Kinetics of extraction of cobalt(II) by quinolinol and its back extraction using $^{58}$Co tracer

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The kinetics of extraction of cobalt(II) by 8-quinolinol has been studied using $^{58}$Co tracer in the pH range 5-6.2 at 29°C and in the temperature range 26.8-44°C for pH 5.2 and 5.4 at an ionic strength 0.1 M. The rate of cobalt(II) extraction by oxine is pseudo-first-order with respect to [oxine]. The kinetics of back extraction of bis(8-quinolinate)cobalt(II) from chloroform to aqueous phase by mineral acids has been also studied. The activation energy, enthalpy and entropy of the extraction reaction have been evaluated.

8-Quinolinol has been used for the determination of a number of metal ions. Ritcey and Lucas have shown that in the extraction of Cu-Fe mixture by Kelex 100, a derivative of 8-quinolinol, some iron is rapidly extracted initially (in less than 1 min), then no further extraction occurs for about 30 min, after which extraction increases with time. The iron initially extracted could be quantitatively accounted for by the oxine in Kelex 100. These results pointed to a significant kinetic role of the oxine impurity in Kelex 100 and led to a study of the kinetics of extraction of Cu and Fe by oxine as a prelude to a study of the Kelex 100 reactions.

Guesnet et al. observed that Co(II) undergoes oxidation by atmospheric oxygen to Co(III), irreversibly, during the course of extraction with 8-quinolinol and Kelex 100. They also reported that the cobalt(II) chelates were poorly strippable from organic phase, but their oxidation could be delayed by the addition of versatic acid and TOPO.

Similar oxidation of Co(II) was observed during the extraction of Co(II) adducts of 2-methyl-8-quinolinol and 4-methyl-8-quinolinol with 2,4-lutidine and 2,4,6-collidine; the adducts were extracted as Co(III) species. A kinetic study of the extraction of the Co(II) chelates in presence of 2,4-lutidine and 2,4,6-collidine revealed that the extraction was first order and the rate of oxidation decreased with the increase in [pyridine]. Kinetics of the adduct formation in the Co(II) chelates of 8-quinolinol and its analogues were also studied spectrophotometrically, in a single phase system. The present work on the kinetics of the extraction of Co(II) was undertaken as a part of our research programme dealing with certain metal adducts of 8-quinolinol in two phase system.

Experimental
Carrier-free $^{58}$Co($^{12}$~71d) was supplied by BRIT, Trombay as CoCl$_2$ in dilute HCl. It was mixed with a few drops of saturated solution of hydroxylamine hydrochloride to prevent the oxidation of Co(II) and was sufficiently diluted with distilled water. Aliquots of $^{58}$Co (0.2 ml) were taken every time for the equilibration study so as to give $2 \times 10^5$ cts/min.

ExcelaR grade 8-quinolinol and chloroform, supplied by Glaxo India, were used for the kinetic study.

A set of Clarke and Lubs buffer solutions was prepared for the pH range 5.0-6.2. Ionic strength was maintained at 0.1 M by adding requisite amount of sodium perchlorate in buffers.

Radioactivity was counted on $2'' \times 2''$ well type Na(Tl) detector system connected to a scintillation spectrometer supplied by ECIL (Hyderabad).

A Kahn type shaking machine was used for the equilibration study. A shaking rate of 250 strokes/min was employed at ambient temperature.

Individual samples were equilibrated in stoppered centrifuge tubes in reciprocated manner for varying time intervals. For the kinetic study at different temperatures, the samples were shaken in 50 ml stoppered conical flasks fitted in a thermostated water bath.

For the kinetic study of stripping, a pre-extracted cobalt(II)-8-quinolinolate solution in chloroform was used and equilibrated with hydrochloric acid of different concentrations with varying time interval.

In the extraction kinetics, samples of the aqueous phase were taken at different time intervals and $^{58}$Co activity was counted; whereas, in the stripping study, samples of the organic phase were taken for counting of the activity.

Results and discussion
In the classical reaction scheme, the rate controlling step is often the stepwise addition reaction of the chelating agent, i.e.,

$$M^{n+} + R \rightarrow \text{Products}$$
When the back reaction is negligible, the rate of metal removed from the aqueous phase is,

\[ \frac{d[M]^-}{dt} = k \cdot (M^{n+}) \cdot (R^-) \]  \hspace{1cm} (1)

where \( k \) is the forward reaction rate constant.

The extraction of cobalt from the start and up to approaching equilibrium can be represented as,

\[ a_0 - a_c \quad \text{at time } t \text{ in the aqueous phase.} \]

Then the rate constant for the forward extraction reaction of the first order is given as\(^2\),

\[ k_c = \frac{a_0 - a_c}{a_0 - a_c} = \ln \frac{a_0 - a_c}{a_0 - a_c} \]  \hspace{1cm} (2)

The rate constant for the back extraction of cobalt is given as,

\[ k_{bc} = \ln \frac{C_0}{C_i} \]  \hspace{1cm} (3)

where \( C_0 \) and \( C_i \) are the cobalt concentrations at the start and at time \( t \) in the organic phase.

The kinetic data obtained for the extraction of cobalt(II) with 8-quinolinol were plotted in accordance with Eq. (2) for different \([8-HQ] \) for respective pH when straight line plots were obtained with varying slopes. Fig. 1 shows typical plots obtained from Eq. 2. These straight line plots confirm that the rate of extraction is pseudo-first order with respect to cobalt(II). The slopes of these plots give directly the value of observed rate constants for the extraction of cobalt(II). The observed rate constants were obtained for various pH values between 5.0 and 6.2. These are given in Table 1. The data show that the observed extraction rate increases with increasing pH and [8-HQ].

The variations of the observed rate constants at various [8-HQ] and pH values were plotted. These plots showed good linear relationships between the log of observed rate constant, [oxine] and pH respectively. The slopes of these plots were found to be -1.48 and 1.

**Stripping of Co(II)**

The formation of CoQ₃ chelate due to oxidation of Co(II) to Co(III) by oxygenation was confirmed by the bathochromic shift observed in the absorption spectrum of CoQ₃ when the \( \lambda_{	ext{max}} \) got shifted from 403 nm to 410 nm\(^3\). The stripping ratio at equilibrium decreased when the time-lapse between the extraction and beginning of stripping increased. Addition of acidic compounds, such as versatic 10 acid or dichloroacetic acid, to the organic phase after extraction with 8-quinolinol decreased the oxidation rate\(^4\).

Back extraction of Co-8-quinolinolate into aqueous phase was tried with mineral acids like HCl, H₂SO₄ as well as with EDTA. Surprisingly, no stripping was observed with EDTA. Results of the back extraction of Co(II) with HCl and H₂SO₄ at various concentrations are given in Table 2 along with the observed rate constants obtained with HCl. From the data obtained it can be seen that HCl is a better stripping agent than H₂SO₄ and it is possible to back-extract cobalt from chloroform in contradiction to an earlier report\(^5\). From the present data, it can be seen that the rate constant of stripping increases very rapidly with the increase in [HCl].

This study elaborates the possibility of the extraction of cobalt(II) with 8-quinolinol at various pH values and at 28°C.

<table>
<thead>
<tr>
<th>[8-HQ] (mol L⁻¹)</th>
<th>( k \times 10^4 ) (s⁻¹) at pH</th>
</tr>
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<tbody>
<tr>
<td>5.0</td>
<td>6.0</td>
</tr>
<tr>
<td>5.2</td>
<td>6.2</td>
</tr>
<tr>
<td>5.4</td>
<td>6.2</td>
</tr>
<tr>
<td>5.6</td>
<td>6.0</td>
</tr>
<tr>
<td>5.8</td>
<td>6.2</td>
</tr>
<tr>
<td>6.0</td>
<td>6.2</td>
</tr>
</tbody>
</table>

Fig. 1: The first order expression as a function of time for different pH \([8-HQ] = 10^{-4} \); curve 1: pH = 5.0; curve 2: pH = 5.2; curve 3: pH = 5.4; curve 4: pH = 5.6; curve 5: pH = 5.8; curve 6: pH = 6.0; curve 7: pH = 6.2.
Table 2—Back extraction of Co(II) from CHCl₃ with HCl and H₂SO₄ and observed back-extraction rate constants with HCl at 28°C

<table>
<thead>
<tr>
<th>[Acid] (mol.L⁻¹)</th>
<th>% Back extn. with H₂SO₄</th>
<th>% Back extn. with HCl</th>
<th>Rate constants × 10⁴ (s⁻¹) with HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.18</td>
<td>7.98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>27.15</td>
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</tr>
<tr>
<td>3</td>
<td>29.1</td>
<td>10.34</td>
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<td>4</td>
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</tr>
<tr>
<td>5</td>
<td>33.36</td>
<td>47.61</td>
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</tr>
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<tr>
<td>6</td>
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<tr>
<td>6.6</td>
<td>100</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>100</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>

During this study, it was observed that the extraction of Co(II) increased markedly with the increase in temperature. The log D value increased from 0.05 at ambient temperature to 0.8 at 43°C. The thermodynamic constants of the extraction reaction could be determined from the experimental data taken at different temperatures. By plotting the log k values obtained against 1/T, the reciprocal of the absolute temperature, Arrhenius plots were obtained. The activation energy, and the pre-exponential factor A were calculated from the slope and the vertical intercept, respectively, of the linear plots by means of the least squares method. From these values, the activation enthalpy $H^\ddagger$ and the activation entropy $S^\ddagger$ were calculated by the following equations,

$$ H^\ddagger = E_a - RT $$

$$ S^\ddagger = R[\ln(Ah/kT) - 1] $$

where $h$ is the planck constant, $k$, the Boltzmann constant and $R$, the gas constant. These values obtained are as follows: $E_a = 19.56$ kJ mol⁻¹, $\Delta H^\ddagger = 17.06$ kJ mol⁻¹, $\Delta S^\ddagger = -200.5$ jK⁻¹ mol⁻¹.

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References