

Kinetic Investigation of the Base Hydrolysis of the Chloropentaamminecobalt(III) Ion in Micellar Sodium Dodecyl Sulfate Solution

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Abstract

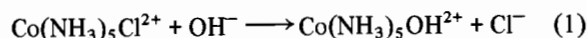
The kinetics of the base hydrolysis of the complex ion chloropentaamminecobalt(III) have been studied by conventional spectrophotometry at 25.0 °C in water and in the presence of the anionic surfactant sodium dodecyl sulfate (SDS) over the SDS concentration range from 1.0×10^{-3} to 7.5×10^{-2} mol dm^{-3} . The hydrolysis rate is strongly inhibited by the surfactant, fitting a model in which the cobalt(III) complex is distributed between water and the micellar pseudo-phase with a binding constant equal to 3.7×10^3 $\text{dm}^3 \text{mol}^{-1}$. The effects of different added electrolytes on the critical micelle concentration of the surfactant and on the hydrolysis rate have also been investigated and discussed.

Introduction

In recent years many investigations [1] have been devoted to the study of the kinetics and mechanisms of reactions which occur in the presence of organized assemblies. Interest for the use of these systems as reaction media has been primarily stimulated by their potential applications in a variety of fields such as photochemical solar energy storage and conversion, catalysis, extraction, polymerization, synthesis, biological membrane and enzyme models. The majority of the reactions examined, however, involve organic substrates, whereas kinetic studies on inorganic reactions are comparatively scarce. Most inorganic reactions investigated in the micellar aggregates concern transition metal complex formations [2–4] and electron transfer processes [5–9] involving aquo-ions and metal complexes with hydrophobic or hydrophilic ligands.

Continuing our investigations on the effect of micelles on the rates of inorganic processes to obtain information about the reaction mechanism in these media and the types of interactions involving both the reactants and the micelles, we have now studied

the kinetics of the base hydrolysis eqn. (1) of the chloropentaamminecobalt(III) cation, $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, in water and in micellar solutions of sodium dodecyl sulfate (SDS) at 25 °C. Additional kinetic measure-



ments have been carried out in the presence of varying amounts of added electrolytes in order to examine salt effects on the reaction rate in the micellar solution. The critical micelle concentration (*cmc*) of the anionic surfactant in various aqueous electrolyte solutions has also been estimated.

Experimental

Materials

Sodium dodecyl sulfate was supplied from Fluka and recrystallized from ethanol. The chloropentaamminecobalt(III) complex was prepared as described elsewhere [10] and characterized by the molar extinction coefficient at the wavelengths of 229 [11] and 550 [12] nm. All the inorganic substances were of reagent grade or very pure products and doubly distilled water was used in preparing all solutions.

Kinetic and Surface Tension Measurements

All kinetic measurements were carried out at 25 °C with excess of hydroxide ion (NaOH) by following the decrease [11] in the absorption at 229 nm with a Beckman DK-2A recording spectrophotometer equipped with a thermostated compartment for 1 cm cells. At constant NaOH concentration the hydrolysis rates always followed a first-order law, except at SDS concentrations very close to the critical micelle concentration, where deviations were observed. The reason for these deviations might be related to the formation of the micellar aggregates (*cf.* *cmc* value in the following). The observed pseudo-first order rate constants k_{obs} , estimated from the slopes of the $\ln(A - A_\infty)$ against time plots (A = absorbance), were reproducible within $\pm 3\%$. Since preliminary measurements showed the independence of k_{obs} on the cobalt(III)

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TABLE I. Critical Micelle Concentrations (*cmc*) of Sodium Dodecyl Sulfate in Water and in Aqueous Electrolyte Solutions at 25 °C

10^2 [MOH] (mol dm ⁻³)	10^2 ([MOH] + [MClO ₄]) (mol dm ⁻³)	10^3 <i>cmc</i> (M ⁺ = Na ⁺) (mol dm ⁻³)	10^3 <i>cmc</i> (M ⁺ = Li ⁺) (mol dm ⁻³)
		8.00	8.00
0.75	0.75	4.50	5.60
1.0	2.0	3.10	4.00
3.0	3.0	2.50	2.80
3.0	4.0	1.95	
1.0	5.0	1.80	
1.0	6.0		1.90
5.0	6.0	1.60	
6.0	6.0	1.55	1.90
1.0	8.0		1.50
1.0	10.0	1.20	

complex concentration, the majority of the kinetic runs were performed with $[\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}] = 4.0 \times 10^{-5}$ mol dm⁻³. The second-order rate constants (k_b) for the base hydrolysis were determined simply as $k_{\text{obs}}/[\text{OH}^-]$, the contribution of the acid hydrolysis (aquation) being negligibly small under the experimental conditions used [12, 13].

Critical micelle concentrations were obtained by a Kruss K10 tensiometer as described previously [9].

Results and Discussion

Kinetics in the Absence of Surfactant

The rate of the hydrolysis reaction (eqn. (1)) in water has been studied at 25 °C and at varying ionic strengths (supporting electrolyte NaClO₄) using $[\text{NaOH}] = 0.010$ mol dm⁻³

There are several kinetic studies of the hydrolysis of the chloropentaamminecobalt(III) ion in alkaline solution in the absence of surfactant, an S_N1CB mechanism being presumably operative [12, 13]. Where comparisons are possible, the second-order rate constants k_b obtained in the present work are in fair agreement with those reported previously. The rate of the base hydrolysis decreases with increasing ionic strength as expected for a reaction between two ions of opposite charge. Figure 1 shows the plot of the logarithm of k_b against the square root of the ionic strength (μ). The solid straight line of this figure is drawn with slope equal to -2.04 in accordance with the primary salt effect in dilute solution. The k_b value obtained at $[\text{NaOH}] = 0.010$ and $[\text{NaClO}_4] = 0.040$ mol dm⁻³ ($\mu = 0.050$ mol dm⁻³) is 0.65 dm³ mol⁻¹ s⁻¹.

Critical Micelle Concentration

Table I assembles the critical micelle concentration (*cmc*) of the anionic surfactant estimated in the present work at 25 °C by surface tension measure-

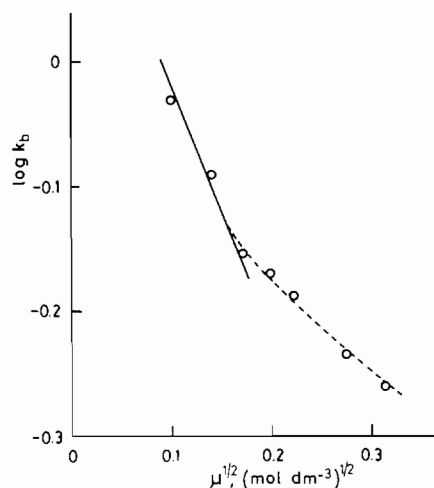


Fig. 1. Plot of $\log k_b$ against $\mu^{1/2}$ in water at 25 °C. The slope of the solid line is equal to -2.04 (see text).

ments in water and in various aqueous electrolyte solutions. As far as we know, no *cmc* values for the SDS surfactant in the presence of these electrolyte mixtures have been previously reported. The *cmc* value of the present work in water is in good agreement with those already reported [14]. Moreover the *cmc* value of 2.3×10^{-3} mol dm⁻³ calculated from previous data [15] in the presence of 0.050 mol dm⁻³ NaCl can be compared with that (1.80×10^{-3} mol dm⁻³) found in this work at $[\text{NaOH}] = 0.010$ and $[\text{NaClO}_4] = 0.040$ mol dm⁻³. The addition of electrolytes reduces the *cmc* of the SDS surfactant [14–17] and, over the salt concentration range used, for a given added cation the *cmc* decrease depends virtually only on the total cationic concentration. Moreover the salt effect on the *cmc* is more significant for Na⁺ than for Li⁺ [14, 17]. It is well known [16, 18] that the increase in the counterion concentration causes a decrease in the surface potential of the micelle. As also found in prev-

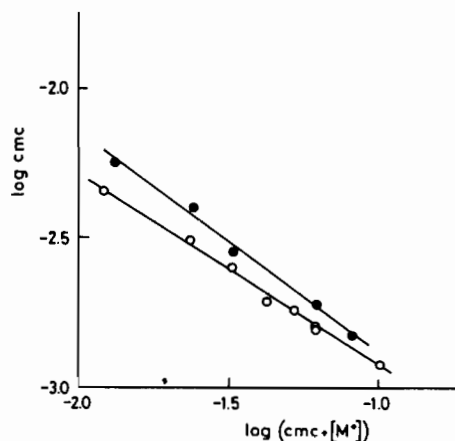


Fig. 2. Plot of $\log cmc$ against $\log (cmc + [M^+])$ for SDS in aqueous electrolyte solution at 25 °C: $M^+ = Li^+$ (●) and Na^+ (○). The line is the least-squares fit according to eqns. (2) and (3).

ious studies [15–17, 19], a straight line is obtained by a logarithmic plot of cmc against the total counterion concentration ($= cmc + [M^+]$), where $[M^+]$ indicates the molarity of the added cation (Fig. 2). The least-squares analysis of the experimental data yields eqns. (2) and (3) for sodium and lithium electrolytes, respectively.

$$\log cmc = -3.559 - 0.633 \log (cmc + [Na^+]) \quad (2)$$

$$\log cmc = -3.608 - 0.726 \log (cmc + [Li^+]) \quad (3)$$

Kinetics in the Presence of Surfactant

The hydrolysis rate in micellar sodium dodecyl sulfate solution has been studied at 25 °C over the $[SDS]$ range from 1.0×10^{-3} to 7.5×10^{-2} mol dm^{-3} using $[NaOH] = 0.01$ mol dm^{-3} , the total sodium concentration of the medium being maintained constant at 0.050 mol dm^{-3} by the addition of sodium perchlorate.

Figure 3 shows that the (apparent) second-order rate constant k_b is not affected by the presence of the anionic surfactant when the concentration of the latter is below the cmc ($= 1.80 \times 10^{-3}$ mol dm^{-3} , see Table I), but a strong rate inhibition is observed just above the estimated cmc . Further increases in $[SDS]$ lead to a continuous decrease in the hydrolysis rate, which remains almost constant at the highest $[SDS]$ values examined.

The observed dependence of the rate constant k_b upon the SDS concentration can be easily analyzed by Berezin's approach [20]. Since the hydroxide ion bearing the same charge sign of the micelles will be repelled by the micelle surface and will be then confined predominantly to the intermicellar aqueous region, the following simple reaction scheme applies to the base hydrolysis under examination:

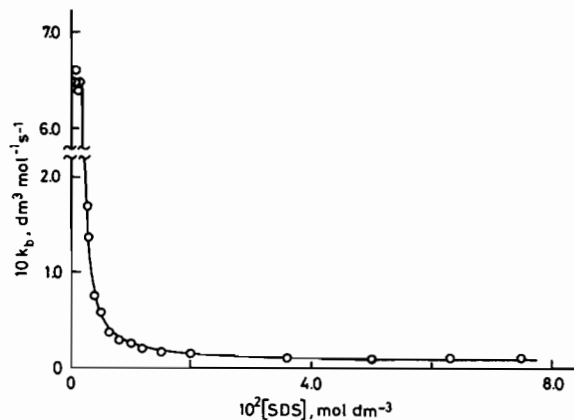
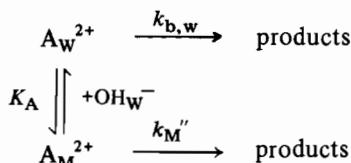


Fig. 3. Plot of k_b against $[SDS]$. The solid line is drawn according to eqn. (5).



According to this scheme the cobalt(III) complex ion ($= A^{2+}$) is partitioned between water (W) and the micellar pseudo-phase (M), K_A ($= [A_M^{2+}] / [A_W^{2+}] C$) being the binding constant of the complex to the SDS micelles and $C = [SDS] - cmc$. Therefore in the most general case two reactions may contribute to the progress of the complex hydrolysis, that is the reactions of the hydroxide ion in the bulk water with the two solubilized complex forms A_W^{2+} and A_M^{2+} , and the (apparent) second-order rate constant k_b is given [4, 6, 9, 20] by eqn. (4), where $k_{b,w}$ indicates the second-order rate constant in the absence of surfactant.

$$k_b = \frac{k_{b,w} + k_M'' K_A C}{1 + K_A C} \quad (4)$$

The non-linear least-squares treatment of the experimental data [21] yields the values of $(7.0 \pm 0.9)10^{-3}$ dm^3 mol^{-1} s^{-1} and $(3.7 \pm 0.2)10^3$ dm^3 mol^{-1} for k_M'' and K_A , respectively. The dependence of the rate constant k_b on the molar surfactant concentration is thus expressed by eqn. (5). Figure 3 shows that the curve drawn using this equation fits very well the experimental data.

$$k_b = \frac{0.65 + 26([SDS] - 1.8 \times 10^{-3})}{1 + 3.7 \times 10^3([SDS] - 1.8 \times 10^{-3})} \quad (5)$$

It should be noted that the hydrolysis rate involving OH_W^- and the complex ion solubilized in the SDS micelles is 93 times smaller than that in aqueous solution, reflecting the difficulty of approach of the hydroxide ion on the negatively charged micellar surface. Similar rate-retarding effects have also been observed previously for some electron transfer [6]

and complexation [4] reactions in the presence of differently charged micelles. Moreover, at the highest [SDS] values examined the second-order rate constant k_b becomes very close to k_M'' and, consequently, the base hydrolysis proceeds primarily following this reaction path.

The binding constant (K) of a species strongly bound to the SDS micelles can be related [7, 8, 20] to the partition coefficient P by the equation $K = P\bar{V}$, where \bar{V} ($= 0.251 \text{ dm}^3 \text{ mol}^{-1}$ [8]) is the partial molar volume of the surfactant monomer in the micelle. Therefore, in the present case the partition coefficient P_A ($= K_A/\bar{V}$) of the cobalt(III) complex between the aqueous phase and the micellar pseudo-phase is equal to 1.5×10^4 , the estimated value of $3.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ being used or K_A . In order to evaluate the relative contributions of the electrostatic and nonelectrostatic interactions to the partition coefficient ($P = P_{el}P_{nel}$), we can make a rough estimate of the electrostatic contribution [7, 8, 20] by means of eqn. (6), where Z is the ionic charge on the associated species and ψ is the surface potential of

$$P_{el} = e^{-Z\psi/25.69} \quad (\text{at } 25^\circ\text{C}) \quad (6)$$

the micelle in millivolts. Using the ψ value of -89 or -115 mV obtained from published data [2, 18] for SDS micelles at $[\text{NaCl}] = 0.050 \text{ mol dm}^{-3}$, we calculate $P_{el} = 1.0 \times 10^3$ or 7.7×10^3 , respectively. If allowance is made for the approximation involved in the evaluation of the P_{el} value, it is apparent that binding of the cobalt(III) complex to the SDS micelles is largely due to electrostatic interactions.

As to the salt effects upon the base hydrolysis (eqn. (1)) in the anionic micellar medium, we have performed kinetic measurements at the SDS concentration of $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ under different experimental conditions of added electrolytes. The experimental conditions used are: (a) $[\text{NaOH}] = 0.010 \text{ mol dm}^{-3}$ and varying NaClO_4 concentrations over the range from 0 to $0.080 \text{ mol dm}^{-3}$; (b) $[\text{NaClO}_4] = 0$ and $[\text{NaOH}]$ ranging from 0.0075 to $0.060 \text{ mol dm}^{-3}$; (c) $[\text{NaClO}_4] = 0.010 \text{ mol dm}^{-3}$ and $[\text{NaOH}] = 0.0050$ – $0.050 \text{ mol dm}^{-3}$; (d) $[\text{LiOH}] = 0.010 \text{ mol dm}^{-3}$ and $[\text{LiClO}_4] = 0$ – $0.070 \text{ mol dm}^{-3}$; (e) $[\text{LiClO}_4] = 0$ and $[\text{LiOH}] = 0.0075$ – $0.060 \text{ mol dm}^{-3}$. The second-order rate constant k_b is plotted against the total electrolyte concentration ($[\text{MOH}] + [\text{MClO}_4] = [\text{M}^+]$) in Fig. 4. This plot shows that the hydrolysis rate increases linearly with increasing the total amount of electrolytes present in solution (*i.e.*, the ionic strength of the medium) and, consequently, depends solely on the total concentration of the added cations. No significant differences are observed for Na^+ and Li^+ ions. The linear least-squares treatment of the data yields eqn. (7) for the dependence of k_b on the total concentration of added cation, $[\text{M}^+]$, at $[\text{SDS}] =$

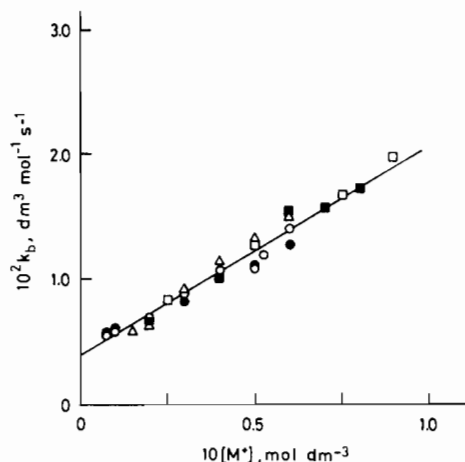


Fig. 4. Plot of k_b against total concentration of added cation at $[\text{SDS}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$: experimental conditions a (\square), b (\circ), c (\triangle), d (\blacksquare), and e (\bullet) described in the text. The straight line is the least-squares fit according to eqn. (7).

$5.0 \times 10^{-2} \text{ mol dm}^{-3}$. The straight line of Fig. 4 represents the least-squares fit.

$$k_b = 3.80 \times 10^{-3} + 0.171 [\text{M}^+] \quad (7)$$

The observed trend of the salt effects upon the hydrolysis rate in the surfactant medium is opposite to that found above (*cf.* Fig. 1) for the reaction in water. These findings might be qualitatively interpreted by bearing in mind that at the high SDS concentration examined the base hydrolysis occurs primarily through the pathway (k_M'') involving the cobalt(III) complex associated with the micelle and the aqueous hydroxide ion. Since added cations and the complex ions compete for binding sites on the micelle, the addition of univalent cationic species would cause a partial expulsion of the reactive cobalt(III) complex from the anionic micelle, implying a rate-retarding effect on the reaction path k_M'' . On the other hand, the decrease in the surface potential of the micelle with increasing ionic strength [16, 18] would facilitate the approach of the reacting aqueous hydroxide ion to the negative micellar surface with a consequent enhancement of the reaction rate. Therefore, the observed positive salt effects on the hydrolysis rate in the presence of $5.0 \times 10^{-2} \text{ mol dm}^{-3}$ SDS would be the result of the partial compensation of these two opposite salt effects on the pathway k_M'' , the second effect outweighing the first one.

Acknowledgements

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