Studies on synthesis, determination of CMC values, kinetics and the mechanism of iron(II) reduction of surfactant-Co(III)-ethylenediamine complexes in aqueous acid medium

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Studies on synthesis, determination of CMC values, kinetics and the mechanism of iron(II) reduction of surfactant–Co(III)–ethylenediamine complexes in aqueous acid medium

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The surfactant–Co(III) complexes of the type *cis*-[Co(en)$_2$AX]$^{2+}$ (A = Tetradecylamine, X = Cl$^-$, Br$^-$) were synthesised from corresponding dihalogeno complexes by the ligand substitution method. The critical micelle concentration (CMC) values of these surfactant complexes in aqueous solution were obtained from conductance measurements. The kinetics and mechanism of iron(II) reduction of surfactant–Co(III) complexes, *cis*-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl](ClO$_4$)$_2$ and *cis*-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Br] (ClO$_4$)$_2$ ions were studied spectrophotometrically in an aqueous acid medium by following the disappearance of Co(III) using an excess of the reductant under pseudo-first-order conditions: [Fe(II)] = 0.25 mol dm^{-3}, [H$^+$] = 0.1 mol dm^{-3}, [μ] = 1.0 mol dm^{-3} ionic strength in a nitrogen atmosphere at 303, 308 and 313 K. The reaction was found to be of second order and showed acid independence in the range [H$^+$] = 0.05–0.25 mol dm^{-3}. The second-order rate constant increased with surfactant–Co(III) concentration and the presence of aggregation of the complex itself altered the reaction rate. The effects of [Fe(II)], [H$^+$] and [μ] on the rate were determined. Activation and thermodynamic parameters were computed. It is suggested that the reaction of [Fe(II)] with Co(III) complex proceeds by an inner-sphere mechanism.

Keywords: surfactant–cobalt(III); micelle; reduction; thermodynamic parameters; kinetics

1. 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]. Metallosurfactants 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

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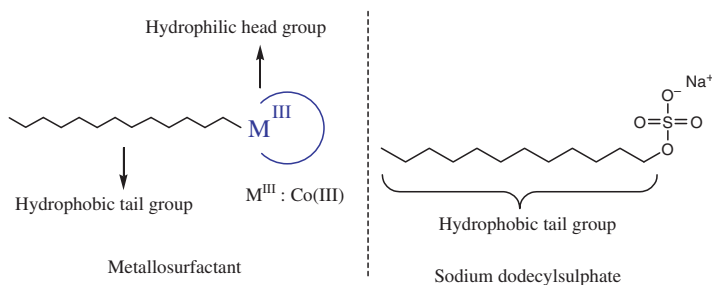
Scheme 1. Structure of metallosurfactant and surfactant.

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 [2–4]. 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.

Electron transfer (ET) processes are fundamentally important to many branches of chemistry and biology. A feature of modern coordination chemistry is its expanding ability to mimic form and structure in biology. This had largely been achieved using a principle which had itself been borrowed from biology: the self-assembly of well-defined and complex molecular entities from constituent subunits in solution. Unlike biology, however, self-assembly in coordination chemistry occurs through the formation of coordinate bonds rather than weak inter- or intramolecular interactions. Self-assembly in coordination chemistry consequently provides an important and powerful entry into supramolecular engineering and the associated fields of solid-state and crystal engineering [5,6]. It potentially also affords novel catalytic systems [7] which may ultimately be induced to offer the selectivity and usefulness of biological catalysts. In the last century, numerous works [1–18] were performed on the nature of the self-assembly process and the interactions of these structures with salts, alcohols, proteins and other compounds.

A growing number of applications have been developed to study the metallo-surfactants in this context. Surface-active materials were major building blocks of many physical, chemical and biological systems. They were introduced into several commercial products such as antiseptic agents in cosmetics and as germicides [19], and also found a wide range of applications because of their unique solution properties such as detergency, solublisation and surface-wetting capabilities, in diverse areas such as mining, petroleum and pharmaceutical industries. It has been observed [20–24] that several redox reactions in micellar media were influenced by the hydrophobic and electrostatic forces and for a given set of reactions the observed rate depends on the extent of association between the reactants and micellar aggregates. Most of the chemical reactions investigated were simple organic and inorganic systems. On the other hand, relatively few works have been carried out on the electron-transfer reactions for transition metal ions complexes with lipophilic ligands [25–30]. Redox reactions of metallosurfactants have been the subject of continued interest in their own right, especially in the context of ET processes. Owing to their importance in molecular synthesis and electrochemical reactions in a wide

range of homogeneous and heterogeneous processes in many chemical and bio-chemical systems, ET reactions have been the subject of many theoretical and experimental studies. Most reactions of inorganic complexes in micellar and in microemulsion systems occur at rates markedly different from those in aqueous solution. During the course of studying the effects of metallosurfactants on chemical reactions, catalytic effects were observed [31–34] above their CMC. Such systems offered the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as the local microenvironment on the reactivity. Cobalt(III) complexes, by virtue of their abundance and diversity, have played a fundamental role in our understanding of the structural, spectroscopic and electrochemical properties of coordination compounds. We were interested in the synthesis and micelle-forming properties of Co(III) complexes containing lipophilic ligands for a long time [33–36]. As in biology, such compounds may exhibit novel physical and chemical properties with interesting and useful associated applications. Studies on the ET chemistry of Co(III) metallosurfactants have received a sustained high level of attention, due to their relevance in various redox processes in biological systems and act as promising agents for antitumour [37], anthelmintic [38], anti-parasitic [39], antibiotic [40] and antimicrobial activities [41]. In this study, some of the interesting results concern the kinetics of electron transfer between Co(III) metallosurfactants with Fe(II) in aqueous acid medium.

2. Experimental details

2.1. *Materials*

All the reagents were of analytical grade from Aldrich and Merck were used as received. The deionised H_2O used had conductivity $<10^{-6}\,S\,m^{-1}$ and was obtained from a milli-Q water system. Pure N_2 gas was bubbled through the reaction solutions to remove dissolved O_2. Oxidant solutions were shielded from light with aluminium foil.

2.2. *Instrumentation*

Infrared (IR) spectra were recorded on a Jasco 460 plus spectrometer using the potassium bromide discs method. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer using DMSO as solvent. Electronic absorption spectra were taken in 10^{-3} M perchloric acid medium recorded on a Varian Cary 500 scan UV–Vis–NIR spectrophotometer. C, H and N were estimated using a Perkin–Elmer 2400 CHN instrument. Conductivity studies were done in aqueous solutions of the complexes with an Elico conductivity bridge-type CM 82 and a dip-type cell with a cell constant of 1.0.

2.3. *Synthesis of oxidant*

2.3.1. *cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl](ClO$_4$)$_2$*

trans-[Co(en)$_2$Cl$_2$]Cl [42] (3.0 g) was dissolved in water (20 ml) and tetradecylamine (2.5 g) in ethanol (10 mL) was added drop by drop over a period of 30 min. The green

solution gradually became brown during the reaction. The mixture was set aside at room temperature for two days until no further change was observed. Afterwards a saturated solution of sodium perchlorate in very dilute perchloric acid was added. Slowly a pasty solid mass separated out and it was filtered off, washed with small amounts of alcohol followed by acetone, and then it was dried over air. The semi-dried solid was further dried in a drying pistol over fused calcium chloride and stored in vacuum desiccators.

2.3.2. *cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Br](ClO$_4$)$_2$*

This complex was synthesised by adopting the same method as described for the synthesis of the complex *cis*-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl](ClO$_4$)$_2$ except that in place of *trans*-[Co(en)$_2$Cl$_2$]Cl, *trans*-[Co(en)$_2$Br$_2$]Br [43] (3.0 g) was used.

Safety note: Caution! Perchlorate salts of surfactant–Co(III) complexes containing organic ligands are potentially explosive! Although we have experienced no problems with the compounds reported in this work, they should only be handled in small quantities and never scraped from sintered glass frits nor heated in the solid state.

2.4. *Preparation of reductant*

A stock solution of Fe(ClO$_4$)$_2$ was prepared by dissolving pure Fe powder in a slight excess of HClO$_4$ under a N$_2$ atmosphere. These solutions were prepared just prior to use for kinetic measurements. The ionic strength of the solution was adjusted by the addition of NaClO$_4$. The concentrations of Fe(II), H$_2$ and perchlorate ions in solution were determined by a method similar to that reported in the literature [44]. The free-acid content of iron solution was measured by passing it through a Dowex 50 W X-8 strong cation-exchange resin in the H$^+$ form to obtain [H$^+$] equivalent to the metal-ion concentration along with free acid, and then subtracting the metal equivalent from these. An aqueous solution of NaClO$_4$ was standardised by passing through a Dowex 50 W X-8 strong cation-exchange resin in the H$^+$ form and titrating the liberated acid with standard NaOH to a phenolphthalein end-point. The total acid content of the reaction mixtures was calculated as added acid plus that produced by the hydrolysis of ferric ion.

2.5. *Determination of CMC*

The CMC values of the complexes were calculated using electrical conductance data measured using a digital 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 Barthel *et al.* [45]. Various concentrations of surfactant–Co(III) complexes were prepared in the range of 10^{-5}–10^{-2} mol dm^{-3}. All measurements were performed in a double-walled glass container, which was maintained at the desired temperature (± 0.1 K) using a circulating water bath. The conductivity of these solutions was measured at 303–313 K. The conductance was measured after thorough mixing and temperature equilibrating at each dilution.

The measurement was started with a dilute solution and the subsequent concentrated solutions were prepared by adding a previously prepared stock solution. The establishment of equilibrium was checked by taking a series of reading after 15 min intervals until no significant change occurred.

2.6. *Kinetic measurements*

The reactant solution (containing the complexes, $NaClO_4$ and $HClO_4$) was made, omitting iron(II), and was thermostatted. A 1 cm path length cuvette was used to achieve optimum optical densities at the concentrations chosen. All the 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 minimise leakage of air while introducing the requisite amount of Fe(II) with a hypodermic syringe to initiate reaction and was followed on a Varian Cary 500 Scan UV–Vis–NIR spectrophotometer equipped with the 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 surfactant–Co(III) complex. All kinetic measurements were performed under pseudo-first-order conditions with the Fe(II) in excess over the surfactant–Co(III) complex. The concentration of $Fe(ClO_4)_2$ used was 0.25 mol dm^{-3} and the concentration of surfactant–Co(III) complex was chosen typically above their CMC values in the 3.0–7.0×10^{-3} 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, no change in the absorbance was noted. The second-order rate constant, k, for the Fe(II) reduction of the Co(III) complex defined by $-d[Co(III)]/dt = k$ [Co(III)][Fe(II)] was calculated from the concentration of iron(II) and the slope of the $\log(A_t - A_\alpha)$ versus time plot, which is equal to $-k$ [Fe(II)]/2.303, where A_t is the absorbance at time t; A_α, the absorbance after all the Co(III) complex has been reduced to Co(II) and k, the rate constant. Usually, the value of A_α 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 indicating systematic errors were noted, and the average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time.

2.7. *Effect of [Fe(II)]*

Figure 1 gives the pseudo-first-order rate constant (k_p) for a series of runs at various concentrations of Fe(II) for the chloro/bromo systems at fixed Co(III) concentration. Plots of $\log(A_t - A_\alpha)$ 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 [Fe(II)]. This shows that the reaction is first-order with respect to [Fe(II)]. Plots of $k_p(s)^{-1}$ versus [Fe(II)] generated straight lines, passing through origin,
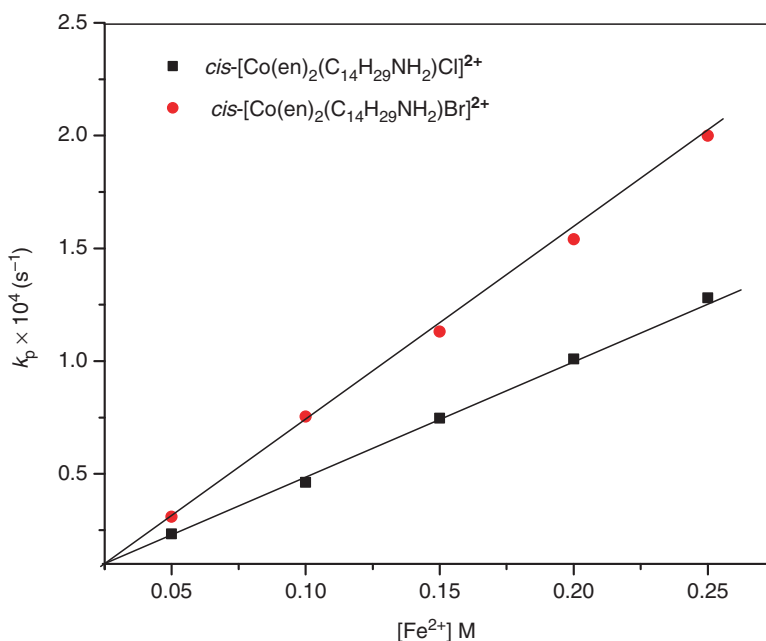
Figure 1. Effect of [Fe(II)] on pseudo-first-order rate constants: ([Co(III)] = $6.0 \times 10^{-3} \, \text{mol dm}^{-3}$; $[\mu] = 1.0 \, \text{mol dm}^{-3}$; $[\text{H}^+] = 0.10 \, \text{mol dm}^{-3}$; T = 308 K).

confirming the first-order dependence of reaction rate with respect to [Fe(II)]. Such a kinetic behaviour, with no intercept in the plots of $k_p(\text{s})^{-1}$ versus [Fe(II)], indicates that the complex formed is too unstable to be detected. Independence of the calculated values of k upon the concentration of Fe(II) confirms the second-order kinetics.

2.8. Stoichiometry

The stoichiometry of the reaction was determined by estimating Fe(III) and Co(II) present in the product mixture. Fe(III) was determined spectrophotometrically by Kitson's method [46] and Co(II) was determined [47] as $[\text{CoCl}_4]^{2-}$ at 690 nm in an excess of HCl. The ratio Fe(III) : Co(II) was found to be 1 : 1 in the reactions studied, indicating 1 : 1 stoichiometry.

3. Results

3.1. Spectroscopic characterisation

The wavelength of the first absorption maximum in aqueous perchlorate medium of complexes is given in Table 1. It has been observed that the absorption spectra [48,49] of the *cis* and *trans* forms of $[\text{Co(en)}_2(\text{NH}_3)\text{Y}]^{n+}$ cations (Y = Cl or H_2O) showed some differences in the longest-wavelength absorption band (d–d transition). The *trans* form showed a lower intensity band ($\varepsilon < 50 \, \text{M}^{-1} \, \text{cm}^{-1}$) whereas the *cis* form showed a higher intensity band ($\varepsilon > 70 \, \text{M}^{-1} \, \text{cm}^{-1}$). This observation can be

Table 1. Microanalysis of surfactant–cobalt(III) complexes.

Complexes	$^a\lambda_{max}$ (ε)	Yield (%)	% Found (Calculated)				
			Co	C	H	N	Cl/Br
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl]$^{2+}$	513 (91)	67	9.53 (9.40)	34.61 (34.49)	7.48 (7.56)	11.35 (11.17)	5.72 (5.65)
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Br]$^{2+}$	521 (93)	62	8.86 (8.78)	32.57 (32.20)	7.41 (7.05)	10.38 (10.43)	12.08 (11.90)

Note: $^a\lambda$ in nm; ε in M^{-1} cm^{-1}.

used to determine the geometrical configuration of the present cations, whose longest-wavelength absorption maxima are shown in Table 1. By comparing the spectra of the corresponding butylamine complexes [43], it reveals that both the ordinary and the surfactant complexes have the same structure and the replacement of lower aliphatic amine ligands by long chain aliphatic amine ligands does not affect the symmetry of the surfactant complexes.

Infrared spectroscopy is used to distinguish the mode of coordination of the ligand with the central metal ion. Various workers have employed [48,50–53] the NH$_2$ deformation mode in the 1700–1500 cm^{-1} region, CH$_2$ rocking mode in the 900–850 cm^{-1} region and Co–N stretching mode in the 610–500 cm^{-1} region to distinguish between the *cis*- and *trans*-isomers of cobalt(III)–ethylenediamine complexes. The *cis*-isomers always show two peaks, whereas the *trans*-isomers usually have only one peak in the CH$_2$ rocking region. In the present study, the NH$_2$ deformation mode shows two bands in the region 1600–1530 cm^{-1}, two bands for the CH$_2$ or NH$_2$ twist mode in the region 1060–980 cm^{-1} [53] and two bands for the CH$_2$ rock mode in the region 900–850 cm^{-1}. In the surfactant–Co(III) complexes, the bands exhibit around 2925 and 2853 cm^{-1} can be assigned to C–H asymmetric and symmetric stretching vibration of aliphatic CH$_2$ of tetradecylamine. Perchlorate bands at *ca* 1100 and 620 cm^{-1} belong to an ionic species; this means that this counter-ion is not involved in the cobalt–ligand coordination [54]. The IR spectroscopic data therefore clearly indicate a *cis* configuration for the surfactant–cobalt(III) complexes.

The ^{1}H NMR spectra offer a conclusive proof of the configuration of the isomers in solution. The *cis*- and *trans*-isomers of [Co(en)$_2$X$_2$]$^+$ ions have different symmetry properties, and this factor appears to govern the difference in their NMR spectra. The *cis*-isomers possess C$_2$-symmetry with the two-fold axis in the plane of cobalt and two X groups, and this makes –CH$_2$CH$_2$– groups equivalent provided that the cobalt–ethylenediamine rings have the same conformation. Moreover, in complexes of the type *cis*-[Co(en)$_2$X$_2$]$^{n+}$ there are four pairs of equivalent nitrogen protons, but in complexes of the type *cis*-[Co(en)$_2$XY]$^{n+}$, although some protons are similarly orientated, no two protons are in identical situations. In complexes of the type *trans*-[Co(en)$_2$X$_2$]$^{n+}$ all the protons are equivalent, but in complexes of the type *trans*-[Co(en)$_2$XY]$^{n+}$ all the protons on one side of the plane of the ethylenediamine ring will experience a different field from those on the other side. It is possible that if the ligands X and Y differed greatly in size, inversion of the chelate ring would be

hindered or even inhibited. In the case of *trans* complexes, two separate proton resonances of equal area would be observed if inversion was inhibited, while with *cis* complexes a most complex pattern would result. In *trans*-isomers, however, with D_{2h} symmetry, the amine and methylene protons of ethylenediamine appear as a singlet at 3 ppm. In the present study of *cis* complexes, due to lower symmetry, methylene protons of ethylenediamine show a absorption around 2.1–2.7 ppm. The methylene protons of the long-chain moiety (tetradecylamine) give rise to a multiplet usually at 1.25–1.7 ppm, whereas the terminal methyl group of the hydrocarbon chain substituent gives triplet around 0.86 ppm. ^{13}C NMR spectrum of surfactant–cobalt(III) complexes exhibits only one signal around 35–40 ppm because of merging of tetradecylamine and chelating ligands signals. For long-chain tetradecylamne, the aliphatic methylene carbons of all the surfactant–cobalt(III) complexes appeared around 15–40 ppm and terminal carbon atom appeared around 14 ppm.

3.2. *CMC values*

The CMC values were computed from the slope of [Co(III)] versus specific conductance data. The complex concentration at which the micellisation starts was 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 determined 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 equations of the form $y = mx + c$ and solving the two equations simultaneously to obtain the point of intersection. Least-squares analysis was employed and correlation coefficients were greater than 0.98 in all the cases. The conductivity measurements at three different temperatures have been repeated three times and the accuracy of the CMC values was found within $\pm 3\%$ error. Figure 2 illustrates the plot for the complex *cis*-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl](ClO$_4$)$_2$; similar plot

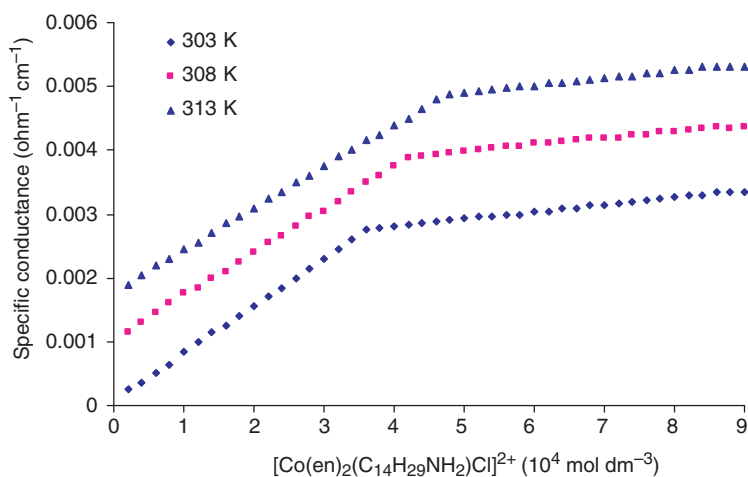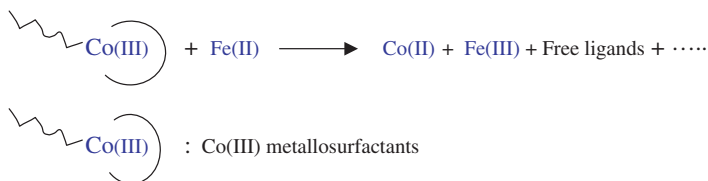Figure 2. Electrical conductivity vs. [Co(III)] in aqueous solution.

Table 2. CMC values of surfactant–cobalt(III) complexes.

Complexes	CMC $\times 10^4$ (mol dm^{-3})			ΔG^0_{mic} (kJ mol^{-1})	ΔH^0_{mic} (kJ mol^{-1})	$T\Delta S^0_{mic}$ (kJ mol^{-1})
	303 K	308 K	313 K			
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl]$^{2+}$	3.6	4.2	4.7	-34.4 ± 0.1	-15.6 ± 0.3	18.8 ± 0.1
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Br]$^{2+}$	3.1	3.6	4.2	-36.2 ± 0.3	-16.7 ± 0.2	19.5 ± 0.1

Scheme 2. Electron transfer for reactions of Co(III) and Fe(III).

was obtained (not shown) for the other complex. Table 2 shows the values of the CMCs of surfactant–cobalt(III)–ethylenediamine complexes as a function of temperature. It was found that CMC values increase on increasing the temperature for a given system. This behaviour may be related to two competitive effects. Firstly, a temperature increase causes a decrease in hydration in the hydrophilic group, which favours micellisation. Secondly, a temperature increase also causes a disruption of the water surrounding the hydrophobic group, and this retards micellisation. The relative magnitude of these two opposing effects will determine the CMC behaviour. It is observed that by changing the ion from Cl$^-$ to Br$^-$, the CMC decreases. It may be 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 which decreases the charge repulsion between the polar groups and thus facilitates the micellisation.

3.3. *Electron-transfer kinetics*

Kinetic data obey the first-order rate equation with respect to both the Co(III) and Fe(II) complexes,

$$-d[Co(III)]/dt = -d[Fe(II)]/dt = k[Co(III)][Fe(II)]$$

corresponding to the chemical process (Scheme 2), since Fe(II)X is the only Fe(III) species produced in the reaction, although it would dissociate into Fe(III) and X$^-$ under experimental the conditions.

Table 3 shows the values of the measured second-order rate constant of the specific rates of *cis*-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)X](ClO$_4$)$_2$ (X = Cl or Br) with Fe(II) at three different temperatures (303, 308 and 313 K) in aqueous solution at fixed [Fe(II)], ionic strength and acid concentration. In all cases, log($A_t - A_\alpha$) versus t plot were substantially linear for at least two half-lives. The second-order rate constant

Table 3. Second-order rate constants for the reduction of [Co(III)] by [Fe(II)] in aqueous solution.

Oxidising agents	$[Co(III)] \times 10^3$ $(mol\,dm^{-3})$	$k \times 10^4$ $(dm^3\,mol^{-1}\,S^{-1})$		
		303 K	308 K	313 K
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl]$^{2+}$	3.0	0.34 ± 0.1	3.02 ± 0.2	4.74 ± 0.2
	4.0	0.52 ± 0.3	4.49 ± 0.1	7.70 ± 0.1
	5.0	0.81 ± 0.1	5.94 ± 0.3	9.05 ± 0.2
	6.0	1.94 ± 0.2	7.22 ± 0.3	11.11 ± 0.3
	7.0	2.32 ± 0.2	8.11 ± 0.2	14.15 ± 0.2
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Br]$^{2+}$	3.0	0.28 ± 0.3	2.17 ± 0.1	4.06 ± 0.1
	4.0	0.39 ± 0.1	3.32 ± 0.1	6.12 ± 0.2
	5.0	0.54 ± 0.3	4.65 ± 0.2	8.05 ± 0.3
	6.0	1.61 ± 0.4	6.39 ± 0.3	10.68 ± 0.1
	7.0	2.16 ± 0.2	7.08 ± 0.1	12.77 ± 0.3

Note: $[Fe(II)] = 0.25\,mol\,dm^{-3}$; $[\mu] = 1.0\,mol\,dm^{-3}$ (NaClO$_4$); $[H^+] = 0.10\,mol\,dm^{-3}$.
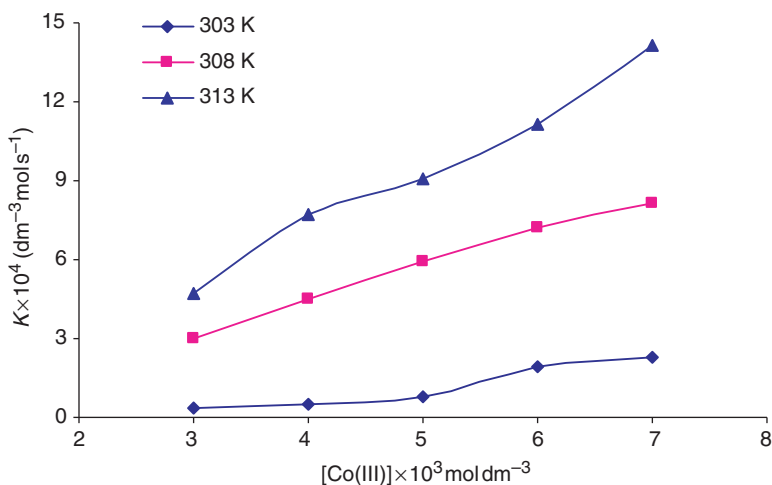
Figure 3. Plot of [Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl]$^{2+}$ vs. k, ($[Fe(II)] = 0.25\,mol\,dm^{-3}$; $[\mu] = 1.0\,mol\,dm^{-3}$ (NaClO$_4$); $[H^+] = 0.10\,mol\,dm^{-3}$).

for the Fe(II) reduction of Co(III) complexes was obtained from the slope of such a plot. The $\log(A_t - A_\alpha)$ versus t plots were linear up to 200 min in all the cases, so the effect of aquation of Co(III) complexes could be neglected. The relatively low reduction rate of *cis*-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)X](ClO$_4$)$_2$ (X = Cl or Br), as compared with that of the corresponding CoN$_4$Cl$_2^+$, may be mainly due to its dipositive charge. As was evident from Table 3, a relatively small increase in the rate with an increase in the concentration was observed (Figures 3 and 4). It may be due to the presence of aggregation of the complex itself to form a self-micelle, which leads to catalysis or acceleration of the reaction rate. Second-order rate constants in water were,
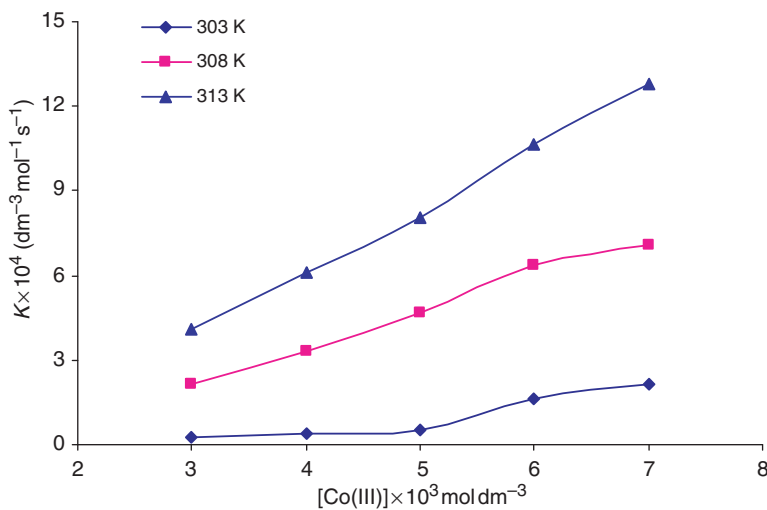
Figure 4. Plot of $[Co(en)_2(C_{14}H_{29}NH_2)Br]^{2+}$ vs. k, ($[Fe(II)] = 0.25\,mol\,dm^{-3}$; $[\mu] = 1.0\,mol\,dm^{-3}$ (NaClO$_4$); $[H^+] = 0.10\,mol\,dm^{-3}$).

by definition, independent of reactant concentrations, except for medium effects. But the rate constants in self-micelles depend on reactant concentrations in the micellar region (3.0–$7.0 \times 10^{-3}\,mol\,dm^{-3}$), and observed second-order rate constants will change if the stoichiometric reactant concentration is kept constant and that of the micelles is changed. As a result, observed micellar rate enhancements cannot be analysed without considering the extent to which changes in overall concentrations affect local concentrations in the micelles or other association colloids. Similar trends in the rate enhancement were also observed for the dodecylamine Co(III) complexes [34,35]. It may be attributed to the aggregation of the complex itself to form micelles (self-micelles formed by themselves), which leads to catalyse or accelerate the reaction rate. The acceleration in the rate may be due to the (a) binding of the reactants in a small volume of Stern layer of the micelle, thus leading to a considerable concentration effect; (b) possibility that the transition state is stabilised more than the initial state in the micellar pseudo-phase, leading to the lowering of activation energy; (c) aggregation of cobalt(III) complex with molecules provide bridges between iron with more than one chlorine/bromine atom of the cobalt centre simultaneously, so that the electron transfer would be effective. Moreover, the pseudo-first-order rate constants for bimolecular reactions are generally larger in the micellar pseudo-phase than in the aqueous pseudo-phase. Such micellar catalyses on rates of bimolecular reactions have been easily explained in terms of proximity effects – with micelles assisting reactions by bringing the reactants together or inhibiting them by keeping the reactants apart. Micelles of functional surfactants, where one of the reactants is held up with the head group, generally show very large catalyse for the rates of bimolecular reactions. Such catalysis cannot be easily explained only in terms of the proximity effects. Although micelles are dynamic aggregates, the translational degree of freedom of a surfactant molecule is expected to be lower in the micellar pseudo-phase than in the aqueous phase. Because each monomer in

a micelle of functional surfactant is acting as a reactant, the loss of translational degree of freedom in the micellar pseudo-phase may be attributed to the entire or large part of catalysis exhibited by these micelles. The complete loss of translational degree of freedom of one of the reactant molecules has been ascribed to the major part of rate enhancement in the intramolecular reactions compared to analogous intermolecular reactions. At the simplest level, the quantitative application of the pseudo-phase treatment involves the assumption that, once [surfactant] exceeds the CMC, micelles from additional surfactant generates more micelles. However, in many reactions, rates change at [surfactant] below the CMC in water [1–18]. This behaviour is common for reactions of very hydrophobic compounds and in the presence of polyvalent counterions, and is understandable in terms of reactant-induced micellisation. Induced micellisation does not explain all observations on chemical reactivity in very dilute surfactant, and it can associate with reagents to generate assemblies that are kinetically more effective than normal micelles.

3.4. *Effect of hydrogen-ion concentration*

The influence of $[H^+]$ on the reaction rate was studied by varying the concentration of $HClO_4$ (0.05–0.25 mol dm^{-3}) keeping [Co(III)], [Fe(II)] and temperature constant at 6.0×10^{-3}, 0.25 mol dm^{-3} and 308 K, respectively. In each case, the ionic strength was maintained constant at 1.0 mol dm^{-3} by the addition of $NaClO_4$. The results obtained indicate that the second-order rate constant was independent of the hydrogen-ion concentration (Figure 5). Such a kinetic behaviour indicates the
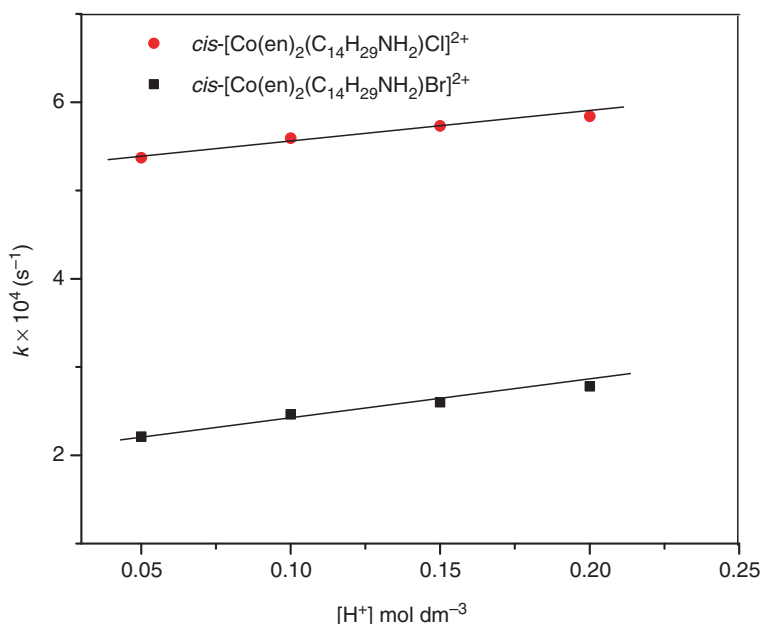

Figure 5. Effect of $[H^+]$ on k, ([Co(III)] = 6.0×10^{-3} mol dm^{-3}; [Fe(II)] = 0.25 mol dm^{-3}; $[\mu]$ = 1.0 mol dm^{-3}; $[H^+]$ = HClO$_4$ (0.05–0.25 mol dm^{-3}); T = 308 K).

non-existence of any protonation equilibrium with respect to both [Fe(II)] and [Co(III)] under the prevailing experimental conditions.

3.5. *Effect of ionic strength (μ)*

The influence of varying the concentration of ionic strength on the reaction rate was studied by the addition of $NaClO_4$ from 0.5 to 2.0 mol dm^{-3} keeping [Co(III)], [Fe(II)], [H$^+$] and temperature constant at 6.0×10^{-3}, 0.25, 0.10 mol dm^{-3} and 308 K, respectively. The value of k was found to increase with an increase in ionic strength (Figure 6).

3.6. *Non-bridging ligand effect*

Non-bridging ligand effects were previously classified [55,56] in the following three categories: (a) effects of geometry – relative rates of reduction of various pairs of *cis*- and *trans*-isomers; (b) effects of changing the nature of one non-bridging ligand – variation in rates along a series of constant *cis* or *trans* geometries; (c) effects of chelation – change in rate upon substitution of ammonia by ethylenediamine. It was evident from the literature that *cis*-Co(en)$_2$XCl^{n+} (X = Cl$^-$, Br$^-$ and RNH$_2$) reacts with Fe(II) via the chloride-bridged activated complex [55–58], so it is reasonable to assume a similar mechanism for our reactions. In such reactions of Co(III) complexes, it had been suggested that the effect of a non-bridging *cis*-ligand on the rate is of minor importance [55,56]. However, detailed information about the effect
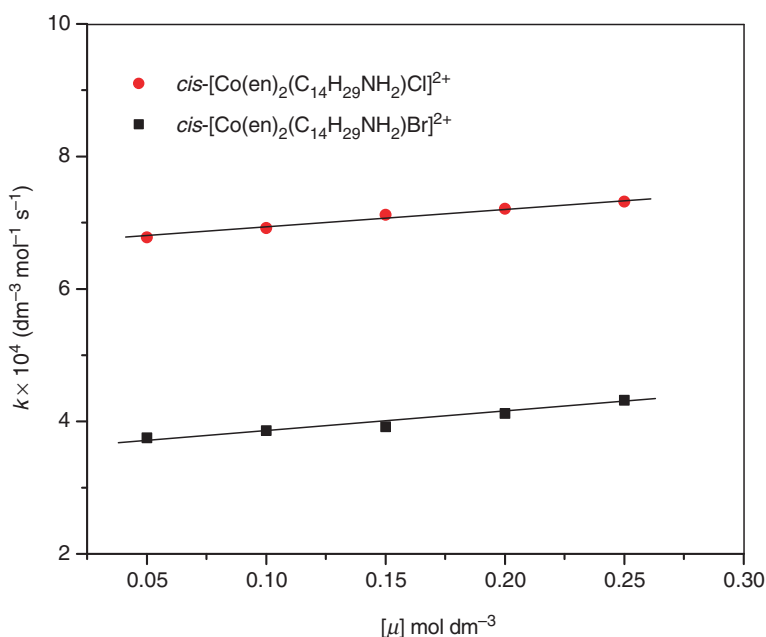

Figure 6. Effect of ionic strength on k, ([Co(III) = 6.0×10^{-3} mol dm^{-3}; [Fe(II) = 0.25 mol dm^{-3}; [μ] = 1.0 mol dm^{-3} (NaClO$_4$); [H$^+$] = 0.10 mol dm^{-3}; T = 308 K).

of the *cis*-ligand of the X was previously discussed in the literatures [55,56]. The results for the *cis*-isomer conform to those previously obtained in the reduction of *cis*-Co(en)$_2$XCl^{n+} (X = Cl$^-$; Br$^-$ and RNH$_2$) by Fe(II), indicating that effect (b) was the important factor for variation in the rate. Moreover, in the case of the lower alkylamine ligands from methylamine to butylamine [57], the reactivity successively decreases with an increase in the size of the amine ligand, but in the present study the reactivity increases suggesting that the formation of micelles by the complex itself catalyse the reaction. This suggests that the introduction of a higher long-chain alkylamine group into the non-bridging *cis*-ligand facilitates the reaction rate. The presence of a higher long-chain alkylamine group in the non-bridging ligand may stabilise the activated complex due to an increase in the solvation energy relative to that of the activated complex formed by the corresponding lower alkylamine ligand complex and Fe(II).

3.7. *Temperature dependence*

The temperature effect on (k) was studied at three different temperatures (303, 308 and 313 K) in order to obtain the thermodynamic parameters (Table 3) for the reaction between surfactant–Co(III) complexes and Fe(II). From the transition state theory,

$$\ln(k/T) = \ln(k_B/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT,$$

where values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ were determined by plotting $\ln(k/T)$ *versus* $1/T$. From the slope, the value of $\Delta H^{\neq}$ was calculated ($-\Delta H^{\neq} = R$) and from the intercept $[\ln(k_B/h) + \Delta S^{\neq}/R]$ the value of $\Delta S^{\neq}$ was calculated. The values of entropy of activation ($\Delta S^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) are given in Table 4. A meaningful mechanistic explanation was not possible, however, as seen from the table the trends in the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values with increasing Co(III) concentration were mainly due to the electrostatic attraction between the reductant and the oxidant micelle in the micellar phase. The $\Delta H^{\neq}$ obtained in this study was reasonable when compared to those values obtained for lower amines. $\Delta S^{\neq}$ values show that the transition state was well structured in the micellar phase. The positive

Table 4. Thermodynamic parameters for surfactant–cobalt(III) complexes.

Oxidising agents	[Co(III)] × 10^3 (mol dm^{-3})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (kJ mol^{-1})
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Cl]$^{2+}$	3.0	105.28	187.19
	4.0	98.51	175.63
	5.0	92.17	170.28
	6.0	87.62	159.94
	7.0	85.06	137.32
cis-[Co(en)$_2$(C$_{14}$H$_{29}$NH$_2$)Br]$^{2+}$	3.0	103.62	177.83
	4.0	95.43	168.52
	5.0	89.55	159.69
	6.0	84.37	151.07
	7.0	81.62	139.46

values of $\Delta S^{\neq}$ clearly indicate that the micellisation was 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 were entropy-driven processes.

3.8. *Binding mode of the coordinated halide ion, X^-*

The trend $F^- < Cl^- < Br^- < I^-$ was known as 'normal order' and the reverse was known as 'inverse order'. Several aspects related to the oxidant and reducing agents appear to be significant in determining the trend [56,59]. $[Co(NH_3)_5X]^{2+}$ with Fe(II) shows an inverse order [56], which may be treated according to the decreasing stabilities of Fe(II)X in the order: $FeCl^{2+} > FeBr^{2+}$. It may be thus generalised that if the oxidant was a soft acid, one finds the inverse order and, if hard, normal order, the reductant in both the 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 was mediated by bridging through the halide ion. In the present study, the electron transfer was mediated by halide ion, Cl^-/Br^- and the trend were found to be in 'inverse order'.

4. Conclusions

As mentioned in our previous reports [34–36], the CMC values of Co(III) metallo-surfactants in the present study are also very low compared to that of simple organic surfactant, dodecylammonium chloride (CMC $= 1.5 \times 10^{-2}$ mol dm^{-3}) indicating that, these metal–surfactant complexes have more capacity to associate themselves forming aggregates compared to those of ordinary synthetic organic surfactants. This suggests that the introduction of a metal complex to the hydrophilic part of the amphiphile can remarkably enhance the ability of aggregation. Therefore, amphiphilic metal complexes are expected to be used to construct a variety of aggregation morphologies.

Electron transfer is one of the primary reactions of transition metal complexes. Its rate depends on the concentration of the oxidant and the reductant. The nature of the bridging ligand is important for inner-sphere reactions. The role of the bridging ligand is the most important feature of inner sphere reactions and has dominated research on reactivity towards electron transfer by inner-sphere mechanism.

The present study allows definition of the mechanistic factors at play in the reduction of the transition-metal ion complexes with the long-chain amines and the effect of micellisation in the corresponding metalloaggregates. It is suggested that the reduction of Fe(II) with Co(III) complex proceeds by inner-sphere mechanism. Most information about the mechanism of the reaction comes from the experimentally rate law: $-d[Co(III)]/dt = -d[Fe(II)]/dt = k[Co(III)] [Fe(II)]$. Other clues to the mechanism come from comparisons of the rates of related reactions, investigations of the temperature dependence, ionic strength dependence of the reaction rates and kinetically controlled reaction products. The [H$^+$] independence for all the metallosurfactants studied is of special significance. Thus, the kinetic benefits of the aggregates mainly derive from concentration effects due to the

transfer of the substrate into the pseudo-phase and form the effect of bringing into proximity the reagents, as in most cases of functionalised micelles or vesicles. A lipophilic long-chain can introduce an extra-orientation requirement in the supramolecular assembly between the metal–ion complex and the Fe(II) existing in the micelle by the hydrophobic interactions.

We attempt to provide some idea of the kinetic effects of metallosurfactants on inorganic redox reactions. There are many other kinetic studies not cited in this work due to length requirements. However, the main features in understanding most of the kinetic data obtained in this area of knowledge have been considered. Some points remain without answers, for instance, the development of a kinetic model that permits the quantitative explanation of the surfactant kinetic effects on inorganic redox reactions for the whole surfactant concentration range, below and above the CMC, when pre-micellar and micellar kinetic effect are operative. Much effort is still needed in this field (in terms of pseudo-phase ion exchange and mass action kinetic models). Many interesting behaviours may be seen as more studies of this type are performed.

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