Kinetic studies on the solvent extraction of iron(III) from aqueous solution with 1-phenyl-3-methyl-4-(p-nitrobenzoyl)pyrazol-5-one dissolved in chloroform: Rate of forward extraction

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The rate of forward extraction of iron(III) from aqueous solution using 1-phenyl-3-methyl-4-(p-nitrobenzoyl)pyrazol-5-one, HNP in chloroform has been investigated at various conditions. Experimental observation shows that the rate of forward extraction is first order each with respect to \([\text{Fe(III)}]\) and \([\text{HNP}]_{\text{org}}\), and inverse first order with respect to \([\text{H}^+]\). The rate of forward extraction of Fe(III) is proposed to be controlled by the formation of the first complex between \(\text{Fe(H}_2\text{O)}_5^{2+}\) or \(\text{Fe(H}_2\text{O)}_5\text{OH}^{2+}\) and the extractant anion, \(\text{NP}^-\). The rate constant, \(k_f\) for the forward extraction and the extraction equilibrium constant, \(K_{\text{ex}}\) have been determined respectively as \(5.83 \times 10^2\) s\(^{-1}\) and 0.18.

Solvent extraction studies of iron(III) have been undertaken by various workers\(^1\) using \(\beta\)-diketones, especially the acyl pyrazolones and their derivatives, but studies on their rates of extraction have been limited. The rate of extraction of iron(III) using thenoyltrifluoroacetone (HTTA) has been reported to be governed by slow formation of the first complex between iron and HTTA anion in the aqueous phase\(^5\). Kinetic studies on the extraction of Fe(III) using \(\beta\)-isopropyltriptolide, alkylphosphoric acid and 8-hydroxyquinoline have also been reported\(^8\)\(^{11}\).

However, kinetic studies on the extraction of iron(III) using nitro derivatives are almost lacking. It is on this premise that the present study was undertaken. Eigen\(^12\), nevertheless, postulated that the rate of extraction of metal ions from aqueous solutions is slow when the charge is large and/or the radius is small. This has been attributed to the slow substitution of the coordinated water molecules. Herein we report the kinetics of extraction of iron(III) with 1-phenyl-3-methyl-4-(p-nitrobenzoyl)pyrazol-5-one (HNP) in chloroform and its possible mechanism.

Experimental

The HNP was prepared from high grade \(p\)-nitrobenzoyl chloride and 1-phenyl-3-methyl-5-pyrazolone (HPMP), which was prepared from analytical grade ethylacetoacetate and phenylhydrazine\(^13\).\(^{14}\). The nitropyrazolone was recrystallized from ethanol and dissolved in chloroform to obtain the desired concentrations. All other reagents were of analytical grades, except otherwise stated.

The stock solution of Fe(III) was prepared by dissolving ferric ammonium sulphate (0.2169) in 0.1 M \(\text{H}_2\text{SO}_4\) solution (250 ml). Further dilutions were made by adding appropriate amounts of distilled water and/or suitable buffer solutions (KCI/HCl and NaAc/HAc) to desired \(p\text{H}\). The PYE Unicam SP8-100 spectrophotometer was used for all spectrophotometric measurements, and TOA Digital \(p\text{H}\) meter model HIM-208 for \(p\text{H}\) measurements.

Extraction procedure

The details of the extraction procedure are essentially the same as those described elsewhere\(^2\)\(^7\). The studies on the rate of forward extraction were carried out by mixing equal volumes (4 ml) of 4.5 \(\times 10^{-5}\) M Fe(III) solution and 0.002-0.05 \(M\) HNP in chloroform in stoppered extraction bottles. Each mixture was agitated for a specific time interval (5-240 mins) by means of a mechanical shaker at a speed so high that no acceleration of the extraction rate was observed on further increase in the extraction speed. This eliminated the effects due to material transport (diffusion) and interfacial effects in the system\(^15\). After extraction, the phases were allowed 30 min settling time, after which aqueous aliquots were taken for analysis. The concentration of Fe(III) in the aqueous phase was determined spectrophotometrically\(^16\) using 1,10-phenanthroline at 480 nm, while that in the organic phase was determined by difference. All experiments were conducted at 26 ± 0.5°C and constant ionic strength of 0.3 M, maintained by the use of sodium sulphate. Preliminary experiments show that sulphate ions had no effect on extractions.

The extraction equilibrium of Fe(III) with HNP was achieved by agitating aqueous solutions of
Fe(III) at pH 3 with various concentrations of HNP in chloroform solution for 45 min. The distribution ratio, D, of Fe(III) in each case was calculated as the ratio of the concentration of Fe(III) in the organic phase to that in the aqueous phase. From the extraction data, the extraction equilibrium constant, $K_{ex}$ was computed as follows:

$$\text{Fe(III)_{aq}} + 3\text{HNP}_{\text{org}} \rightarrow K_{ex}\text{Fe(NP)}_{3\text{org}} + 3\text{H}^+ \quad \ldots (1)$$

$$K_{ex} = \frac{[\text{Fe(NP)}_{3\text{org}} [\text{H}^+]^3]}{[\text{Fe(III)}]_{\text{aq}} [\text{HNP}]_{\text{org}}^3} \quad \ldots (2)$$

$$D = \frac{[\text{H}^+]_{\text{aq}} [\text{HNP}]_{\text{org}}^{-3}}{[\text{Fe(III)}]_{\text{aq}}^{-1}} \quad \ldots (3)$$

and

$$D = K_{ex}[\text{HNP}]_{\text{org}}^{-3} \quad \ldots (4)$$

where D is the distribution ratio,

$$\frac{[\text{Fe(NP)}_{3\text{org}}]}{[\text{Fe(III)}]_{\text{aq}}}$$

From Eq. 4

$$\log D = \log K_{ex} + 3\log[\text{HNP}]_{\text{org}} + 3\text{pH} \quad \ldots (5)$$

**Results and discussion**

**Extraction equilibrium**

The data in Table 1 show the variation of distribution ratio with extractant concentration. A plot of log-log values of D versus [HNP]org was linear with a slope of 3.0. This meant that three moles of HNP were involved in complexation with one mole of Fe(III) ion, and representing a third-power dependence of D on [HNP]org, as depicted in Eqs (4) and (5). The value of $\log K_{ex}$ was calculated as -0.75.

**Kinetics of reaction**

The rate of extraction was followed as the rate of disappearance of Fe(III)aq, and fitted to Eq. (6)

$$-\frac{d\text{Fe(III)}}{dt} = K_r[\text{Fe(III)}]^y[\text{HNP}]^y[\text{H}^+]^{-1} \quad \ldots (6)$$

**Table 1—Extraction equilibrium data (pH = 3)**

<table>
<thead>
<tr>
<th>log HNP</th>
<th>log D</th>
<th>log $K_{ex}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.70</td>
<td>0.10</td>
<td>-0.80</td>
</tr>
<tr>
<td>-2.50</td>
<td>0.70</td>
<td>-0.80</td>
</tr>
<tr>
<td>-2.40</td>
<td>0.95</td>
<td>-0.85</td>
</tr>
<tr>
<td>-2.30</td>
<td>1.30</td>
<td>-0.80</td>
</tr>
<tr>
<td>-2.25</td>
<td>1.60</td>
<td>-0.65</td>
</tr>
<tr>
<td>-2.00</td>
<td>2.35</td>
<td>-0.65</td>
</tr>
<tr>
<td>-1.82</td>
<td>2.65</td>
<td>-0.68</td>
</tr>
</tbody>
</table>

Ave $\log K_{ex}$ = -0.75 and $K_{ex}$ = -0.18

**Fig. 1—Rate of forward extraction of Fe(III) with respect to [H+] [HNP] = 0.02 M, slope = $S_{H^+}$**
Table 2(a)—Kinetic data ([HNP]org = 0.02 M, [Fe(III)] = 1.8 \times 10^{-7} \text{ mM})

<table>
<thead>
<tr>
<th>$-\frac{d[\text{Fe(III)}]}{dt}$</th>
<th>$[\text{H}^+]$</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0004</td>
<td>0.32</td>
<td>$3.6 \times 10^4$</td>
</tr>
<tr>
<td>0.001</td>
<td>0.10</td>
<td>$3.5 \times 10^4$</td>
</tr>
<tr>
<td>0.005</td>
<td>0.03</td>
<td>$3.8 \times 10^4$</td>
</tr>
<tr>
<td>0.0122</td>
<td>0.01</td>
<td>$3.4 \times 10^4$</td>
</tr>
<tr>
<td>0.038</td>
<td>0.0032</td>
<td>$3.5 \times 10^4$</td>
</tr>
<tr>
<td>0.182</td>
<td>0.00063</td>
<td>$3.2 \times 10^4$</td>
</tr>
</tbody>
</table>

Ave $K_f = 3.50 \times 10^4 \text{ min}^{-1}$

Ave $K_f = 5.83 \times 10^2 \text{s}^{-1}$.

(b)—Kinetic Data ([H+] = 0.01 M, [Fe(III)] = 1.8 \times 10^{-7} \text{ mM})

<table>
<thead>
<tr>
<th>$-\frac{d[\text{Fe(III)}]}{dt}$</th>
<th>HNP</th>
<th>$K_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0013</td>
<td>0.002</td>
<td>$3.55 \times 10^4$</td>
</tr>
<tr>
<td>0.0033</td>
<td>0.005</td>
<td>$3.67 \times 10^4$</td>
</tr>
<tr>
<td>0.0063</td>
<td>0.010</td>
<td>$3.5 \times 10^4$</td>
</tr>
<tr>
<td>0.0096</td>
<td>0.015</td>
<td>$3.54 \times 10^4$</td>
</tr>
<tr>
<td>0.0133</td>
<td>0.02</td>
<td>$3.69 \times 10^4$</td>
</tr>
</tbody>
</table>

Ave $K_f = 3.59 \times 10^4 \text{ min}^{-1}$

Ave $K_f = 5.97 \times 10^2 \text{s}^{-1}$.

**Mechanism**

The rate law shows that the determining step is the formation of the first complex between iron (III) ion and the extractant anion, NP⁻.

Fe(III) + NP⁻ $\rightleftharpoons [\text{Fe(NP)}]^2{+}$ ... (10)

because

$[\text{NP}] = K_{\text{HNP}} \cdot \frac{[\text{HNP}]}{[\text{H}^+]}$ ... (11)

where $K_{\text{HNP}}$ is the dissociation constant of HNP. Since the actual complex formed during extraction is Fe(NP)$_3$$_{\text{org}}$, the addition of second and third ligands must be fast.

The actual mechanism may be the formation of ion pair followed by a slow dissociative step (Eigen and Wilkens)$^{17,18}$ leading

$\text{Fe(H}_2\text{O)}^\delta{+} + \text{Fe(H}_2\text{O)}^\delta{+} \text{NP}^-$ $\rightarrow \text{Fe(H}_2\text{O)}^\delta{+} \text{NP}^-$ ... (12)

$\text{Fe(H}_2\text{O)}^\delta{+} \text{NP}^-$ $\rightarrow \text{Fe([H}_2\text{O)}_4 \text{NP})^2{+} + 2\text{H}_2\text{O}$ ... (13)

to the formation of the first chelate ring of monopyrazolonato-tetraaquo-iron complex. It is expected that this step is followed by more rapid successive reaction, to produce a neutral tris-pyrazolonato-iron chelate, which eventually is transferred to the bulk organic phase, steric factors notwithstanding.

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**References**