Micellar Effects on Interaction of Proton & Metal Ions with Oxalatopentaamminecobalt(III) & on Rates of Aquation of Resulting Species

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The effect of sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) on the protonation equilibrium of oxalatopentaamminecobalt(III) is examined at 21°C. SDS in the concentration range of 0.02-0.08 mol dm⁻³, increases the pK of (NH₃)₅CoOCO₂H²⁺ by a factor of ~2. CTAB exerts no such effect on the pK of the substrate. The binuclear complexation equilibria involving Zn²⁺ and Al³⁺ and the oxalato complex are also strongly influenced by SDS. This is attributed to the partitioning of the multiple-charged binuclear species, (NH₃)₅CoOCO₂M⁺⁺⁺⁺ into the anionic pseudo-phase of SDS micelle. The micelle bound species of Al³⁺ is somewhat stabilized towards water substitution at the cobalt(III) centre.

The study of the effect of micelle forming surfactant, cetyltrimethylammonium bromide (CTAB), on the base hydrolysis of cis-(ammine)(5-NO₂salicylatolbistethylenediaminelcobalt (III) complex demonstrated that (i) phenoxide form of this substrate could be reversibly bound to the cationic micelle, and (ii) the micelle-bound complex underwent base hydrolysis at slightly faster rate than the free complex in the aqueous phase. We were led to believe that the mechanism of hydrolysis of this substrate in the micellar pseudo-phase of CTAB is not different from that in the aqueous phase. But the micelle altered the rate profile via an ion-exchange equilibrium process. This work prompted us to use similar cationic cobalt (III) substrates and study their kinetics and equilibrium behaviour in aqueous medium in the presence of both cationic and anionic surfactants. In this paper data are presented (i) on the effects of sodium dodecyl sulphate (SDS) and CTAB on the interaction of H⁺ and metal ions with oxalatopentaamminecobalt (III) and (ii) on the kinetics of aquation of resulting species.

Materials and Methods

Hoxalatopentaamminecobalt (III) diperchlorate was prepared as described earlier² and its purity checked by analysis of Co and oxalate which agreed within ±0.2% with the calculated values. All other reagents were of either AR grade or extrapure quality. SDS was purified by repeated crystallization from ethanol and its purity checked by cmc determination. CTAB was 99.8% pure as indicated by Br analysis. pH measurement was made using an ECIL pH meter model 5651; saturated NaCl was used as the electrolyte for the reference electrode. The meter was standardised against standard buffers of pH 4.00 and 9.20. The spectral measurements were made with a Varian-Cary 634S UV-visible spectrophotometer using 1.00 cm matched quartz cells.

The kinetics of hydrolysis of the oxalato complex was followed spectrophotometrically at 40°C. The cell compartment of the spectrophotometer was thermostated to the desired temperature. Runs were made under pseudo-first order conditions and the rate constants were calculated from the gradients of the plots of log (A₁ - A₂) against time (s) where A₁ and A₂ denote the absorbances at time t and for complete aquation of the complex respectively. A₁ was taken to be the value of A₄ at ~ 10⁻⁴.

Results and Discussion

Effect of SDS on acid dissociation equilibrium of the complex

The acid dissociation equilibrium of the oxalato complex in aqueous medium in the absence of SDS may be represented by Eq. (1)

\[
\text{K}_1 \quad (\text{NH}_3)_5\text{CoOCOCO}_2\text{H}^+ \rightleftharpoons (\text{NH}_3)_5\text{CoOCOCO}_2^+ + \text{H}^+ \quad ... (1)
\]

The values of K₁ at 28°C reported earlier³ are 2.1 \times 10⁻² and 1.03 \times 10⁻² mol dm⁻³ at Φ = 0 and 0.3 mol dm⁻³ respectively. The absorbance data of the complex at pH 9.01 ± 0.05 (borate buffer), 0 ≤ [SDS] ≤ 0.08 mol dm⁻³ and the [complex] = 5.04 \times 10⁻⁴ mol dm⁻³ show that the extinction coefficient (in dm³ mol⁻¹ cm⁻¹) at λ 280 (ε = 2412), 290 (2046), 300 (1655) and 320 nm (855) are changed, respectively, to 2534,
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Table 1—Effect of Varying [SDS] on Extinction Coefficient of Oxalatopentaamminecobalt (III)

<table>
<thead>
<tr>
<th>[SDS]_T (mol dm⁻³)</th>
<th>[HClO₄] (mol dm⁻³)</th>
<th>pH</th>
<th>ε_{obs} (dm³ mol⁻¹ cm⁻¹) at 280 nm</th>
<th>290 nm</th>
<th>300 nm</th>
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<tr>
<td>0 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>1.99</td>
<td>1845 1487 1155</td>
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<td></td>
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<tr>
<td>0.02 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.19</td>
<td>978.9 600.3 372.3</td>
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<td></td>
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<td>0.03 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.26</td>
<td>997.7 608.7 374.4</td>
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<tr>
<td>0.04 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.32</td>
<td>1012 629.6 393.2</td>
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<td></td>
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<tr>
<td>0.05 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.36</td>
<td>1054 669.3 439.2</td>
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<td></td>
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<tr>
<td>0.06 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.39</td>
<td>1089 719.3 478.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.07 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.43</td>
<td>1140 755.0 499.9</td>
<td></td>
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</tr>
<tr>
<td>0.08 0.01 0.00 0.00</td>
<td>0.01 0.01 0.00 0.00</td>
<td>2.48</td>
<td>1179 790.3 529.3</td>
<td></td>
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</tr>
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</table>

2125, 1677 and 833 dm³ mol⁻¹ cm⁻¹ in the presence of 0.01 mol dm⁻³ SDS. Beyond this [SDS] the change in the extinction coefficient at these pH values is insignificant. At this pH the complex exists exclusively in the ionized form, (NH₃)₅CoC₂O₄ and therefore, the interaction between the cationic species and the anionic micelle of SDS cannot be ruled out.

The absorbance data of the oxalato complex in the pH range of 2 to 4, 0 ≤ [SDS]_T ≤ 0.08 mol dm⁻³ and [complex]_T in the range of (4.78 to 5.52) × 10⁻⁴ mol dm⁻³ (see Table 1) indicate that SDS has significant effect on the absorbance of the acidified oxalato complex. Simultaneously the surfactant also alters the pH of the medium though to a small extent. This behaviour may be interpreted in terms of the pseudo-phase ion-exchange equilibrium for H⁺ and the substrate as shown in Scheme 1, where Dn = micellized surfactant, X_M or X_W (X = ROX⁻ and H⁺) denote the species X in the micellar pseudo-phase (M) or in aqueous phase (W) respectively, and [X]_T = [X]_W + [X]_M, the concentration being referred to the total solution volume. The absorbance of the solution is given by

\[ A = \varepsilon_1^M [\text{ROXH}^+]+\varepsilon_2^W [\text{ROXH}^+] + \varepsilon_2^M [\text{ROX}^+]+\varepsilon_2^W [\text{ROX}^+] \] ...

where \( \varepsilon_1 \) and \( \varepsilon_2 \) denote the molar extinction coefficients of the species ROXH²⁺ and ROX⁻ respectively. From the consideration that \( \varepsilon_2^M = \varepsilon_2^W = \varepsilon_2 \) we assume \( \varepsilon_1^M = \varepsilon_1^W = \varepsilon_1 \) which reduces Eq. (2) to the form

\[ \varepsilon_{\text{obs}}[\text{complex}]_T = \varepsilon_1 [\text{ROXH}^+]+\varepsilon_2 [\text{ROX}^+] \] ...

Defining the acid dissociation constant of the complex in the presence of SDS by Eq. (4),

\[ K_1(\text{app}) = \frac{[\text{ROX}^+]_T [\text{H}^+]}{[\text{ROXH}^+]_T} \] ...

Eq. (3) can easily be transformed to Eq. (5)

\[ K_1(\text{app}) = \frac{\varepsilon_{\text{obs}} - \varepsilon_1 [\text{H}^+]}{\varepsilon_2 - \varepsilon_1} \] ...

Table 2 presents the calculated values of \( K_1(\text{app}) \). It is interesting to note that the values of \( K_1(\text{app}) \) in the pH range 2.19 to 2.43 and 3.83 to 4.12, 0.02 ≤ [SDS]_T ≤ 0.08 mol dm⁻³, [complex]_T = (4.78 to 5.52) × 10⁻⁴ mol dm⁻³ and temp. = 28°C are virtually constant, the values in the pH range 3.83-4.12 being only 3 times lower than those in the pH range 2.19-2.43. These data, however, are significantly lower than the value of \( K_1 \) in the aqueous phase (≈ 10⁻² mol dm⁻³) which cannot be accounted for in terms of ionic strength effect. In other words the present case demonstrates enhancement of the basicity of the half-bonded oxalate due to its incorporation into the anionic pseudo-phase of SDS micelle. We attribute the difference in the two sets of values of \( K_1(\text{app}) \) to the effect of added H⁺ ion (added as HClO₄) which competes with the complex ions for micellar binding and in turn displaces the latter from the micellar phase to the aqueous phase.

Referring to Eq. (4) it can be easily shown that

\[ K_1(\text{app}) = K_1(1 + K_{\text{Dn}}^M [\text{Dn}])/(1 + K_{\text{Dn}}^M [\text{Dn}]) \] ...

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where \([Dn] = [SDS]_T - \text{cmc}\); \(K_{ox}\) and \(K_{oxH}\) are the micellar binding constants of the species \((\text{NH}_3)_3\text{CoC}_2\text{O}_4^+\) and its acid form respectively. The cmc of SDS in the absence of extraneous ions is 0.008 mol dm\(^{-3}\) (ref. 5). Usually added salts reduce cmc value significantly (cmc = 0.0023 and 0.0005 mol dm\(^{-3}\) at \([\text{NaCl}]_T = 0.05\) and 0.506 mol dm\(^{-3}\) respectively and temp. = 25°C). In the present case since \([SDS]_T > > \text{cmc}\) the calculated values of \(K_{i(app)}\) are found to be independent of \([SDS]_T\) once pH is held constant. In accord with Eq. (6) this amounts to the valid assumption: \(K_{ox}[Dn] > > 1\) and \(K_{oxH}[Dn] > > 1\). Hence under the experimental condition Eq. (6) yields, 
\[
K_{i(app)} = K_1(K_{ox}/K_{oxH}) \quad \ldots (7)
\]

Thus the micellar binding of both the complex species must be strong so that the values of \(K_{i(app)}\) do not reflect SDS-dependence. From Eq. (7) \(K_{ox}/K_{oxH} = 24\) and 72 at pH in the range 2.2-2.4 and 3.8-4.1 respectively taking \(K_1 = 2.1 \times 10^{-2}\) mol dm\(^{-3}\). The ratio of the micellar binding constants are of right order of magnitude considering the charges of the substrates.

The effect of CTAB on the UV absorption spectrum of the oxalato complex has also been examined under the conditions \([\text{complex}]_T = 5.0 \times 10^{-4}\) mol dm\(^{-3}\), 0 \(< [\text{CTAB}]_T < 0.08\) mol dm\(^{-3}\) and pH = 3.44. The spectrum of the complex is unaffected in the region 280-300 nm. Hence the possibility of binding of the ion, \([\text{(NH}_3)_3\text{CoOCOCO}_2\text{O}_4]^+\), with the cationic CTAB micelle is ruled out.

Effect of SDS on complexation equilibria of \((\text{NH}_3)_3\text{CoC}_2\text{O}_4^+\) with Zn\(^{2+}\) and Al\(^{3+}\)

The spectrophotometric data for Zn\(^{2+}\)-\((\text{NH}_3)_3\text{CoC}_2\text{O}_4^+\) and Al\(^{3+}\)-\((\text{NH}_3)_3\text{CoC}_2\text{O}_4^+\) systems in the presence of \([SDS]_T = 0.04\) and 0.02 mol dm\(^{-3}\) show that \(e_{obs}\) (300 nm) values are virtually constant (372 to 387 dm\(^{-1}\) mol\(^{-1}\) cm\(^{-1}\)) in the range of \([\text{Zn}^{2+}]_T = 0.01\) to 0.08 mol dm\(^{-3}\). \(e_{obs}\) values for Al\(^{3+}\) system do not show any trend with \([\text{Al}^{3+}]_T\) (173, 150, 171, 146 and 123 dm\(^{-3}\) mol\(^{-1}\) cm\(^{-1}\) at \([\text{Al}^{3+}]_T = (9.98, 19.97, 5.15, 15.14\) and 25.12\) \(\times 10^{-4}\) mol dm\(^{-3}\) respectively); but these values are significantly lower than those for the species \([\text{(NH}_3)_3\text{CoC}_2\text{O}_4\text{H}]^{2+}\) and \([\text{(NH}_3)_3\text{CoC}_2\text{O}_4]^+\) (see Tables 1 and 2). Assuming that the metal ions do not have any effect on the acid dissociation equilibrium of the oxalato complex in the presence of SDS, \(K_1\) (app) has been calculated as stated earlier. The values of \(K_1\) (app) in the presence of Zn\(^{2+}\) show small shift (from \(5.8 \times 10^{-4}\) to \(8.3 \times 10^{-4}\) mol dm\(^{-3}\)) when \([\text{Zn}^{2+}]_T\) is varied from 0.005 to 0.08 mol dm\(^{-3}\) and are negative for SDS-Al\(^{3+}\)-oxalato complex system (since \(e_{obs} < e_1\)). Lindman et al.\(^{7}\) have shown that VO\(^{2+}\) strongly interacts with the SDS micelle and gets virtually completely bound to its micellar pseudo-phase at \([\text{VO}^{2+}]_T = 0.005\) mol dm\(^{-3}\) once cmc is exceeded. Similar behaviour is expected for Zn\(^{2+}\) and Al\(^{3+}\). Since \([\text{Zn}^{2+}]_T\) ranged from 0.005 to 0.08 mol dm\(^{-3}\), keeping \([SDS]_T = 0.04\) mol dm\(^{-3}\), it is quite expected that not the whole of Zn\(^{2+}\) would be bound to the micellar pseudo-phase. On the other hand this may be the most likely possibility for Al\(^{3+}\) as \([SDS]_T > 8[\text{Al}^{3+}]_T\) is maintained. This would mean that Zn\(^{2+}\) and Al\(^{3+}\) will displace the micellar bound Na\(^+\) and the oxalato complex species into the aqueous pseudo-phase. The ion-exchange process in turn would result in marked enhancement of \(K_1\) (app) (from \(10^{-4}\) to \(10^{-2}\)) which, however, is not the case. Therefore, the spectrophotometric data indirectly indicate that the multiple charged binuclear species, \((\text{NH}_3)_3\text{CoC}_2\text{O}_4\text{M}^{(n+1)+}\) (\(n=2\) for Zn\(^{2+}\) and 3 for Al\(^{3+}\)) are virtually completely partitioned into the anionic micellar pseudo-phase of SDS. The present work further illustrates that micellization of SDS persists in the presence of multivalent metal ions used particularly in the presence of Zn\(^{2+}\) even when \([\text{Zn}^{2+}]_T\) is higher than \([SDS]_T\).

Rate data

The rate of aquation of the oxalato complex has been studied in the presence of Al\(^{3+}\) at varying [SDS]. Some kinetic runs have also been made at 40°C to examine the effects of [SDS] on the H\(^+\) - and Zn\(^{2+}\)-catalysed aquation of the complex. \([\text{Zn}^{2+}]_T, \text{pH}\) and \([SDS]_T\) have been adjusted in the range used for the equilibrium measurements. No marked effect of varying [SDS] is observed. Data presented in Table 3 refer to a situation when the binuclear species, \((\text{NH}_3)_3\text{CoC}_2\text{O}_4\text{Al}^{4+}\), is expected to be completely partitioned into the SDS micelle. The micellar binding of the binuclear species appears to result in considerable rate enhancement of the overall aquation of the complex considering the fact that the overall aquation rate constant of the complex at \([\text{Al}^{3+}]_T\)

<table>
<thead>
<tr>
<th>([\text{Al}^{3+}]_T)</th>
<th>([SDS]_T)</th>
<th>\text{pH}</th>
<th>(10^3k_{obs}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>0.00</td>
<td>2.24</td>
<td>0.44±0.06*</td>
</tr>
<tr>
<td>0.003</td>
<td>0.02</td>
<td>2.26</td>
<td>6.6±0.8†</td>
</tr>
<tr>
<td>0.003</td>
<td>0.04</td>
<td>3.16</td>
<td>4.5</td>
</tr>
<tr>
<td>0.003</td>
<td>0.06</td>
<td>3.27</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Mean of duplicate runs
†Mean of triplicate runs

Table 3 — Rate Data for Hydrolysis of Oxalato-Rhenodiaminecobalt(III) Ion in Presence of SDS and Al\(^{3+}\)

\([\lambda = 270\text{ nm}; \text{complex}]_T = (2.5-3.0) \times 10^{-4}\) mol dm\(^{-3}\); temp. = 40.5±0.1°C}
\[ [\text{SDS}]_T = 0, \ pH = 2-3, \ \text{and} \ \text{temp.} = 40^\circ C \] is extremely small \((\sim 10^{-7} \ \text{s}^{-1})\). From the published data\(^3\), we have, however, calculated a value of \(9.7 \times 10^{-5} \ \text{s}^{-1}\) for the pseudo-first order rate constant of aquation of the binuclear species of \(\text{Al}^{3+}\). Taking the corresponding rate constant in the micellar phase as \((5 \pm 1) \times 10^{-5} \ \text{s}^{-1}\) (see Table 3) it appears revealing that there is indeed no significant micellar effect on the reaction rate once the binuclear complexation is driven to completion. The binuclear species, \((\text{NH}_3)_2\text{CoC}_2\text{O}_4\text{Al}^{4+}\), is efficiently exchanged into the anionic pseudo-phase of SDS micelle so that the concentration limit of \(\text{Al}^{3+}\) for the complete complexation of the oxalato complex with \(\text{Al}^{3+}\) is reduced significantly. The slight retardation of aquation of the binuclear species by SDS could be due to environmental effect, the electrostatic repulsion between the leaving groups in the \(I_d\) transition state, \([(\text{NH}_3)_2\text{Co}^{3+} ... \text{C}_2\text{O}_4\text{Al}^{1+}, \ \text{H}_2\text{O}]^*\) being reduced due to the anionic microenvironment of the micelle.

Acknowledgement

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References