

Studies on cobalt(III) metallosurfactants. Kinetics and mechanism of reduction of cobalt(III) by iron(II) in aqueous acid medium

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Received 9 August 2005; accepted 22 August 2005

Abstract

The kinetics and mechanism of reduction of the surfactant complex ions, *cis*-chloro/bromo(dodecylamine)(triethylenetetramine)cobalt(III) by iron(II) in aqueous solution were studied at 303, 308 and 313 K by spectrophotometry under pseudo-first-order conditions using an excess of the reductant. The second-order rate constant increases with cobalt(III) concentration and the presence of aggregation of the complex itself alters the reaction rate. The reductions are acid-independent in the range $[H^+] = 0.05\text{--}0.25\text{ mol dm}^{-3}$. Variation of ionic strength (μ) influences the reaction rate. Activation and thermodynamic parameters have been computed. It is suggested that the reaction of $Fe^{2+}(aq)$ with the cobalt(III) complex proceeds by an inner-sphere mechanism. The critical micelle concentration (CMC) values of these surfactant metal complexes in aqueous solution were obtained from conductance measurements. Specific conductivity data (at 303, 308 and 313 K) served for the evaluation of the temperature-dependent CMC and the standard Gibbs energy of micellization (ΔG_m^0).

Introduction

Surfactants, sometimes called *surface-active* agents or detergents, are among the most versatile chemicals available. They have applications in many areas, including chemistry (chemical kinetics or equilibria), biology (as membrane mimetics) and Pharmacy [1]. Metallo-surfactants are a special type of surfactant, where a coordination complex (containing a central metal ion with surrounding ligands coordinated to the metal) acts as the surfactant (Scheme 1).

Like any other well-known surfactant, e.g. sodium dodecyl sulfate (SDS), these surfactant–metal complexes also form micelles at a specific concentration called critical micelle concentration (CMC) in aqueous solution. In recent times, there are some reports from various research groups on metallosurfactants of a various nature and their micelle forming properties [2–5]. In all these surfactant-metal complexes, the metal complex entity containing the central metal ion with its primary coordination sphere acts as the head group and the hydrophobic entity of one or more ligands act as a tail part.

Studies on the chemistry of the electron transfer reaction of cobalt(III) complexes have received a sustained high level of attention from the scientific

community for decades, due to their relevance in various redox processes in biological systems, and act as a promising agent for antitumor [6], anthelmintic [7], antiparasitic [8], antibiotics [9] and antimicrobial activities [10]. Numerous studies have been performed addressing the dependence of electron transfer on different environments including metalloproteins [11], Vitamin B₁₂ [12], liquids [13, 14], micelles [15], vesicles [16] and DNA [10]. Electron transfer in a restricted geometry system such as micelles, reverse micelles and vesicles attract a great deal of interest, because of their potential to prolong the lifetime of charge-transfer states, a goal of electron-transfer studies aiming to utilize solar energy [17, 18] and as molecular switches [19]. We have been interested in the synthesis and micelle-forming properties of many surfactant–metal complexes for a long- time [20, 21]. In this paper we present some of the interesting results on the study of kinetics of electron-transfer between cobalt(III)–surfactant complexes with iron(II) in aqueous acid medium.

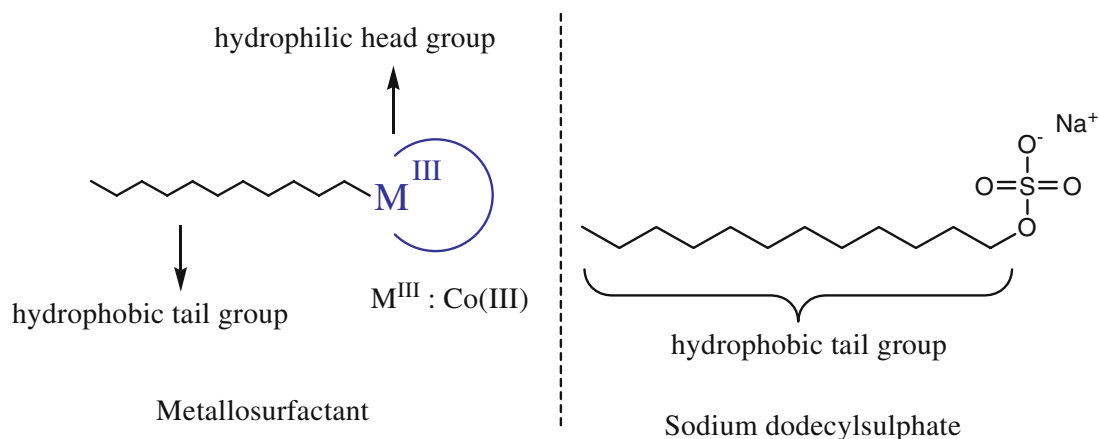
Experimental

Materials

All reagents were of analytical grade (Aldrich and Merck) and were used as received. Ultra pure H₂O, obtained by deionizing distilled H₂O using a Milli-Q

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Scheme 1.

Reagent Grade water system, was used for preparative work and to make up solutions for all physical measurements.

Preparation of oxidant

The surfactant cobalt(III) complexes were used as oxidants which were prepared by a similar method to that reported earlier [21].

Preparation of reductant

$\text{Fe}(\text{ClO}_4)_2$ was prepared in solution by dissolving pure Fe powder in a slight excess of HClO_4 . The concentrations of Fe^{2+} , hydrogen and perchlorate ions in the solution were determined by a method similar to that reported in the literature [22]. The ionic strength of the solution was adjusted by the addition of NaClO_4 solution.

Determination of the CMC

The CMC of these complexes were determined conductometrically using a specific conductivity meter (Elico CM 82). The conductivity cell (dip-type with a cell constant of 1.0) was calibrated with KCl solutions in the appropriate concentration range. The cell constant was calculated using molar conductivity data for KCl published by Shedlivosky [23] and by Chambers *et al.* [24]. Various concentrations of cobalt(III)–surfactant complex were prepared in the 10^{-5} to 10^{-1} mol dm^{-3} range in aqueous solution. The conductivities of these solutions were measured at 303, 308 and 313 K. The temperature of the thermostat was maintained constant within ± 0.01 K. At least one set of 30 specific conductance readings for thirty different concentrations of complex was noted in order to obtain the CMC for each system.

Kinetic measurements

The reactant solution (containing the complex, NaClO_4 and HClO_4 was made up, omitting iron(II), and

thermostatted. A 1 cm path length cuvette was used to achieve optimum optical densities at the concentrations chosen. All solutions were degassed in order to avoid any Fe^{II} air oxidation. After thorough purging with pure N_2 for *ca.* 30 min, the Fe^{II} solution was transferred to the cuvette sealed with a serum cap. A pool of Hg was created on the membrane of the cap to minimize leakage of air while introducing the requisite amount of iron(II) with a hypodermic syringe to initiate reaction and were followed on a Varian Cary 500 Scan UV–Vis–NIR spectrophotometer equipped with Water Peltier System (PCB 150). The temperature was controlled within ± 0.01 K. The decrease in the absorbance was followed at the maximum visible absorption of the cobalt(III) complex. All kinetic measurements were performed under pseudo-first order conditions with the iron(II) in excess over the cobalt complex. The concentration of $\text{Fe}(\text{ClO}_4)_2$ used was 0.25 mol dm^{-3} and the concentration of cobalt(III) complex was chosen typically in the 3.0 – $7.0 \times 10^{-3} \text{ mol dm}^{-3}$ region. The ionic strength was maintained at 1.0 M in all the runs using NaClO_4 . Studies were also carried out in the absence of Fe^{II} where the absorbance of the complex was monitored as a function of time for the same period as in the case of the redox studies, and no change in the absorbance was noted. The second-order rate constant k , for the iron(II) reduction of the cobalt(III) complex defined by $-\text{d}[\text{Co}^{\text{III}}]/\text{d}t = k[\text{Co}^{\text{III}}][\text{Fe}^{\text{II}}]$ was calculated from the concentration of iron(II) and the slope of the $\log(A_t - A_\infty)$ versus time plot, which is equal to $-k[\text{Fe}^{2+}]/2.303$, where A_t is the absorbance at time t ; A_∞ , the absorbance after all the cobalt(III) complex has been reduced to Co^{II} , and k , the rate constant. Usually the value of A_∞ was measured at times corresponding to 10 half-lives. All the first-order plots were linear, with a correlation coefficient of 0.999. Each rate constant reported was the average result of triplicate runs. Rate constants obtained from successive half-life values within a single run agreed to within $\pm 5\%$. No trends indicative of systematic errors were noted, and average values did not differ significantly from those obtained

from least-squares treatment of logarithmic plots of absorbance differences against reaction time.

Stoichiometry

The stoichiometry of the reaction was determined by estimating Fe^{III} and Co^{II} present in the product mixture. Iron(III) was determined [25] as the thiocyanate complex having a maximum absorption at 480 nm by reference to the calibration curve, and cobalt(II) was determined [26] as [CoCl₄]²⁻ at 690 nm in an excess of HCl. The ratio Fe^{III}:Co^{II} was found to be 1:1.

Results and discussion

The cobalt(III)–surfactant complexes synthesized in the present study were characterized by UV–Visible, IR and NMR spectra and checked by comparing the spectra with those reported earlier [21, 27]. The purity of the complexes was checked by cobalt [26], elemental, halide analyses, which were found to be in good agreement with that of the calculated value (Table 1).

The uniqueness of the cobalt(III)–surfactant coordination complexes lies in the fact that the bond between the head group and the tail part of the surfactant–cobalt(III) complex is a coordinate bond and the surfactant contains a higher charge on the head group, unlike common surfactants (SDS). At the same time, like the common surfactants, these cobalt(III)–surfactant coordination compounds form foam in aqueous solution when mechanically disturbed, like shaking, and these complexes dissolve slowly in water. Sometimes we have to sonicate to get a homogeneous solution.

The CMC values were computed from the slope of [Co^{III}] versus specific conductance data. The complex concentration at which the micellization starts is evident from the change in the slope of the plot and that particular concentration is the CMC under the experimental conditions. The CMC values were measured at three different temperatures (303, 308 and 313 K). At all temperatures a break in the conductance versus concentration plots, characteristic of micelle formation was observed. The CMC values were determined by fitting the data points above and below the break to two equation of the form $y = mx + c$ and solving the two equations simultaneously to obtain the point of interaction. Least-squares analysis was employed and correlation coefficients were greater than 0.99 in all cases. The conductivity measurements at three different temperatures were repeated three times and the accuracy of the CMC values was found with in $\pm 2\%$ error. Table 2, illustrates the CMC values for the complexes cis -[Co(trien)(C₁₂H₂₅NH₂)Cl]²⁺ and cis -[Co(trien)(C₁₂H₂₅NH₂)Br]²⁺ respectively as a function of temperature (Figure 1). It is found that CMC values increase on increasing the temperature for a given system. This behavior may be related to two competitive effects. Firstly, a temperature increase causes a

Table 1. Microanalysis of cobalt(III) complexes

Complexes	λ_{max}	(Calc) Found %				
		Co	C	H	N	Cl/Br
cis - α -[Co(trien)-(C ₁₂ H ₂₅ NH ₂)Cl] ²⁺	485	(9.1)	(37.2)	(6.5)	(10.8)	(5.4)
		9.0	37.2	6.3	10.9	5.2
cis - α -[Co(trien)-(C ₁₂ H ₂₅ NH ₂)Br] ²⁺	490	(8.5)	(34.8)	(6.1)	(10.1)	(11.5)
		8.4	34.5	5.9	9.8	11.3

Table 2. CMC values of cobalt(III) complexes

Complexes	CMC $\times 10^3$ (mol dm ⁻³)			ΔG_{mic}^0 (kJ mol ⁻¹)
	303 K	308 K	313 K	
cis - α -[Co(trien)-(C ₁₂ H ₂₅ NH ₂)Cl] ²⁺	1.0 \pm 0.1	1.50 \pm 0.1	1.82 \pm 0.1	-32.3 \pm 0.4
cis - α -[Co(trien)-(C ₁₂ H ₂₅ NH ₂)Br] ²⁺	1.1 \pm 0.1	1.42 \pm 0.1	1.64 \pm 0.1	-31.9 \pm 0.3

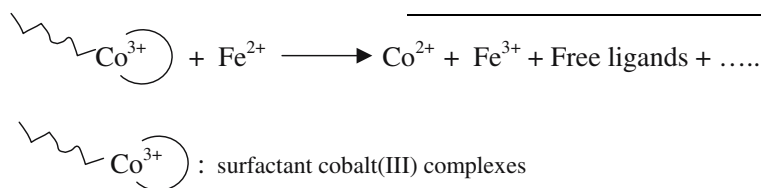
decrease in hydration in the hydrophilic group, which favors micellization. Secondly, a temperature increase also causes disruption of the water surrounding the hydrophobic group, and this retards micellization. The relative magnitude of these two opposing effects will determine CMC behavior. It is observed that by changing the ion from Cl⁻ to Br⁻, CMC decreases. This is due to the increase in the size of the ion in the coordination sphere, which makes it more weakly hydrated. Weakly hydrated ions can be adsorbed more readily in the micellar surface that decreases the charge repulsion between the polar group and thus facilitates the micellization. Assuming that micellization occurs according to the charged pseudo-phase separation model [28], the standard Gibbs free energy of micellization, ΔG_m^0 , for the cationic surfactant was calculated from the relation mentioned in the literature [29]. Our data shows that the free energy of micellization is similar to data reported for common surfactants [30]. As mentioned in our previous reports [20, 21], the CMC values of this cobalt(III)–surfactant coordination complexes are also very low compared to that of simple organic surfactant, dodecylammonium chloride (CMC = 1.5×10^{-2} mol dm⁻³). Thus it is suggested that these metal surfactant complexes have more capacity to associate themselves forming aggregates compared to those of ordinary synthetic organic surfactants. Moreover, introduction of a metal complex to the hydrophilic part of the amphiphile can remarkably enhance the ability for aggregation.

Electron-transfer kinetics

Kinetic data obey the rate equation first order with respect to both the cobalt(III) complex and iron(II).

$$-d[Co^{III}]/dt = -d[Fe^{II}]/dt = k [Co^{III}] [Fe^{II}] \quad (1)$$

corresponding to the chemical process



since FeCl^{2+} is the only Fe^{III} species produced in the reaction, though it would dissociate into Fe^{3+} and Cl^- under the experimental conditions.

Table 3, shows the values of the measured second-order rate constant of the specific rates of *cis*-Co(trien)(C₁₂H₂₅NH₂)X²⁺ with Fe^{2+} at three different temperatures (303, 308 and 313 K) in neat aqueous solution at our fixed $[\text{Fe}^{2+}]$, ionic strength and acid concentration. In all cases, the $\log(A_t - A_\infty)$ versus t plots were substantially linear for at least two half-lives. The second-order rate constant for the Fe^{2+} reduction of cobalt(III) complexes was obtained from the slope of such plot. The $\log(A_t - A_\infty)$ versus t plots were linear up to 200 min in all cases, so the effect of aquation of cobalt(III) complexes could be neglected. The relatively low reduction rate of *cis*-Co(trien)(C₁₂H₂₅NH₂)X²⁺ as compared with that of the corresponding $\text{CoN}_4\text{Cl}_2^+$ may be mainly due to its dipositive charge. It is evident from the Table 3, that a relatively small increase in the rate with an increase in the concentration was observed (Figures 2

and 3). This is due to the presence of aggregation of the complex itself to form a micelle, which leads to an increase in the reaction rate. Aggregation of the cobalt(III) complex molecule makes iron have a bridge with more than one chlorine/bromine atom of cobalt center simultaneously, so that the electron transfer would be effective.

Effect of $[\text{Fe}^{2+}]$

Figure 4 gives the pseudo-first order rate constant (k_p) for a series of runs at various concentrations of iron(II) for the chloro/bromo systems at fixed cobalt(III) concentration. Plots of $\log(A_t - A_\infty)$ versus time were linear and the pseudo first-order rate constant (k_p , s⁻¹) evaluated from these plots was found to increase with an increase in $[\text{Fe}^{2+}]$. This shows that the reaction exhibits first order with respect to $[\text{Fe}^{2+}]$. Plots of k_p (s⁻¹) versus $[\text{Fe}^{2+}]$ gave straight lines passing through the origin confirming the first-order dependence of reaction rate with respect to $[\text{Fe}^{2+}]$. Such a kinetic

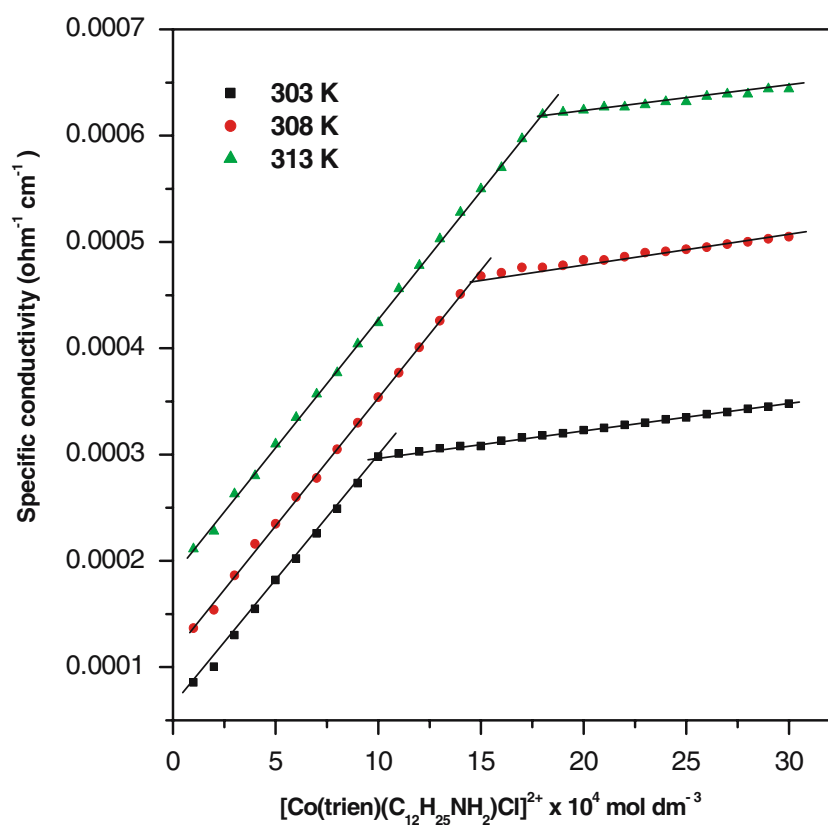


Fig. 1. Electrical conductivity versus $[\text{Co}^{\text{III}}]$ in aqueous solution.

Table 3. Second-order rate constants for the reduction of $[\text{Co}^{3+}]$ by $[\text{Fe}^{2+}]$ in aqueous solution

Oxidizing agent	$[\text{Co}^{\text{III}}]$ $\times 10^3$ mol dm^{-3}	$k \times 10^4$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)		
		303 K	308 K	313 K
<i>cis</i> - α -[Co(trien)- ($\text{C}_{12}\text{H}_{25}\text{NH}_2$)Cl] $^{2+}$	3.0	0.49 ± 0.2	2.93 ± 0.4	5.08 ± 0.3
	4.0	0.64 ± 0.3	4.75 ± 0.5	8.02 ± 0.2
	5.0	0.79 ± 0.1	6.12 ± 0.2	9.21 ± 0.2
	6.0	0.99 ± 0.1	7.50 ± 0.1	11.16 ± 0.2
	7.0	1.52 ± 0.1	8.53 ± 0.1	14.32 ± 0.1
<i>cis</i> - α -[Co(trien)- ($\text{C}_{12}\text{H}_{25}\text{NH}_2$)Br] $^{2+}$	3.0	0.43 ± 0.3	1.94 ± 0.1	3.86 ± 0.5
	4.0	0.57 ± 0.2	2.48 ± 0.1	5.31 ± 0.1
	5.0	0.70 ± 0.5	3.10 ± 0.3	8.41 ± 0.3
	6.0	0.97 ± 0.2	4.01 ± 0.2	10.87 ± 0.2
	7.0	1.23 ± 0.1	5.35 ± 0.5	12.74 ± 0.1

$[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$

behavior with no intercept in the plots of k_p (s^{-1}) versus $[\text{Fe}^{2+}]$ indicates the complex formed is too unstable to be detected. Independence of the calculated values of k upon the concentration of iron(II) confirms second-order kinetics.

Effect of ionic strength (μ)

All the reactions were studied in sodium perchlorate medium. The effect of ionic strength on the rate of the

reaction was studied by varying the concentration of sodium perchlorate from 0.50 to 2.0 mol m^{-3} at fixed concentrations of cobalt(III), Fe^{II} and H^+ . A relatively small increase in rate with increasing ionic strength was observed k versus Ionic strength (Figure 5). The effect of ionic strength is such that electrostatic interaction seems to be mainly responsible for the overall precursor complex formation.

Effect of $[\text{H}^+]$

All the reactions were studied in perchloric acid medium. The variation of acid concentration with k was studied at fixed $[\text{Co}^{3+}]$, $[\text{Fe}^{2+}]$, $[\mu]$. The results obtained indicate that the second-order rate constant is independent of the hydrogen-ion concentration (Figure 6). Such a kinetic behavior indicates the nonexistence of any protonation equilibrium with respect to both $[\text{Fe}^{2+}]$ and $[\text{Co}^{3+}]$ under the present experimental conditions employed.

Temperature dependence

The effect of temperature on (k) was studied at three different temperature (Table 3) viz., 303, 308 and 313 K, in order to obtain the thermodynamic parameters for the reaction between cobalt(III) surfactant complexes and Fe^{2+} .

From the transition state theory,

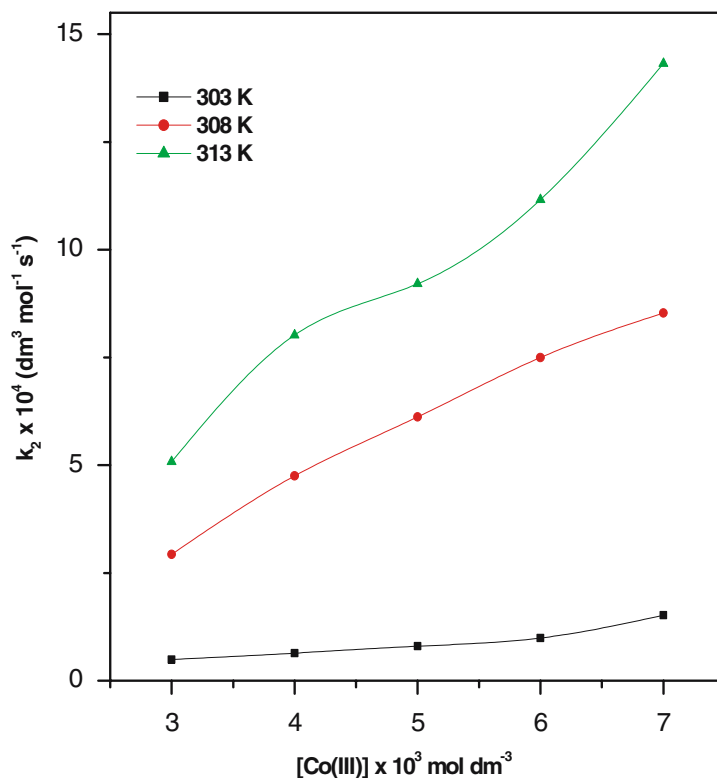


Fig. 2. Plot of $[\text{Co(trien)(C}_{12}\text{H}_{25}\text{NH}_2)\text{Cl}]^{2+}$ versus k , ($[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$).

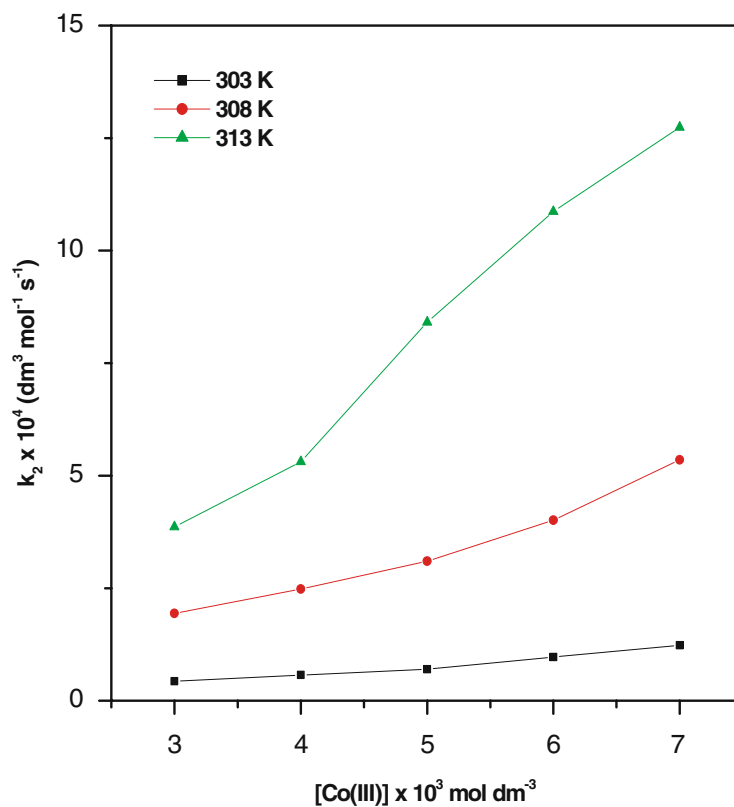


Fig. 3. Plot of $[\text{Co}(\text{trien})(\text{C}_{12}\text{H}_{25}\text{NH}_2)\text{Br}]^{2+}$ versus k_2 , ($[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$).

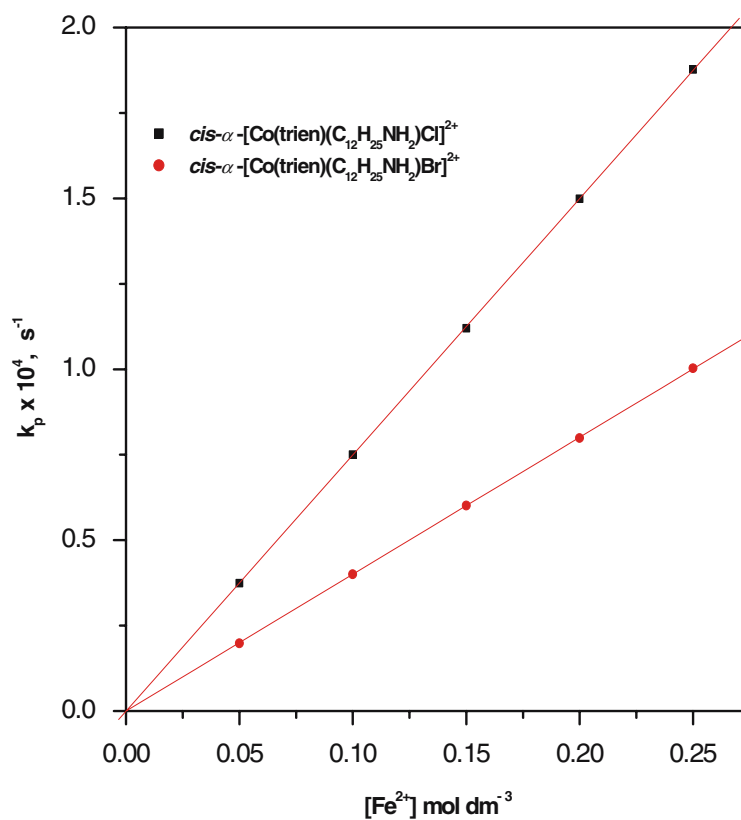


Fig. 4. Effect of $[\text{Fe}^{2+}]$ on pseudo-first-order rate constant, ($[\text{Co}^{\text{III}}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$; Temp = 308 K).

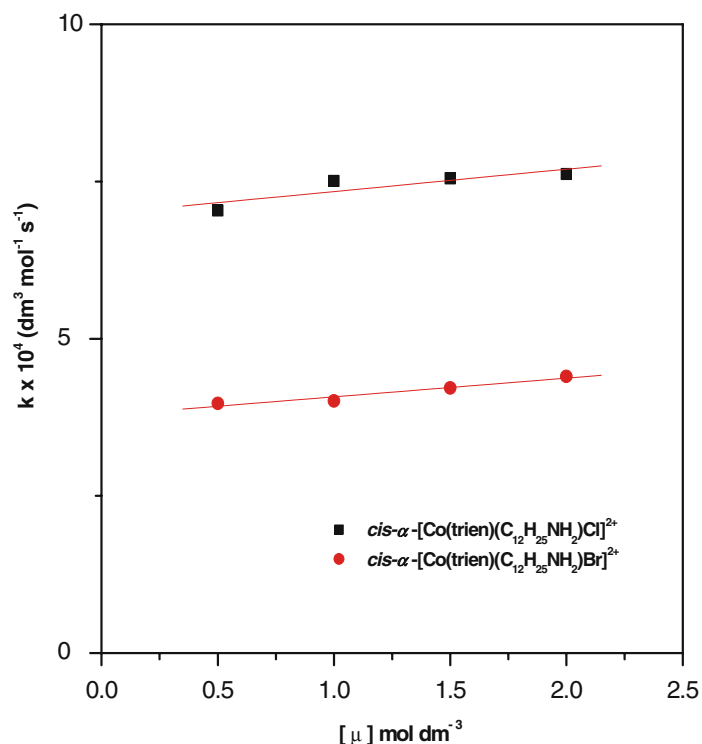


Fig. 5. Effect of Ionic strength on k , ($[\text{Co}^{\text{III}}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Fe}(\text{II})] = 0.25 \text{ mol dm}^{-3}$; $\mu = (\text{NaClO}_4)$; $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$; Temp = 308 K)

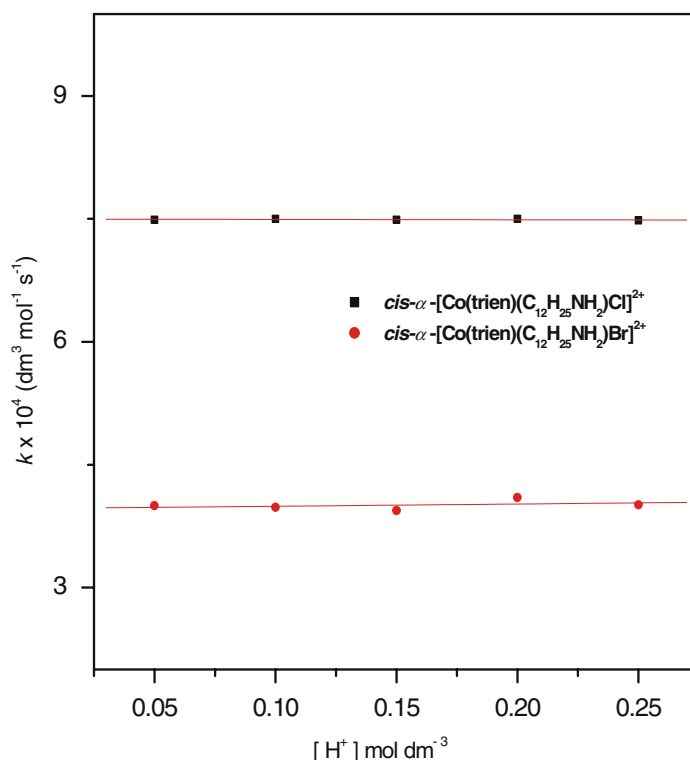


Fig. 6. Effect of $[\text{H}^+]$ on k , ($[\text{Co}^{\text{III}}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Fe}(\text{II})] = 0.25 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$; $[\text{H}^+] = \text{HClO}_4 \text{ mol dm}^{-3}$; Temp = 308 K).

$$\ln(k/T) = \ln(k_B/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

the values of ΔS^\ddagger and ΔH^\ddagger were determined by plotting $\ln(k/T)$ versus $1/T$. From the slope, the value of ΔH^\ddagger were calculated ($-\Delta H^\ddagger/R$) and from the intercept

$[\ln(k_B/h) + \Delta S^\ddagger/R]$ the value of ΔS^\ddagger was calculated. The value of entropy of activation (ΔS^\ddagger) and enthalpy of activation (ΔH^\ddagger) are given in Table 4. A meaningful mechanistic explanation is not possible, however as seen from the table, there is a decrease in the ΔH^\ddagger and ΔS^\ddagger

Table 4. Thermodynamic parameters

Oxidizing agent	[Complex] × 10 ³ mol dm ⁻³	ΔH [‡] (kJ mol ⁻¹)	ΔS [‡] (JK ⁻¹)
<i>cis</i> -α-[Co(trien)- (C ₁₂ H ₂₅ NH ₂)Cl] ²⁺	4.0	165.4	224.1
	5.0	162.9	217.4
	6.0	159.3	207.4
	7.0	146.0	166.7
<i>cis</i> -α-[Co(trien)- (C ₁₂ H ₂₅ NH ₂)Br] ²⁺	5.0	158.8	203.3
	6.0	153.8	189.0
	7.0	149.9	177.9

values with increasing cobalt(III) concentration. This is due to the electrostatic attraction between the reductant and the oxidant micelle in the micellar phase. The ΔH[‡] obtained in this study is reasonable when compared to those values obtained for lower amines. ΔS[‡] shows that the transition state is well structured in the micellar phase. The positive values of ΔS[‡] clearly indicate that the micellization is governed mainly by hydrophobic interactions between the surfactant cations, resulting in the breakdown of the structured water surrounding the hydrophobic groups, and indicates that the cationic surfactants are entropy driven processes. It is evident from the literature that *cis*-Co(trien)XClⁿ⁺ (X = Cl⁻, Br⁻, RNH₂) react with Fe²⁺ via the chloride-bridged activated complex [30, 31], so it is reasonable to assume a similar mechanism for our reactions. The order of effectiveness is Co(trien)Cl₂⁺ > Co(trien)(C₁₂H₂₅NH₂)Cl⁻ > Co(trien)(C₁₂H₂₅NH₂)Br⁻. Introduction of higher alkylamine into the nonbridging *cis*-ligand facilitates the reaction rate. Moreover, the presence of a higher alkylamine group in the nonbridging ligand increases the solvation energy and stabilizes the activated complex.

Binding mode of the coordinated halide ion, X⁻

The trend: F⁻ < Cl⁻ < Br⁻ < I⁻ is known as 'normal order' and the reverse is known as 'inverse order'. Several aspects related to the oxidant and reducing agents appear to be significant in determining the trend [33]. [Co(NH₃)₅X]²⁺ with Fe^{II} showing an inverse order [33], which may be ascribed to the decreasing stabilities of FeX²⁺ in order: FeCl²⁺ > FeBr²⁺. It may be thus generalized that if the oxidant is a soft acid, one finds the inverse order and, if hard, the normal order, the reductant in both cases being a hard acid. Hence, based on the above arguments, one should expect an inverse trend for the Fe^{II} reduction of halogenocobalt(III)-complexes if the electron transfer is mediated by bridging through the halide ion. In the present study, the electron transfer is mediated by halide ion, Cl⁻/Br⁻ and the trend is found to be in 'inverse order'.

We conclude that, the title reaction proceeds via an inner-sphere pathway in aqueous solution and the

formation of micelles by the title complex leads to alter the reaction rate.

Acknowledgement

Sponsorship of this work by the University Grants Commission (No.F.12-9/2001/SR-I) is gratefully acknowledged.

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