise generated by direct Fourier transformation of the unsmoothed $\Delta_{\text{Fe}}(k)$ in figure 1. Removal of this noise by the straight line shown, and back transformation to k -space produced the full curve through the data in figure 1. The equivalent Fe^{3+} radial distribution function, $G_{\text{Fe}}(r)$, (dashed curve) suitably scaled for concentration differences, for a 1.5M $\text{Fe}(\text{NO}_3)_3$ heavy water solution is reproduced for comparative purposes.

$\Delta_{\text{Fe}}(k)$ and $G_{\text{Fe}}(r)$ are presented in figures 1 and 2. The former confirms that the isotopic substitution method is feasible for iron and demonstrates that useful information can be obtained for iron salt solutions at significantly lower concentrations; perhaps a factor of five lower! The existence of structure at $k < 1 \text{ \AA}^{-1}$ is an indication that strong ion-ion correlations are present in the solution (see, for example, Neilson and Enderby 1983); the exact nature of these would require a second-order difference experiment which, with present technology, is only feasible for the determination of the $S_{\text{FeCl}}(k)$ and $S_{\text{ClCl}}(k)$ correlations.

The form of $G_{\text{Fe}}(r)$ (figure 2) confirms the existence of a well defined first hydration shell around the iron ions. The peaks centred at 2.13 \AA and 2.75 \AA can readily be identified with $\text{Fe} \dots \text{O}$ and $\text{Fe} \dots \text{D}$ nearest-neighbour correlations, respectively (table 2). Integration over these peaks confirms the six-fold hydration structure characteristic of the ferrous ($\text{Fe}(\text{II})$) cation, with ratios of 6:12 for the areas of the two peaks and therefore no evidence of hydrolysis. The observation that $G(r)$ tends to $G(0)$ in the intermediate region $3.1 \leq r \leq 3.9 \text{ \AA}$, between the first and second hydration shells points to a relatively stable aquated cation: $[\text{Fe}(\text{D}_2\text{O})_6]^{2+}$. It then becomes meaningful to define the $\text{Fe}^{2+} \dots \text{D}_2\text{O}$ conformation in terms of the tilt angle $\bar{\theta}$ between the $\text{Fe} \dots \text{O}$ axis and the bisector of the $\text{D}\hat{\text{O}}\text{D}$ angle. With $r_{\text{OD}} = 0.98 \text{ \AA}$, $\text{D}\hat{\text{O}}\text{D} = 104.5^\circ$ and the values of r_{FeO} and r_{FeD} in table 1, $\bar{\theta}$ is computed to be $32(15)^\circ$.

Although the shape of $G_{\text{Fe}}(r)$ beyond 3 \AA is relatively structureless, there is evidence that a second shell exists over the range $3.9 \leq r \leq 5.3 \text{ \AA}$ which is commensurate with that of the second shell of Fe^{3+} in a number of solutions (Herdman and Neilson 1992).

Table 2. Structural properties of Fe^{2+} in 1 molal iron chloride in heavy water and Fe^{3+} in 1.5 molal iron nitrate in heavy water. Δ is the full width at half maximum of the peaks. The mean angle of tilt, $\bar{\theta}$, is defined as the angle between the bisector of the water molecule and the Fe...O axis, and is calculated on the basis of a rigid water molecule with $r_{\text{OD}} = 0.98 \text{ \AA}$ and $\text{DOD} = 104.5^\circ$.

Cation	$r_{\text{FeO}}(\text{\AA})$	$\Delta_{\text{FeO}}(\text{\AA})$	$\bar{n}_{\text{Fe}}^{\text{D}}$	$r_{\text{FeD}}(\text{\AA})$	$\Delta_{\text{FeD}}(\text{\AA})$	$\bar{n}_{\text{Fe}}^{\text{O}}$	$\bar{\theta}$
Fe^{2+}	2.13(2)	0.28(2)	6.0(3)	2.75(5)	0.36(3)	12.1(5)	32(15) $^\circ$
Fe^{3+}	2.01(2)	0.32(2)	6.0(2)	2.68(3)	0.40(3)	12.0(5)	20(15) $^\circ$

These results can be compared directly with the earlier study of Herdman and Neilson (1992) on ferric (Fe^{3+}) hydration in aqueous solution (figure 2; table 2). The relative shift in mean Fe^{n+} ...O and Fe^{n+} ...D distances might be anticipated on quantitative grounds from their ionic radii, $r(\text{Fe}^{3+}) = 0.53 \text{ \AA}$; $r(\text{Fe}^{2+}) = 0.75 \text{ \AA}$. The tilt angle for the ferrous and ferric ions is computed to be $32^\circ \pm 15^\circ$ and $20^\circ \pm 15^\circ$, respectively. It is clear that both ions have a similar effect on the water, albeit that there is a tendency of the Fe^{3+} ... D_2O moiety towards a more planar configuration.

The above results and those for Fe^{3+} already contained in Herdman and Neilson (1992) are in satisfactory agreement with those derived from other experimental and theoretical investigations. A number of x-ray and EXAFS studies on aqueous solutions of ferric and ferrous salts by, among others, Camaniti and Magini (1979), Sham *et al* (1980) and Ohtaki *et al* (1976) show that the respective ranges of nearest neighbour Fe^{2+} ...O and Fe^{3+} ...O correlations of the hexa aquo species are $2.095 \leq r \leq 2.12 \text{ \AA}$ and $1.99 \leq r \leq 2.04 \text{ \AA}$. Furthermore, work on single-crystal hydrated salts by Bauer (1964) sets the Fe^{2+} ...O distance at 2.12 \AA in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and work by Hair and Beattie (1977) gives the Fe^{3+} ...O distance as 1.99 \AA . Molecular dynamics simulations have also been carried out in order to understand the classical redox reaction: $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$. From the viewpoint of the neutron results, the most relevant studies are those of Kneifel *et al* (1989) and Guárdia and Padró (1990). Both groups give details of the Fe^{2+} and Fe^{3+} environment which are in reasonable agreement with experiment. The results of Kneifel *et al* (1989), which were obtained from the ion-water potentials of Bopp with an appropriate parameterization, give $r_{\text{FeO}} = 2.20 \text{ \AA}$ and $r_{\text{FeD}} = 2.89 \text{ \AA}$ for Fe^{2+} and $r_{\text{FeO}} = 2.03 \text{ \AA}$ and $r_{\text{FeD}} = 2.81 \text{ \AA}$ for Fe^{3+} , most of which are appreciably larger than the experimental values. Interestingly, however, their calculations of the mean values of tilt angles, $\bar{\theta}$, give 14° for Fe^{2+} and 10° for Fe^{3+} , which agree well with the experimental values, within error (table 2). By contrast, the study of Guárdia and Padró (1990) gives inter-atomic distances for Fe^{2+} of $r_{\text{FeO}} = 2.08 \text{ \AA}$, and similar values for θ to that of Kneifel *et al* (1989).

The above results for $[\text{Fe}^{2+}]_{\text{aq}}$ and those of the earlier study by Herdman and Neilson (1992) on $[\text{Fe}^{3+}]_{\text{aq}}$ provide the first quantitative details of the atomic conformation of these ions in concentrated aqueous solution. With the current technology, it is anticipated that neutron diffraction work at the level of the second-order isotopic difference (Neilson and Enderby 1983) will allow the determination of the radial distribution functions $g_{\text{FeCl}}(r)$ and $g_{\text{ClCl}}(r)$ in iron chloride solutions; a knowledge of these functions will provide useful experimental insights into the nature of the classical redox reaction referred to above.

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