Iron(III) complexation in hydrothermal solutions –
An experimental and theoretical study

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Iron(III) hydrolysis and chloro complexation in hydrothermal solutions was studied experimentally and theoretically to 200°C at water vapour saturation pressure. The strong ligand-to-metal charge transitions at wavelengths below 400 nm were used to obtain number of absorbing species, molar absorptivities ($\epsilon$), and equilibrium formation constants using principle component analysis of the spectra. Density-functional-theory calculations of the ground state geometries, energies and UV-Vis absorption spectra were made of iron(III) hydroxo and chloro complexes with up to four chlorine atoms. In acid chloride free solutions Fe$^{3+}$, occupying octahedral coordination, hydrolysis to form FeOH$^2+$. With increasing chloride concentration and temperature, iron(III) chloride complexes become important with FeCl$^{2+}$, FeCl$_2^+$, FeCl$_3$(aq) and FeCl$_4$ forming. The progressive addition of Cl$^-$ to the Fe$^{3+}$ ion the complex geometry changes from octahedral to tetrahedral coordination of the FeCl$_4$ ion, whereas FeCl$_3$(aq) is either tetrahedral or trigonal dipyramidal. The respective formation constants were derived experimentally between 25 and 200°C.

Introduction

A knowledge of the stability of iron complexes in hydrothermal solutions is important for quantitative interpretation of the chemical behaviour of iron in hydrothermal systems. It is generally accepted that iron is predominantly transported as Fe(II) species in reduced acid fluids whereas Fe(III) hydroxy complexes become also important in reduced alkaline solutions. Previous studies on iron transport have mainly focused on the complexation of Fe(II) with chloride ligands and the hydrolysis of Fe(II) and Fe(III) in hydrothermal solutions [e.g. 1-8]. Previous studies on Fe(III) complexes stabilities in hydrothermal solutions have only been carried out to 90°C [9-10].

The aim of this study was, therefore, to experimentally determine the stability of Fe(III) hydrolysis and chloro complex stabilities in hydrothermal solutions and complex structure using spectrophotometric measurements and theoretical calculations.

Methods

All solutions were prepared from double distilled, deionised water on the molal scale from aqueous stock solutions of Fe(III) chloride and Fe(III) perchlorate, standardised hydrochloric and perchloric acid and sodium chloride.

The UV-Vis spectra of 58 solutions were measured with a Varian Cary 4E spectrophotometer from 190 to 500 nm. Data were collected at seven temperatures between 25 and 200°C and ~20 bars above the saturated water vapour pressure. The experiments were carried out using a flow-through, gold-lined optical cell with silica window, an online vacuum degasser system, HPLC pump and a back-pressure regulator [11]. All the parts in contact with the experimental solutions were made of inert PEEK or gold lined. All spectra were collected during flow-through mode and equilibrium solution composition was assessed using a kinetic solution program and was obtained when the absorbance readings in the 190 to 500 nm range was stable which typically occurred within 15 minutes.

The total Fe concentrations ranged from 6.184×10$^{-5}$ to 1.652×10$^{-3}$ mol kg$^{-1}$. The HCl concentration was between 1.260×10$^{-3}$ and 0.128 mol kg$^{-1}$; the NaCl concentration was between 0 and 1.805 mol kg$^{-1}$; and the HClO$_4$ concentration was between 0 and 0.398 mol kg$^{-1}$. 
Beer’s law was used to relate the absorbance measurements to the molarity of absorbing species using principle component analysis [12-14]. The molal scale of the analytical results were converted to the molar scale of the Beer’s law using densities of HClO₄, HCl and NaCl solutions [15-17]. Individual ion activity coefficients were estimated using a modified Debye-Hückel equation [18].

In order to gain insight into the molecular structures and electronic transitions of the title compounds, we have also undertaken a systematic quantum chemical study of the most stable complexes and their corresponding vertical excitation energies. Several mixed Fe(III) aquo-chloro complexes have been chosen as theoretical targets for the present study. All calculations were performed using the Gaussian03 suite of programs [19]. Complex structures were optimised at the B3LYP level. We applied the LanL2DZ effective core potential scheme for Iron. The other atoms (H, O, Cl) were described by Pople-style split valence basis sets up to 6-311+G(3df,3dp). Electronic

Figure 1: The lowest energy geometries of the Fe(III) aquo-chloro and aquo-hydroxo complex series as determined at the B3LYP/LANL2DZ level of theory.
Table 1. Theoretical and Experimental Bond Lengths (Å) for the Fe(III) aquo-chloro complex series

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Exp.</th>
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<tr>
<td></td>
<td>Fe-O</td>
<td>Fe-O</td>
</tr>
<tr>
<td></td>
<td>Fe-Cl</td>
<td>Fe-Cl</td>
</tr>
<tr>
<td>Fe(H₂O)₆³⁺</td>
<td>2.06</td>
<td>2.01b, 2.10e</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.99b, 2.03d</td>
</tr>
<tr>
<td>FeCl(H₂O)₅²⁺</td>
<td>2.10-2.15</td>
<td>2.00g</td>
</tr>
<tr>
<td></td>
<td>2.18</td>
<td>2.28g</td>
</tr>
<tr>
<td>trans-FeCl₂(H₂O)₄⁺</td>
<td>2.13</td>
<td>2.08f</td>
</tr>
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<td></td>
<td>2.23</td>
<td>2.29f</td>
</tr>
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<td>cis-FeCl₂(H₂O)₃⁺</td>
<td>2.13-2.24</td>
<td>2.19, 2.00e</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>2.28e</td>
</tr>
<tr>
<td>FeCl₃(H₂O)₂⁰</td>
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<td>2.04e</td>
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<td>2.27</td>
<td>-</td>
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<td></td>
<td>2.23</td>
<td>-</td>
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<tr>
<td>FeCl₄⁻</td>
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<td>2.25b</td>
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<tr>
<td></td>
<td>2.26</td>
<td>2.24f</td>
</tr>
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</table>

*aNeutron Diffraction [20]; bEXAFS [22]; cEXAFS [21]; dX-ray Diffraction [24];
EXAFS [23]; eX-ray Diffraction [25].

excitations were evaluated at the B3LYP level using the ECP LanL2DZ for iron and 6-311+G(3df,3dp) basis sets for H, O and Cl.

Results and discussion

Complex geometries

Figure 1 depicts optimized ground state geometries for the aquated Fe(III) ion as well as the mono-, di-, tri- and tetrachloro Fe(III) complexes. Also shown are two additional Fe(III) aquo-hydroxo complexes together with experimentally derived structural data from neutron scattering [20], EXAFS [21-23] and X-ray diffraction measurements [24-25]. From Figure 1 it may be seen that the Fe(III) hexahydrate complex has a characteristic T₆ structure in which water molecules coordinate the central metal ion in a pseudo-octahedral arrangement. The calculated Fe-O bond distance is around 2.06 Å and lies well within the range of experimentally determined values (2.10 Å [22] and 1.99 Å [21]).

Several features highlight the substantial distortion in the coordination geometry of the Fe(III) hexahydrate complex upon substitution of one water molecule with a chloride ion: (i) Fe-O bond lengths in FeCl(H₂O)₅²⁺ complex (a2) vary significantly from 2.104 to 2.138 Å and give rise to an average Fe-O bond distance (2.126 Å) that is around 0.06 Å longer than for the hexahydrate (a1) and (ii) the angles subtended by the water molecules in FeCl(H₂O)₅²⁺ (a2) (average 83.9) are significantly smaller than those subtended by water in the regular Fe(H₂O)₆⁵⁺ octahedral complex (a1). Substitution of a second water molecule with a Cl⁻ leads to the formation of two principal conformers, the trans-FeCl₂(H₂O)₄⁻ (a3) and cis-FeCl₂(H₂O)₄⁻ complexes (a4). The average Fe-O and Fe-Cl bond distances in the trans-FeCl₂(H₂O)₄⁻ complex (a3) are 2.129 and 2.266 Å, respectively, and are in fair agreement with Fe-O and Fe-Cl bond distances obtained from EXAFS [23] and X-ray diffraction [25] measurements (Table 1). It should be noted that the calculated average Fe-Cl bond distance in the cis isomer (a4) is 2.191 Å, which is considerably shorter (by around 0.1 Å) than the measured values of 2.29 [25] and 2.30 Å [23] for the dichloro complex. In this context it should also be remarked, that for the cis and trans isomers of the dichloro complex, the complete basis set limit energies are -2487.475375 and -2487.484910 Hartrees, respectively, and are in fair agreement with Fe-O and Fe-Cl bond distances obtained from EXAFS [23] and X-ray diffraction [25] measurements (Table 1). We therefore anticipate that the trans isomer (a3) is thermodynamically most stable arrangement of the FeCl₂(H₂O)₄⁻ complex and would likely predominate in aqueous solution. The replacement of an equatorial water molecule in trans-FeCl₂(H₂O)₄⁻ by a chloride ion yields the octahedral trichloro FeCl₃(H₂O)₃ complex (a6) (note, we also considered the trigonal bipyramidal complex a5 here). However, we are not aware of any experimental studies that have directly probed the structure of the octahedral trichloro complex a6. Interestingly, there are experimental EXAFS...
distance data that appear to point to the existence of an intermediate “FeCl₃(H₂O)₂” complex in highly concentrated FeCl₃ solutions (> 4mol L⁻¹) in which Fe-Cl and Fe-O distances were found to be around 2.22 and 1.93 Å [23] (see Figure 1, a5). However, Asakura et al. [23] suggest that in highly concentrated FeCl₃ solutions the solute is partly present as FeCl₂(H₂O)⁴⁺ and FeCl₄⁻ without any indication for the existence of either FeCl₃(H₂O)₂ or FeCl₃(H₂O)₃ complexes (i.e., Fe-Cl and Fe-O distances and coordination numbers for FeCl₃(H₂O)₃ reported by Magini and Radnai [25] are considered to be smeared out, average values of the di- and tetra-chloro complex rather than real distances of a tri-chloro complex). The theoretical Fe-Cl distance in the tetrahedral FeCl₄⁻ complex is 2.256 Å (a7), which is very close to the value of 2.25 [23] and 2.24 Å [25] obtained from EXAFS.

We also performed a suite of preliminary time-dependent density functional (i.e. B3LYP-level) calculations on the electronic absorption spectra of the above Fe(III) aquo-chloro complexes and results thereof are shown in Figure 2. We wish to emphasize here that the goal of this effort is to identify the relative positions and intensities of absorption bands of the stepwise complexes; no attempt was made to test for the effect of the functional, basis set size and continuum solvation on band position and intensity). As may be seen from Figure 2 all complexes exhibit characteristic electronic transitions that are shifted in position and intensity as a function of the stepwise replacement of water with chloride ions.

**Absorbance spectra**

UV-Vis spectra of Fe(III)+H₂O±HCl±HClO₄±NaCl solutions were collected between 25 and 200°C at saturated water vapour pressure. Principle component analysis of the results reviled the numbers of absorbing species, which was found to depend on temperature. At 25 and 50°C four absorbing species were identified considered to be Fe⁵⁺, FeOH⁵⁺, FeCl⁵⁺ and FeCl₃⁻. At 100°C only 3 species were identified, FeOH⁺, FeCl⁺ and FeCl₂⁺ and FeCl₃(aq) appeared at t ≥150°C. At the far UV end of the spectra Cl⁻ and ClO₄⁻ absorbing species and their bands shifted to higher wavelength with increasing temperature. However, this spectral range was not included in the final data interpretation.

The major electronic transitions for Fe(III) hydorxy and chloro complexes are attributed to ligand-to-metal charge transfers (LMCT) (Fig. 3). One major band was recognised for Fe⁵⁺, shifting from λ_max = 240 to 242 nm at 25 to 200 °C, respectively. For FeOH⁺ two major electron transitions were observed at λ_max = 205 nm at 25 °C shifting to 207 nm 100 °C and λ_max = 297 nm at 25 °C shifting to 301 nm at 200 °C. In acid solutions with increasing chloride concentration two major bands appears at λ_max = 222 and 333 nm due to the formation of FeCl⁺ and at λ_max = 339 nm for FeCl₂⁺ at 25°C. The transitions for FeCl⁺ and FeCl₂⁺ occur at very similar wavelengths. However, FeCl₃⁻ spectral are much more intensive and have a

![Figure 2: Theoretical oscillator strengths of the vertical transitions for Fe(III) aquo-chloro and aquo-hydroxo complexes in the uv-vis range.](image-url)
transitions are much more intensive broader wavelength range. This similarity resulted in great difficulties in resolving accurate molar absorptivities for FeCl2+ and FeCl3+. At \( t \geq 150 \)°C FeCl3(aq) became an important species with two peak maxima at \( \lambda_{\text{max}} = 313 \) and 360 nm. These changes in absorption of FeCl3(aq) are considered to arise from the change in the geometry of the iron(III) chloro complexes.

**Equilibrium formation constants**

The values for the equilibrium formation constant obtained in this study according to the reactions

\[
\begin{align*}
\text{Fe}^{3+} + \text{H}_2\text{O} & = \text{FeOH}^{2+} + \text{H}^+ & \beta_{10} \\
\text{Fe}^{3+} + \text{Cl}^- & = \text{FeCl}^{2+} & \beta_{01} \\
\text{Fe}^{3+} + 2\text{Cl}^- & = \text{FeCl}_2^{2+} & \beta_{02} \\
\text{Fe}^{3+} + 3\text{Cl}^- & = \text{FeCl}_3(\text{aq}) & \beta_{03}
\end{align*}
\]

are listed in Table 2 and plotted in Fig. 4. For \( \beta_{10} \) our results are in excellent agreement with those of Zotov and Kotova [3-4]). For Fe(III) chloride complexes, the results obtained in this work are very similar to those reported by Tagirov et al. [9] for \( \beta_{02} \) and agree within experimental values of Liu et al. [10] for \( \beta_{02} \) and \( \beta_{03} \) at \( t <100 \)°C. No experimental data are available at higher temperatures for Fe(III) chloride complexes.

![Figure 3: Molar absorptivities at 25°C and 150°C for various Fe(III) species in acid chloride solutions.](image)

At temperatures between 25 and 100°C Fe\(^{3+}\) and/or FeOH\(^{2+}\) were major absorbing species in our experimental runs as well as FeCl\(^{2+}\) and FeCl\(^{3+}\) and therefore the values for \( \beta_{10} \), \( \beta_{01} \) and \( \beta_{02} \) were accurately obtained. On the other hand, at \( t \geq 150 \)°C Fe\(^{3+}\) and FeOH\(^{2+}\) were only significant in 1-3 experiments containing chloride (>5% of total iron). Therefore, much higher uncertainties are associated with the cumulative formation constants at the highest temperatures. However, the stepwise formation constants \( K_{02} \) and \( K_{03} \) were associated with much lower errors especially at the higher temperatures as these were major species in the fitting calculations.

In order to derive smooth equilibrium formation constants, the experimental formation constants were fitted to a density model [27]. The resulting constants extrapolated outside the experimental conditions are listed in Table 2 and plotted in Fig. 4.

**Conclusions**

The Fe\(^{3+}\) hydrolysis and Cl\(^-\) complexation in acid solutions were studied experimentally to 200 °C by UV-Vis spectrophotometry and theoretically using density-functional-theory calculations. In acid chloride free solutions Fe\(^{3+}\), occupying octahedral coordination ([Fe(H\(_2\)O)\(_6\)]\(^{3+}\)), hydrolysis to form [Fe(OH)(H\(_2\)O)\(_5\)]\(^2+\). With increasing chloride concentration and temperature Fe(III) chloride complexes become increasingly important with [Fe(Cl)(H\(_2\)O)\(_5\)]\(^2+\), trans-[Fe(Cl)\(_2\)(H\(_2\)O)\(_4\)]\(^+\), [Fe(Cl)\(_3\)(H\(_2\)O)\(_3\)]\(^0\) (or [Fe(Cl)\(_3\)(H\(_2\)O)\(_2\)]\(^0\)) and FeCl\(^4-\) forming. Upon addition of Cl\(^-\) to the Fe\(^{3+}\) ion the geometry of the Fe(III) chloro complexes changes.

![Figure 4: Equilibrium formation constants for Fe(III) hydrolysis and chloro complexation as a function of temperature at water vapour saturation pressure.](image)
from octahedral to tetrahedral coordination of the FeCl$_4$\(^{-}\) ion, whereas FeCl$_3$(aq) is either tetrahedral or trigonal dipyramidal. The respective formation constants were derived experimentally between 25 and 200°C.

**Table 2. Equilibrium formation constants for chloroiron(III) complexes obtained in this study\(^*\)**

<table>
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<tr>
<th>°C</th>
<th>log$\beta_{1,0}$</th>
<th>log$\beta_{0,1}$</th>
<th>log$\beta_{0,2}$</th>
<th>log$\beta_{0,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>-2.18±0.01</td>
<td>1.42±0.02</td>
<td>1.98±0.08</td>
<td>0.72</td>
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<tr>
<td>50</td>
<td>-1.71±0.04</td>
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</tr>
<tr>
<td>100</td>
<td>-0.68±0.07</td>
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<tr>
<td>150</td>
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</tr>
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<td>300</td>
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<td>6.75</td>
<td>12.88</td>
<td>16.12</td>
</tr>
</tbody>
</table>

\(^*\) Values in italics are calculated using density function.

**Literature**


[17] J.M. Simonson, C.S. Oakes and R.J. Bodnar: Densities of NaCl(aq) to the temperature 523 K at pressures to 40 MPa measured with a


