Micellar Effects on Reactions of Complex Ions in Solution: Retardation of Base Hydrolysis of (Isothiocyanato) (Imidazole) Bis(ethylenediamine) Cobalt(III) by Sodium Dodecyl Sulphate

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The rate of base hydrolysis of cis-(isothiocyanato)(imidazole)bis(ethylenediamine)cobalt(III) ion has been studied at 40.0 ±0.1°C in the presence of sodium dodecyl sulphate (SDS). The micellized surfactant strongly retards the rate of base hydrolysis of the imidazolato conjugate base species, cis-[en₂Co(im)NCS]⁺ (Cb⁺). The rate data at 0.01 ≤[SDS] ≤0.15, [OH⁻]₀ = 0.02 and 0.04 mol dm⁻³ could be satisfactorily analysed in terms of the pseudo-phase ion-exchange equilibrium model, Cb⁺ + Na⁺ ⇋ CbNa⁺ + Na⁺, where W and M denote the aqueous phase and the micellar pseudo-phase respectively. Independent spectrophotometric measurements establish the micellar binding of Cb⁺. Data analysis is consistent with the fact that the fully-micelle incorporated conjugate base species, CbNa⁺, is inert to base hydrolysis. It, however, undergoes spontaneous aquation in the micellar pseudo-phase at a rate much slower than that in the aqueous phase. This is believed to be due to the difference in the polarity of the microenvironment of the reactant in both the phases.

In the preceding papers¹⁻³ we have shown the effect of cationic and anionic micelles on the aquation and base hydrolysis of carboxylatopentaminecobalt(III) complexes. cis-(Isothiocyanato)(imidazole)bis(ethylenediamine)cobalt(III) is known to undergo deprotonation at the imino group of the coordinated imidazole⁴ in mild alkaline medium to generate the monopositive imidazolato conjugate base, cis-[en₂Co(im)NCS]⁺ (Cb⁺). Anionic micelle of sodium dodecyl sulphate (SDS) is a multivalent macroanion and hence interaction between Cb⁺ and the anionic micelle of SDS is expected. The present work has been undertaken to test the applicability of the pseudo-phase ion-exchange model for Cb⁺. Besides, selective partitioning of Cb⁺ to the anionic micelle is expected to inhibit the second order base hydrolysis of the conjugate base species, thereby enabling its spontaneous aquation amenable to kinetic investigation in the micellar phase. This will provide indirect support to the proposed spontaneous aquation path of Cb⁺ in aqueous medium and help clarifying ambiguity in the mechanism of the base hydrolysis of cis-[en₂Co(imH)NCS]⁺ as pointed out in our earlier paper⁴.

Materials and Methods

The synthesis and characterization of cis-(isothiocyanato) (imidazole)bis(ethylenediamine)cobalt(III) diperchlorate have been described elsewhere⁵. Sodium dodecyl sulphate (Fluka, AG) was purified by repeated crystallization from ethanol⁶, air-dried, stored over fused calcium chloride and its purity checked by determination of its cmc (=0.008 mol dm⁻³)⁶. All other chemicals used were of AR grade.

As before¹, the kinetic measurements were made spectrophotometrically using a Varian-Cary UV-visible spectrophotometer model 634S in the [complex] range of (1.7-2.0) × 10⁻⁴ mol dm⁻³. The rate of decrease of absorbance was followed at 310 nm at which the complex was the only significantly absorbing species (ε₃₁₀nm = 2034 dm³ mol⁻¹ cm⁻¹ in 0.02 mol dm⁻³ NaOH). The kinetic runs were carried out at 40°C under pseudo-first order conditions and the observed rate constants (kₐ) were calculated from the gradients of the plots of ln(A₀ - Aₙ) against t(s) using a least squares computer program adopted to IBM 1130 computer of the Utkal University. The standard deviation of the rate constant for any run was better than 1% and duplicate runs reproduced the rate constants within 5%.

Results and Discussion

Interaction of cis-[en₂Co(imNCS)⁺ (Cb⁺)] with SDS micelle

The c-s-[en₂Co(imH)NCS]²⁺ is a weak acid with pKₐ = 10.6 ± 0.1 at 25°C and ionic strength (I) = 0.3 mol dm⁻³ for the coordinated imidazole⁴. A lower value of pKₐ at lower ionic strength and at higher temperature¹ is expected. Complete deprotonation of NH of the coordinated imidazole at [OH⁻] = 0.02 and 0.04 mol dm⁻³ (35°C), is also indicated as the zero time absorption spectrum (extrapolated; 280-370 nm) of the relatively more absorbing conjugate base cis-[en₂Co(im)NCS]⁺ is independent of [OH⁻]₀. SDS
has very little effect on the absorption spectrum of the conjugate acid species. The absorption spectrum of the imidazolato species (Cb$^+$) is, however, strongly modified by SDS (see Fig. 1). Hence a strong interaction between the anionic micelle of SDS and Cb$^+$ is indicated. Micellar binding of Cb$^+$ results in shifting of its $A_{\text{max}}$ from 310 nm to 320 nm. Figure 2 depicts the variation of $e_{\text{obs}}$ of Cb$^+$ at 330 nm (35°C) with [SDS]$\_T$ at $[\text{NaOH}]_T = 0.02$ and 0.04 mol dm$^{-3}$ is in keeping with a value of 0.002 mol dm$^{-3}$ for cmc. $\beta$ was taken as an adjustable parameter in the range 0.6 to 0.8 as it has often been used. With $\epsilon_{\text{cb}} = (19.76 \pm 0.10) \times 10^2$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (330 nm), the absorbance data at [SDS]$\_T = 0.005, 0.01, 0.02, 0.05, 0.1$ and 0.15 mol dm$^{-3}$ ([NaOH]$\_T = 0.02$ and 0.04 mol dm$^{-3}$) were fitted to Eq. (4) by an iterative least squares computer program using $X = [\text{Na}^+]_T / (\beta - m_{\text{cb}})[\text{Dn}]$ in the first iteration step. The

\begin{equation}
K_{\text{ex}} = m_{\text{cb}}^5 \frac{[\text{Na}^+]_T - (\beta - m_{\text{cb}})^5 [\text{Dn}]}{(\beta - m_{\text{cb}})^5 ([\text{cb}^+]_T - m_{\text{cb}}^5 [\text{Dn}])} \quad \ldots (2)
\end{equation}

where

\begin{equation}
\beta = m_{\text{cb}} + m_{\text{Na}} = [\text{Cb}^+_\text{w}] / [\text{Dn}] + [\text{Na}^+] / [\text{Dn}], \quad [\text{Dn}] = [\text{SDS}]_T - \text{cmc}, \quad [\text{Na}^+]_T = [\text{NaOH}]_T + [\text{SDS}]_T, \quad \text{and} \quad [\text{Cb}^+]_T = [\text{complex}]_T.
\end{equation}

The concentrations are expressed in terms of total solution volume and the activity coefficient ratios, $\gamma_{\text{Na}}(\text{Na}^+) / \gamma_{\text{Na}}(\text{Cb}^+)$, are assumed to be unity. The micellar binding parameter $m_{\text{cb}}$ can be expressed as

\begin{equation}
m_{\text{cb}}^5 = \frac{[e_{\text{obs}} - \epsilon_{\text{cb}}]}{[\epsilon_{\text{cb}} - e_{\text{obs}}]} x [\text{cb}^+]_T / [\text{Dn}] \quad \ldots (3)
\end{equation}

where $\epsilon_{\text{cb}}$, $\epsilon_{\text{cb}}^w$ and $e_{\text{obs}}$ respectively denote the molar extinction coefficients of Cb$^+$ in the micellar pseudo-phase, aqueous phase and when it is distributed in both the phases. On rearranging Eq. (2) yields Eq. (4)

\begin{equation}
(e_{\text{obs}} - \epsilon_{\text{cb}}^w) = (e_{\text{cb}} - \epsilon_{\text{cb}}^w) + [(e_{\text{cb}} - \epsilon_{\text{cb}}^w) K_{\text{ex}}] x \quad \ldots (4)
\end{equation}

where $X = [\text{Na}^+]_T / (\beta - m_{\text{cb}})[\text{Dn}] - 1$. It has been reported earlier that cmc of SDS is very strongly sensitive to the electrolyte concentration (cmc = 0.008, 0.0023, 0.00094 and 0.00051 mol dm$^{-3}$ at [NaCl] = 0, 0.05, 0.20 and 0.50 mol dm$^{-3}$ respectively). The variation of $e_{\text{obs}}$ with [SDS] at [NaOH]$\_T = 0.02$ and 0.04 mol dm$^{-3}$ is in keeping with a value of 0.002 mol dm$^{-3}$ for cmc. $\beta$ was taken as an adjustable parameter in the range 0.6 to 0.8 as it has often been used. With $\epsilon_{\text{cb}} = (19.76 \pm 0.10) \times 10^2$ dm$^3$ mol$^{-1}$ cm$^{-1}$ (330 nm), the absorbance data at [SDS]$\_T = 0.005, 0.01, 0.02, 0.05, 0.1$ and 0.15 mol dm$^{-3}$ ([NaOH]$\_T = 0.02$ and 0.04 mol dm$^{-3}$) were fitted to Eq. (4) by an iterative least squares computer program using $X = [\text{Na}^+]_T / (\beta [\text{Dn}]) - 1$ in the first iteration step. The

\begin{table}[h]
\centering
\caption{Least Squares Best Values of Parameters of Eq. (4) for Different Values of $\beta$}
\begin{tabular}{cccc}
\hline
$\beta$ & $10^2(e_{\text{cb}}^w - \epsilon_{\text{cb}})$ & $10^2([\epsilon_{\text{cb}}^w - \epsilon_{\text{cb}}] K_{\text{ex}})$ & $K_{\text{ex}}$
\hline
0.80 & 0.206 ± 0.009 & 0.0108 ± 0.0029 & 19.1 ± 5.1
0.75 & 0.206 ± 0.009 & 0.0101 ± 0.0027 & 20.4 ± 5.5
0.72 & 0.205 ± 0.010 & 0.0096 ± 0.0025 & 21.3 ± 5.8
0.70 & 0.205 ± 0.010 & 0.0093 ± 0.0023 & 21.9 ± 6.0
0.65 & 0.205 ± 0.010 & 0.0086 ± 0.0023 & 23.8 ± 6.5
0.60 & 0.204 ± 0.012 & 0.0078 ± 0.0021 & 25.9 ± 7.1
\hline
\end{tabular}
\end{table}
Table 2 — Rate Data for Base Hydrolysis of cis-(en)$_2$Co(im)NCS$^+$ in Aqueous SDS,NaOH Medium at 40.0 ± 0.1°C

<table>
<thead>
<tr>
<th>[SDS]$_T$ (mol dm$^{-3}$)</th>
<th>$10^3 k_v(s^{-1})^a$ at [NaOH]$_T$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.02</td>
</tr>
<tr>
<td>0.00</td>
<td>21.0 ± 0.2</td>
</tr>
<tr>
<td>0.002</td>
<td>21.2 ± 1.2</td>
</tr>
<tr>
<td>0.005</td>
<td>17.4 ± 0.2</td>
</tr>
<tr>
<td>0.010</td>
<td>10.6 ± 0.3</td>
</tr>
<tr>
<td>0.020</td>
<td>5.96 ± 0.4</td>
</tr>
<tr>
<td>0.040</td>
<td>2.34 ± 0.2</td>
</tr>
<tr>
<td>0.060</td>
<td>2.21 ± 0.5</td>
</tr>
<tr>
<td>0.100</td>
<td>1.87 ± 0.3</td>
</tr>
<tr>
<td>0.150</td>
<td>1.62 ± 0.3</td>
</tr>
</tbody>
</table>

(a) Errors quoted are the least squares standard deviation of ln $(A_0 - A_v)$ versus $v$ plots except for [SDS] = 0.002 mol dm$^{-3}$.

(b) Mean of duplicate runs.

calculated values of the parameters $(e_m^w - e_m^w)^{-1}$ and $K_{ex}$ within error limits (see Table 1) turned out to be insensitive to the chosen value of $\beta$. The average value of $K_{ex}$ turned out to be 22.1 ± 2.4 at 35°C. It is pertinent to note that the value of $K_{ex}$ for (CH$_3$)$_4$N$^+$/Na$^+$ exchange reaction in the presence of SDS micelle is reported to be 8.8 at 90°C (ref. 9). A similar calculation for the cis-[en)$_2$Co(im)N$_3$]$^+$/Na$^+$ exchange equilibrium in the presence of SDS micelle also yields $K_{ex}$ = 15.0 ± 1.6 at 35°C (ref. 10).

The rate data at [SDS]$_T$ = 0.01 to 0.15 and [OH$^-$]$_T$ = 0.02 and 0.04 mol dm$^{-3}$ were fitted to Eq. (8), a linearized form of Eq. (5)

$$(k_{obs} - k_v)/y = K_{ex}k_v - k_{eq}K_{ex}$$  ... (8)

by an iterative least squares computer program. The value of $K_{ex}$ obtained from the equilibrium measurement was chosen as the initial guess; $\beta$ and cmc were used as adjustable parameters. For each value of $\beta$ (0.6 to 0.85) and cmc (= 0.001 to 0.004 mol dm$^{-3}$), the iterative least squares procedure yielded the best value of $K_{ex}$ and $(k_{eq}/K_{ex})$ as the gradient and intercept of the plot of $(k_{obs} - k_v)/y$ against $k_v$. Typical plot is presented in Fig. 3. Adjudged from the calculated least squares standard deviation of left hand side of Eq. (8), cmc = 0.002 or 0.003 mol dm$^{-3}$ was most acceptable. The calculated values of $K_{ex}$, $k_{eq}/K_{ex}$ and $k_{eq}$ for different values of $\beta$ and cmc are presented in Table 3. The value of $K_{ex}$ is insensitive to the chosen value of $\beta$ for a given value of cmc for which the calculated value of $k_{eq}$ shows a downward trend with decreasing value of $\beta$. The correlation coefficient of $(k_{obs} - k_v)/y$ versus $k_v$ plot is slightly better for cmc = 0.003 (see Table 2). In the range of $\beta$ = 0.6 to 0.85 the mean value of $K_{ex}$ and $k_{eq}$ respectively turn out to be 16.1 ± 2.1, (1.12 ± 0.15) $\times 10^{-5}$ s$^{-1}$ at cmc = 0.003 mol dm$^{-3}$ and 13.8 ± 1.8.

### Kinetic model

The rate of base hydrolysis of the complex is strongly retarded by SDS (see Table 2). In this respect SDS behaves as a multivalent anion which retards the base hydrolysis of acidoaminecobalt(III) complexes by ion-pairing$^{11,12}$. The plot of $k_v$ against [SDS]$_T$ at a fixed [OH$^-$]$_T$ is observed to be asymptotic with respect to the latter axis. Participation of OH$^-$ into the anionic micelle is unlikely$^{13}$. A reasonable kinetic model, consistent with our observation, is presented in Scheme 1 for which the observed pseudo-first order rate constant $(k_v)$ is given by Eq. (5)

$$k_v = \frac{k_w^v + k_{eq} K_{ex} y}{1 + K_{ex} y}$$  ... (5)

where $k_v$ and $k_w^v$ refer to the same [OH$^-$]$_T$ ($k_v = k_w^v$ at [SDS]$_T$ = 0) and

$$y = (\beta - m_{eq}([Dn] - ([Na^+]_T - (\beta - m_{eq})[Dn])); \ldots (6)$$

Equation (2) on rearrangement yields Eq. (7) from which $m_{eq}$ can be calculated using known values of $\beta$, cmc and $K_{ex}$.

$$m_{eq} = (\frac{k_w^v}{k_{ex} y}) [Dn] - \frac{k_w^v}{k_{ex} y} [k_{ex} [Dn] + [Na^+]_T]$$

$$+ \beta [Dn] [k_{ex} y]; K_{ex} y = 0$$  ... (7)

![Scheme 1](image-url)

Table 3 — Calculated Values of Parameters of Eq. (8)$^a$

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>$K_{ex}$</th>
<th>$10^3 k_{eq}/K_{ex}$ (s$^{-1}$)</th>
<th>$10^3 k_{eq}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>13.6 ± 0.6</td>
<td>1.86 ± 0.25</td>
<td>1.36 ± 0.18</td>
</tr>
<tr>
<td>0.80</td>
<td>14.4 ± 0.6</td>
<td>1.81 ± 0.26</td>
<td>1.26 ± 0.18</td>
</tr>
<tr>
<td>0.75</td>
<td>15.4 ± 0.6</td>
<td>1.79 ± 0.28</td>
<td>1.17 ± 0.18</td>
</tr>
<tr>
<td>0.70</td>
<td>16.5 ± 0.6</td>
<td>1.78 ± 0.29</td>
<td>1.08 ± 0.18</td>
</tr>
<tr>
<td>0.65</td>
<td>17.8 ± 0.7</td>
<td>1.76 ± 0.31</td>
<td>0.99 ± 0.17</td>
</tr>
<tr>
<td>0.60</td>
<td>19.3 ± 0.7</td>
<td>1.74 ± 0.33</td>
<td>0.90 ± 0.17</td>
</tr>
<tr>
<td>0.55</td>
<td>20.7 ± 0.7</td>
<td>1.72 ± 0.35</td>
<td>0.81 ± 0.17</td>
</tr>
</tbody>
</table>

Mean $K_{ex}$ = 16.1 ± 2.1 (13.8 ± 1.8)

Mean $10^3 k_{eq}$ = 1.2 ± 0.15 (0.91 ± 0.19)s$^{-1}$

(a) cmc = 0.002 mol dm$^{-3}$ for values in parantheses (corr. coeff. = 0.992); cmc = 0.003 mol dm$^{-3}$ for all other values (corr. coeff. = 0.994).
(0.91 ± 0.19) \times 10^{-5} \text{s}^{-1} \text{ at cmc} = 0.002 \text{ mol dm}^{-3}. \text{ The values of } K_{eq} \text{ obtained from the kinetic data are in satisfactory agreement with that calculated from the equilibrium measurement.}

It is important to note that the spontaneous aequation path of cis-\left[(\text{en})_2\text{Co(Im)NCS}^-\right]_+ \text{ is observable in the micellar phase. This lends indirect support to the existence of similar path for the conjugate base species, } C_b^+ \text{, in the aqueous phase which was proposed by us earlier.} \text{ The aequation and base hydrolysis rate constants of } C_b^+ \text{ in aqueous phase at zero ionic strength were calculated from the relation (9)}

\[ k_{\text{obs}}^w = k_{aq}^w + k_{OH}^{w,w} + k_{CB}^{w,w} [OH^-] \]  

\text{using the pseudo-first order rate constant } (k_a) \text{ at } [OH^-] = 0.02, 0.04 \text{ and } 0.06 \text{ mol dm}^{-3} \text{ and } [\text{SDS}]_r = 0 \text{ (see Table 2). } \gamma_{OH}^w = \gamma_{CB}^w \text{ was assumed and the activity coefficients were calculated by Davies' equation.} \text{ The values of } k_{aq}^w \text{ and } k_{OH}^{w,w} \text{ turned out to be } 1.5 \times 10^{-4} \text{ s}^{-1} \text{ and } 4.37 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ respectively. It then turns out that } C_b^+ \text{ in the micellar phase aequates } \sim 15 \text{ times slower than in the aqueous phase } (k_{aq}^w/k_{aq}^M \approx 15). \text{ It is, however, quite logical to think, from the consideration of the charge and hydrophilic centres of } C_b^+ \text{, that the conjugate base species is bound to the Stern layer of the micelle.} \text{ Hence the observed rate difference cited above possibly arises due to the difference in the polarity of the microenvironment of the reactant in aqueous and micellar pseudo phases.}

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**References**