Equilibrium and Structural Study of Chloro Complexes of Iron(III) Ion in Acidic Aqueous Solution by Means of X-Ray Absorption Spectroscopy

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EXAFS, Complexation, Formation Constant, Iron(III) Ion, Chloride Ion

Using an extended X-ray absorption fine structure (EXAFS) technique, the formation constant of the pentaaquachloroiron(III) complex was determined to be $3.8 \pm 0.4 \text{ mol}^{-1} \text{ dm}^{3}$ at $25.0 \pm 0.1 ^\circ\text{C}$ in a $1.00 \text{ mol dm}^{-3} \text{ HClO}_4$ aqueous solution. The structures of $[\text{Fe(OH}_2]^3^+ \text{ and [FeCl(OH}_2)5^2+}$ were determined on the basis of the same EXAFS data. The Fe–O bond length (2.05 Å) in the latter is longer than that (2.01 Å) in the former due to the electron donation and charge neutralization by the coordinating chloride ion with the Fe–Cl bond length of 2.26 Å.

1. Introduction

The extended X-ray absorption fine structure (EXAFS) technique is generally accepted as a powerful tool for structural analysis around metal ions [1]. Wide applicability to any sample conditions, such as powder, amorphous, and solution, is an advantage of the EXAFS technique [2]. Recently, in addition to hydration structures [3 - 10], solvation structures in nonaqueous solvents for many metal ions have been determined by means of EXAFS spectroscopy [11 - 23]. We have investigated the solvation structures in nonaqueous solvents, such as 1,1,3,3-tetramethylurea [11], ethylenediamine [12], propylamine [13], 1,3-propanediamine [13], nitrites [14, 15], trimethylphosphate [16], and alcohols [16].

The X-ray absorption brings about the excitation of an inner-shell electron of the absorbing atom to give an excited photoelectron. Because the transition to an excited state and its decay are much faster than the ligand exchange reaction on the metal center, structural information of the metal complexes under equilibria is contained in an X-ray absorption spectrum. In the case of a solution in which the equilibria between $M$, $ML_1$, $ML_2$, $\cdots$, $ML_x$ are achieved according to eq. (1), the normalized EXAFS oscillation, $\chi(k)$, is expressed by the sum of the products of the EXAFS oscillation of each component $(\chi_{ML_i}(k), i = 0, 1, 2, \cdots, x)$ and its mole fraction $(P_{ML_i})$ as eq. (2).

$$M = ML_1 = ML_2 = \cdots = ML_i$$

$$\chi(k) = \sum_{i=0}^{x} P_{ML_i} \chi_{ML_i}(k)$$

It is then suggested that the determination of the equilibrium constants of eq. (1) should be possible on the basis of the EXAFS spectra of sample solutions with a variety of $P_{ML_i}$ as well as by the potentiometric, spectrophotometric, and calorimetric titrations.

By potentiometric titration we can determine the formation constants of complexes in an aqueous solution with high precision, but this method is rarely used in nonaqueous solvents where electrodes do not work well. The spectrophotometric titration is useful to determine the formation constants in both aqueous and nonaqueous solvents only in the case of reactions with a change in the UV/Vis absorption. The calorimetric titration is advantageous to evaluate the formation constants for complexation without such color change. However, these techniques are not useful to detect directly the change in the coordination environment around the metal ion. On the other hand, because EXAFS spectroscopy...
Table I. Compositions of sample solutions for EXAFS measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$C_{Cl}$</th>
<th>$C_{Cl}/C_{Fe}$</th>
<th>Mole fraction$^b$</th>
<th>$[\text{Fe(OH}_2\text{)}_6]^{2+}$</th>
<th>$[\text{FeCl(OH}_2\text{)}_5]^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC0</td>
<td>0</td>
<td>0</td>
<td>1.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>FC1</td>
<td>0.0501</td>
<td>0.258</td>
<td>0.90</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>FC2</td>
<td>0.100</td>
<td>0.515</td>
<td>0.81</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>FC3</td>
<td>0.150</td>
<td>0.773</td>
<td>0.73</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>FC4</td>
<td>0.200</td>
<td>1.03</td>
<td>0.66</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>FC5</td>
<td>0.501</td>
<td>2.57</td>
<td>0.40</td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $C_{Fe} = 0.194$ mol dm$^{-3}$ and $[\text{H}^+] = 1.00$ mol dm$^{-3}$ (HClO$_4$); $^b$ calculated using the formation constant $K_1$ determined by EXAFS, see in text.

Extracts information about short-range interactions and detects directly the coordinating atoms around the metal center, the EXAFS technique will enable the analysis of chemical equilibria with variations in the coordination of metal ions. Uncertainties in the estimation of the background and smooth base absorptions for the data analysis of EXAFS are the origin of the low sensitivity of EXAFS to the coordination number of the metal ion. On using a fixed observation cell in order to keep the background absorption and light-path length unchanged, however, a relative change in X-ray absorbance will be observed in response to a change in the composition of the sample solution. Thus, on this basis we can determine the formation constant of the metal complex in solution. In this study, we have examined the additivity of the EXAFS oscillation (eq. (2)) and demonstrated the determination of the formation constant for complexation of the iron(III) ion with the chloride ion in an acidic aqueous solution. This is the first report on the determination of the formation constant of a metal complex by means of the EXAFS technique.

2. Experimental

2.1. Sample solutions

The sample solutions for the EXAFS measurements were prepared by dissolving adequate amounts of Fe(H$_2$O)$_n$(ClO$_4$)$_3$ (Wako) and NaCl (Wako) in distilled water containing 1.00 mol dm$^{-3}$ HClO$_4$. The concentration of the iron(III) ion was determined by EDTA titration. The concentrations and compositions of the sample solutions are summarized in Table I together with the mole fractions of component species calculated using the formation constant of the pentaaquachloroiron(III) complex determined by EXAFS described later. According to the literature [24], the hydrolysis and polymerization of the aqua iron(III) ion are negligible under the present experimental conditions.

2.2. EXAFS measurement and data analysis

X-ray absorption spectra around the Fe $K$ edge were recorded using station BL-12C at the Photon Factory of the National Laboratory for High Energy Physics [25]. The white synchrotron radiation was monochromatized by a Si(111) double crystal, and the parallelism of the crystals was detuned to 70% of the maximal intensity at 7.111 keV in order to remove the higher-order reflection. The incident and transmitted X-ray intensities were simultaneously measured by the ionization chambers of a length of 17 and 31 cm, filled with N$_2$ gas and with a 1:4 mixture of Ar and N$_2$ gas, respectively. A flow sample cell (path length = 1 cm) with windows made of pyrolytically prepared boron nitride plates (150 $\mu$m, Shinetsu) was used for measurements of a series of EXAFS spectra. In such a series the flow sample cell was never moved geometrically whenever a sample solution was substituted. The geometric fixation of the sample cell is important to analyze quantitatively the observed EXAFS oscillation for the determination of the formation constant. The temperature of the sample solutions was controlled to 25.0 ± 0.1 °C by the thermostated water circulated around the cell.

The background absorption ($\mu_b$) and the base absorption ($\mu_0$) were estimated by fitting the Victoreen equation and a cubic spline function to the observed absorbances in the pre-edge and post-edge regions, respectively. In order to obtain the normalized EXAFS oscillation, $\chi_{obs}(k)$, the residuals obtained by the subtraction of $\mu_b$ and $\mu_0$ from the observed absorbances were divided by the smooth $K$ shell absorbances calculated by referring to the McMaster coefficients using the $\mu_0$ value at 7.224 keV [26]. The values of threshold energy ($E_0$) were first determined at 7.126 keV corresponding to a peak position of the derivative function of the observed X-ray absorption spectrum. The analysis of the $\chi_{obs}(k)$ values was based upon the theoretical EXAFS expression.
\[
\chi_{\text{cal}}(k) = \sum_{j} \left\{ \frac{N_j S_0^2}{kR_j^2} \right\} F_j(k) \sin \left( 2kR_j + \delta_j(k) \right) \exp \left( -2\sigma_j^2 k^2 - \frac{2R_j}{\lambda(k)} \right)
\]

where \( F_j(k), \delta_j(k), \sigma_j^2, \lambda(k), \) and \( S_0^2 \) are the back scattering amplitude from each of \( N_j \) scatterers \( j \) at distance \( R_j \) from the absorbing atom, the photoelectron phase shift, the many-body amplitude reduction factor, respectively. The values of \( F_j(k), \delta_j(k), \) and \( \lambda(k) \) for the \( \text{Fe} - \text{O} \) and \( \text{Fe} - \text{Cl} \) interactions were calculated using the FEFF7 program [27]. In order to refine the structure parameters in eq. (3), the least-squares fitting in the \( R \) space was carried out using the FEFFIT program [28]. Since crystal structure data of the \([\text{Fe(OH}_2\text{)}_6]^{3+}\) ion were not available, we used a virtual compound \([\text{Fe(OH}_2\text{)}_6]^{3+}\) with the \( \text{Fe} - \text{O} \) bond distance of 2.01 Å determined by the X-ray diffraction method [3] as a theoretical standard of FEFF7 to calculate the \( F_j(k), \delta_j(k), \) and \( \lambda(k) \) values for the \( \text{Fe} - \text{O} \) interaction in the \( [\text{Fe(OH}_2\text{)}_6]^{3+}\) ion. Similarly, the model \([\text{FeCl(OH}_2\text{)}_5]^{2+}\) with the \( \text{Fe} - \text{O} \) and \( \text{Fe} - \text{Cl} \) bond distances of 2.02 and 2.30 Å, respectively, was used for the theoretical standard of the \( \text{Fe} - \text{O} \) and \( \text{Fe} - \text{Cl} \) interactions in the \( [\text{FeCl(OH}_2\text{)}_5]^{2+}\) ion. These bond distances are the average values of those observed in the crystal structures of \([\text{FeCl(dimso)}_5]^{2+}\) (dimso = dimethyl sulfoxide) [30] and \([\text{FeCl(dimso)}_5]^{2+}\) (dimso = dimethyl sulfoxide) [30]. The \( \chi_{\text{obs}}(k) \) data were weighted by \( k^3 \) and windowed between 2.4 < \( k < 13.3 \) Å\(^{-1}\) using the Hanning window with \( \Delta k = 0.5 \) Å\(^{-1}\). The obtained structure parameters did not change even if the minimum \( k \) value was increased to 4.5 Å\(^{-1}\). All the fittings were carried out on both the real and imaginary parts of the Fourier transformations in the \( R \) region from 1.0 to 2.1 Å. The \( S_0^2 \) value of 1.19, which was obtained by the fitting for the sample solution FC0 (see Table I) in which only \([\text{Fe(OH}_2\text{)}_6]^{3+}\) was contained, was kept constant for the analyses of the other sample solutions (FC1–FC5) containing various amounts of \([\text{Fe(OH}_2\text{)}_6]^{3+}\) and \([\text{FeCl(OH}_2\text{)}_5]^{2+}\) ions. The \( \Delta E_0 \) value of the \( \text{Fe} - \text{O} \) interaction was set at \(-3.6 \) eV, which was determined for solution FC0. That of the \( \text{Fe} - \text{Cl} \) interaction was first determined as 4.0 eV for solution FC5, in which the largest amount of the \([\text{FeCl(OH}_2\text{)}_5]^{2+}\) ion was contained among the present sample solutions, and was held constant for the other solutions (FC1–FC4). Because the quantities of \([\text{Fe(OH}_2\text{)}_6]^{3+}\) were known by the equilibrium analysis, the \( N \) values of the \( \text{Fe} - \text{O} \) interaction in \([\text{Fe(OH}_2\text{)}_6]^{3+}\) and \([\text{FeCl(OH}_2\text{)}_5]^{2+}\) and the \( \text{Fe} - \text{Cl} \) interaction in the latter were fixed in the course of the fitting procedures with the values calculated according to the compositions given in Table I. Furthermore, since the \( R \) and \( \sigma^2 \) values of \([\text{Fe(OH}_2\text{)}_6]^{3+}\) could be determined by the EXAFS analysis of solution FC0, those values were fixed for the analyses of the other solutions (FC1–FC5). In order to prevent the correlation in the least-squares fitting between the \( \sigma^2 \) values of the \( \text{Fe} - \text{O} \) and the \( \text{Fe} - \text{Cl} \) interactions in \([\text{FeCl(OH}_2\text{)}_5]^{2+}\), the \( \sigma^2 \) value of the former was kept constant as 0.0078 Å\(^2\), which was determined by the analysis of solution FC5, which contained the largest amount of \([\text{FeCl(OH}_2\text{)}_5]^{2+}\) ion.

3. Results and Discussion

3.1. Formation constant of the pentaaquachloroiron(III) complex

Fig. 1 shows the \( k^2 \chi_{\text{obs}}(k) \) curves with the isosbestic points at \( k / \) Å\(^{-1}\) = 2.62, 3.45, 4.00, 5.10, 6.40, 7.08, and 8.02. The existence of the isosbestic points means that only one equilibrium between the hexaaquoiron(III) ion and the chloride ion (reaction 4) exists in the present reaction system and that the additivity of the EXAFS oscillations is held.

\[
[\text{Fe(OH}_2\text{)}_6]^{3+} + \text{Cl}^- \rightleftharpoons [\text{FeCl(OH}_2\text{)}_5]^{2+} + \text{H}_2\text{O} \quad (4)
\]

\[
K_1 = \frac{[\text{FeCl(OH}_2\text{)}_5]^{2+}}{[\text{Fe(OH}_2\text{)}_6]^{3+}[\text{Cl}^-]} \quad (5)
\]
Because relatively large changes in the $k^3 \chi_{obs}(k)$ value were observed at $k / \AA^{-1} = 3.00, 4.25, 5.75, 6.50,$ and $7.30$, we simultaneously used the $k^3 \chi_{obs}(k)$ values at the five $k$ values to determine the formation constant $K_1$ defined by eq. (5) using eqs. (6) - (8).

$$C_{\text{Fe}} = [\text{Fe(OH}_2)_{6}^{3+}] + [\text{FeCl(OH}_2)_{5}^{2+}] \quad (6)$$

$$C_{\text{Cl}} = [\text{Cl}^-] + [\text{FeCl(OH}_2)_{5}^{2+}] \quad (7)$$

$$k^3 \chi_{obs}(k) = \left( k^3 \chi_{\text{Fe}^{3+}}(k) [\text{Fe(OH}_2)_{6}^{3+}] + k^3 \chi_{\text{FeCl}^{2+}}(k) [\text{FeCl(OH}_2)_{5}^{2+}] \right) / C_{\text{Fe}}. \quad (8)$$

The value of $K_1$ was determined to be $3.8 \pm 0.4$ mol$^{-1}$ dm$^3$ at $25.0 \pm 0.1$ °C and [HClO$_4$] = 1.00 mol dm$^{-3}$. Fig. 2 shows the plots of the $k^3 \chi_{obs}(k)$ values against $C_{\text{Cl}}$. The calculated curves obtained using the determined parameters of $k^3 \chi_{\text{Fe}^{3+}}(k)$, $k^3 \chi_{\text{FeCl}^{2+}}(k)$, and $K_1$ excellently reproduce the $k^3 \chi_{obs}(k)$ values.

There were many investigations of the complexation of the iron(III) ion with the chloride ion in acidic aqueous solution [31]. The values of the formation constant determined under conditions similar to our experiments are summarized in Table II [32 - 38]. Our value obtained by the EXAFS in the present study is consistent with those previously reported. This indicates the validity of the procedures of the formation constant determination by means of the EXAFS technique.

### 3.2. Structure of pentaaquachloroiron(III) complex

The absolute values of the Fourier transformation carried out using the $k^3 \chi_{obs}(k)$ values are given in Fig. 3 without the phase-shift correction. Only one peak is observed around 1.60 Å which is attributable to two kinds of Fe–O (Fe–O(0) in [Fe(OH$_2$)$_6$]$^{3+}$ and Fe–O(1) in [FeCl(OH$_2$)$_5$]$^{2+}$) and one kind of Fe–Cl interactions. There is clearly a small increase in the Fourier transform magnitude at the longer side of the main peak with increasing the quantity of [FeCl(OH$_2$)$_5$]$^{2+}$, because the distance of the Fe–Cl
Table III. Structure parameters around the iron(III) ion.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interaction</th>
<th>N</th>
<th>$R$ [Å]</th>
<th>$\sigma^2$ [Å$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC0</td>
<td>Fe–O(O)</td>
<td>6</td>
<td>2.01</td>
<td>0.0073</td>
</tr>
<tr>
<td>FC2</td>
<td>Fe–O(O)</td>
<td>4.83</td>
<td>2.01</td>
<td>0.0073</td>
</tr>
<tr>
<td></td>
<td>Fe–O(1)</td>
<td>0.97</td>
<td>2.05</td>
<td>0.0078</td>
</tr>
<tr>
<td></td>
<td>Fe–Cl</td>
<td>0.19</td>
<td>2.25</td>
<td>0.0032</td>
</tr>
<tr>
<td>FC3</td>
<td>Fe–O(O)</td>
<td>4.36</td>
<td>2.01</td>
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<tr>
<td></td>
<td>Fe–O(1)</td>
<td>1.37</td>
<td>2.05</td>
<td>0.0078</td>
</tr>
<tr>
<td></td>
<td>Fe–Cl</td>
<td>0.27</td>
<td>2.26</td>
<td>0.0050</td>
</tr>
<tr>
<td>FC4</td>
<td>Fe–O(O)</td>
<td>3.95</td>
<td>2.01</td>
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<td></td>
<td>Fe–O(1)</td>
<td>1.71</td>
<td>2.04</td>
<td>0.0078</td>
</tr>
<tr>
<td></td>
<td>Fe–Cl</td>
<td>0.34</td>
<td>2.26</td>
<td>0.0065</td>
</tr>
<tr>
<td>FC5</td>
<td>Fe–O(O)</td>
<td>2.40</td>
<td>2.01</td>
<td>0.0073</td>
</tr>
<tr>
<td></td>
<td>Fe–O(1)</td>
<td>3.00</td>
<td>2.04</td>
<td>0.0078</td>
</tr>
<tr>
<td></td>
<td>Fe–Cl</td>
<td>0.60</td>
<td>2.28</td>
<td>0.0092</td>
</tr>
</tbody>
</table>

a The $E_0$ value for the Fe–O and Fe–Cl interactions are 7.122 and 7.130 keV, respectively, and $S_0^2$ = 1.19; b O(0) and O(1) represent oxygen atoms in [Fe(OH$_2$)$_6$]$^{3+}$ and [FeCl(OH$_2$)$_5$]$^{2+}$, respectively; c fixed during the curve fitting procedure.

Fig. 4. The observed (dots) and calculated (solid lines) values of the imaginary (a) and real (b) parts of the Fourier transformations for solutions FC0 (A) and FC5 (B).

Table IV. Averaged bond lengths in 6-coordinate octahedral monochloro and dichloro iron(III) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$-R$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[FeCl(OH$_2$)$_3$]$^{2+}$</td>
<td>Fe–O</td>
</tr>
<tr>
<td>FeCl(dmf)$_3$:(FeCl)$_3$O</td>
<td>2.05</td>
</tr>
<tr>
<td>FeCl(dms)$_3$:(FeCl)$_3$</td>
<td>2.03</td>
</tr>
<tr>
<td>FeCl(oda)(OH)$_2$</td>
<td>2.03</td>
</tr>
<tr>
<td>FeCl(dmso)$_3$</td>
<td>2.19</td>
</tr>
<tr>
<td>FeCl(dppe)$_3$</td>
<td>2.12</td>
</tr>
<tr>
<td>FeCl(xb)$_3$</td>
<td>2.11</td>
</tr>
</tbody>
</table>

The Fe–Cl bond length in [FeCl(OH$_2$)$_3$]$^{2+}$ is clearly shorter than that of ca. 2.35 Å for the dichloro iron(III) complexes [41 - 43]. The Fe–O bond distance (2.05 Å) in [FeCl(OH$_2$)$_3$]$^{2+}$ is also in agreement with those (2.01 - 2.03 Å) in 6-coordinate octahedral monochloro iron(III) complexes (see Table IV) and is slightly longer than that in [Fe(OH)$_2$)$_6$]$^{3+}$ (2.01 Å). The $\sigma$- and $\pi$-donations by a chloride ion enhance the electronic repulsion on the iron(III) center and reduce the formal charge on the iron(III) ion. These effects contribute to the elongation of the Fe–O bonds in [FeCl(OH$_2$)$_3$]$^{2+}$. Interestingly, according to the crystal structures of [FeCl(dmf)$_3$]$^{2+}$ [29] and [FeCl(dms)$_3$]$^{2+}$ [30], the five Fe–O distances in...
each crystal are not different within to ± 0.03 Å, although the Fe–O bond at the trans position of the chloride ion is expected to be longer than the other four bonds at the cis position. This seems to be due to the π-donation of the chloride ion, which can electronically influence the cis position, in addition to the σ-donation which makes the greatest elongating contribution to a trans ligand. Five similarly elongated Fe–O bonds are then expected for the monochloro iron(III) complexes.

This paper has demonstrated that EXAFS spectroscopy has a unique advantage for analysis of equilibria in solution. The formation constants of metal complexes and the structure parameters around the metal center can be simultaneously determined using the same experimental data. Because organic materials have high transparency to X-rays, the chemical equilibria concerning metal ions in living samples will be also examined in situ by the present EXAFS technique.

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