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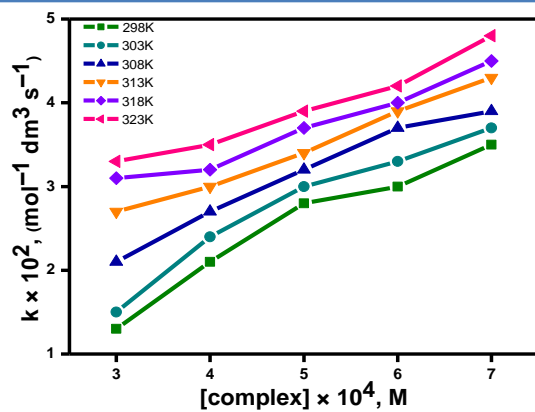
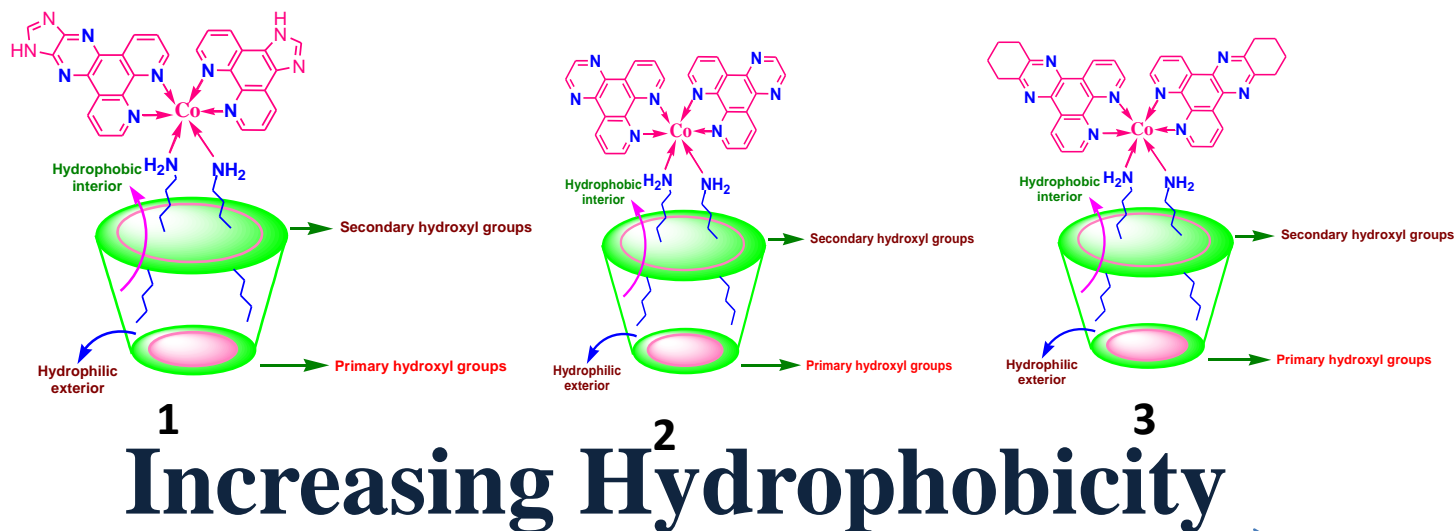


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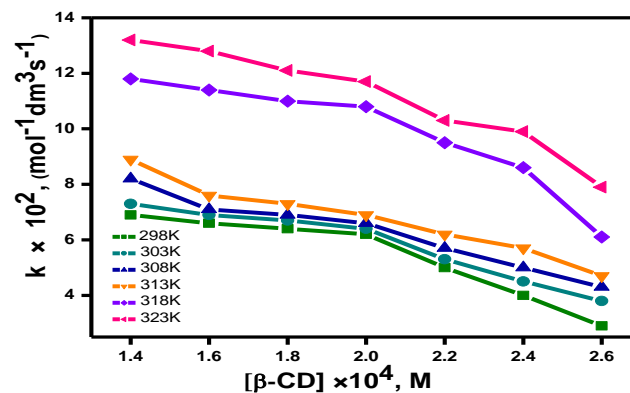
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In Micelles



In β -Cyclodextrins

A Comparative study on Electron Transfer Reaction (ETR) of Surfactant Cobalt(III) Complexes of Aliphatic/Aromatic ligand in micro heterogeneous media: Thermodynamic approach

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Abstract

The kinetics of electron transfer reaction (ETR) between the surfactant cobalt(III) complex ion, Cis-[Co(ip)₂(C₁₂H₂₅NH₂)₂](ClO₄)₃, Cis-[Co(dpq)₂(C₁₂H₂₅NH₂)₂](ClO₄)₃ and Cis-[Co(dpqc)₂(C₁₂H₂₅NH₂)₂](ClO₄)₃ (ip = imidazo[4,5-f][1,10]phenanthroline, dpq = dipyrido[3,2-d:2'-3'-f]quinoxaline, dpqc = dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine, C₁₂H₂₅NH₂=dodecylamine) and Fe²⁺ ion in micelles as well as β-cyclodextrin (β-CD) were studied at different temperatures by spectrophotometric method under pseudo first order conditions using an excess of the reductant. The results of surfactant complex containing aromatic ligands ETR higher than that of aliphatic ligands due to the results have been explained based on the hydrophobic effect. Experimentally the reactions were found to be second order and the electron transfer postulated as outer sphere. The rate constant increases with increase in the concentration of micelles but inclusion of the long aliphatic chain of the surfactant cobalt(III) complexes into β-cyclodextrin decreases the rate of the reaction. Thermodynamic parameters were evaluated.

Key words

Micelles; β-cyclodextrin; Electron transfer; aggregation; surfactant complex

15 Introduction

Outer-sphere electron transfer involving transition metal complexes plays an essential role both *in vivo* [1] and in the operation of molecular scale devices, such as molecular wires and logic gates [2]. Surface-active materials are major building blocks of many physical, chemical, and biological systems. They have been introduced into several commercial products such as antiseptic agents and germicides [3], and have also found a wide range of applications in diverse areas such as mining, petroleum, and pharmaceutical industries. It has been observed that redox reactions in micellar media can be influenced by 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 [4]. Electron transfer reactions of cobalt(III) complexes are very well known because the kinetics of reduction of octahedral cobalt(III) complexes is mostly free from complications arising from reversible electron transfer, aquation, substitution and isomerization reactions. Octahedral cobalt(III) complexes, which are substitutionally inert, are ideal for theoretical and experimental studies. Surfactant cobalt(III) complexes have received a sustained high level of attention for the last few years due to their relevance to various redox processes in biological systems, and their potential as for anthelmintic and antibiotic agents [5]. Numerous studies have addressed the dependence of electron transfer on different environments including micelles [6], vesicles [7] and DNA [8]. The redox processes occurring in biological systems are controlled both by specific geometry of the inner coordination sphere, which mainly controls the operation potential of the metal center, and by the hydrophobic effect offered by the pseudo biological interfaces. Electron transfer in these restricted geometry systems attracts great deal of interest [9,10] because of their potential to prolong the lifetime of charge-transfer states, a goal of electron-transfer studies aiming to utilize solar energy [11]. Majumdar and Mahapatra [12] studied the electron transfer reactions between cobalt(III) and iron(II) complexes in cationic micellar medium (N-cetyl-N,N,N trimethyl ammonium bromide) and also in reverse micellar medium. The rate of the reaction was found to mainly depend on the inter-phase environment of the micelles and reverse micelles. Micelle-forming properties and electron transfer reactions of many surfactant metal complexes have been studied in our laboratory [13-16]. Recently, we have reported on the outer-sphere electron transfer reactions between cis-[Co(en)₂(C₁₂H₂₅NH₂)₂](ClO₄)₃, cis-[Co(trien)(C₁₂H₂₅NH₂)₂](ClO₄)₃ and iron(II) in the micelles formed by these complexes

themselves [17,18]. In all these surfactant metal complexes the coordination complex containing a central metal ion with surrounding ligands coordinated to metal acts as surfactant. In recent times there have been some reports from various research groups on surfactant metal complexes of various natures and their micelle forming properties [19-22]. In all these surfactant metal complexes, the metal complex part containing the central metal ion with its primary coordination sphere acts as the head group and the hydrophobic part of one or more ligands acts as the tail part. Cyclodextrins (CD) are cyclic polysugars composed of glucose units linked by 1-4 α glycoside bonds [23-26]. The hydrophilic (water soluble) outer surface and (water insoluble) hydrophobic cavities provide different environments to change the photophysical properties of the guest molecules. When the substrate comes into a constrained cyclodextrin cavity, the polarity of the guest molecule is rearranged and selectivity, photoreactivity are also modified [27,28]. The effects of cyclodextrin inclusion on the kinetics and mechanism of ligand substitution [29,30] and electron transfer reactions of transition metal complexes in aqueous solution [31,32] have received considerable attention in recent years. The inclusion complexation of these host-guest systems occurs through various weak interactions, such as hydrogen bonding and van der Waals, electrostatic or hydrophobic interaction [33].

In this paper we report a further investigation on the effect of increasing hydrophobicity of the complexes on the kinetics of outer-sphere electron transfer between some surfactant cobalt(III) complexes containing polypyridyl ligands and iron(II) in aqueous media. As these complexes themselves form micelles we have conducted the reactions in micelles created by the surfactant metal complex molecules themselves. We have also studied the inclusion effect of β -cyclodextrin on these reactions. The surfactant complex ions used in the present study are $\text{cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$, $\text{cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$ and $\text{cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$ (ip = imidazo[4,5-f][1,10]phenanthroline, dpq = dipyrido[3,2-d:2'-3'-f]quinoxaline, dpqc = dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine, $\text{C}_{12}\text{H}_{25}\text{NH}_2$ =dodecylamine).

20 Experimental

Materials and methods

Electrolytic grade iron powder (Loba Chemie) and perchloric acid (Loba Chemie) were used to prepare iron(II) perchlorate and to maintain an acidic medium. β -cyclodextrin (β -CD) was purchased from Sigma-Aldrich Chemical Co.(Bangalore, India) and used as such. To prepare buffer solutions anhydrous dibasic sodium phosphate (Na_2HPO_4) and sodium dihydrogen orthophosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) were used. All solvents used were of analytical grade.

Preparation of oxidant / Reductant

The surfactant cobalt(III) complexes, $\text{cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\text{cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ and $\text{cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ used as oxidants were prepared as reported by us earlier [34]. A stock solution of $\text{Fe}(\text{ClO}_4)_2$ was prepared by dissolving pure iron powder in slight excess of perchloric acid. The concentration of Fe^{2+} ion was determined by a method similar to that reported in the literature [35] the ionic strength of the solution was adjusted by the addition of sodium perchlorate solution.

Kinetic measurements

The rate of the reaction was measured spectrophotometrically using a Shimadzu -1800 UV-Visible spectrophotometer equipped with water Peltier system (PCB 150). The temperature was controlled within $\pm 0.01^\circ\text{C}$. A solution containing the desired concentration of β -cyclodextrin and surfactant cobalt(III) complexes in oxygen-free water was placed in a 1-cm cell, which was then covered with a serum cap fitted with a syringe needle. This cell was placed in a thermostated compartment in the spectrophotometer and then the solution containing Fe^{2+} was added anaerobically using the syringe. The reaction was followed by measuring the absorption of the surfactant cobalt(III) complex with time. The decrease in the absorbance was followed at 470

nm for these complexes. All kinetic measurements were performed under pseudo-first order conditions with the Fe^{2+} ion in excess over the cobalt(III) complex. The concentration of $\text{Fe}(\text{ClO}_4)_2$ used was 0.1 mol dm^{-3} region. The ionic strength was maintained at 1.0 mol dm^{-3} and the concentration of cobalt(III) complex was always chosen above their CMC values in the region [34]. The second-order rate constant, k , for the Fe^{2+} ion reduction of the cobalt(III) complex defined by $-\text{d}[\text{Co(III)}]/\text{dt} = k[\text{Co(III)}][\text{Fe}^{2+}]$ was calculated from the concentration of iron(II) and the slope of the pseudo first order plot of $\log(A_t - A_\infty)$ versus time, which is equal to $-k[\text{Fe}^{2+}]/2.303$, where A_t is the absorbance at time t , A_∞ is the absorbance after all the cobalt(III) complex has been reduced to cobalt(II), and k is the second-order rate constant. Usually the value of A_∞ was measured at times corresponding to ten half-lives. All the first-order plots were substantially linear for at least five half-lives, with a correlation coefficient of > 0.999 . Each rate constant reported is the average result of triplicate runs. Rate constants obtained from successive half-life values within a single run agreed to within $\pm 5\%$. No trend indicative of systematic error was noted, and the average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance difference against reaction time.

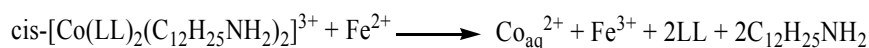
Stoichiometry

The stoichiometry of the reaction was determined by estimating iron(III) and cobalt(II) present in the product mixture. Iron(III) was determined spectrophotometrically by Kitson's method [36] and Co(II) was determined as $[\text{CoCl}_4]^{2-}$ at 690 nm in an excess of HCl [37]. The ratio of Fe(III) to Co(II) was found to be 1:1 in the reactions studied, indicating 1:1 stoichiometry.

Results and Discussion

Electron-transfer kinetics

The reduction of surfactant cobalt(III) complexes, $\text{cis}[\text{Co}(\text{LL})_2(\text{DA})_2]^{3+}$ by Fe^{2+} , proceeds according to the overall reaction as indicated below:



where LL = ip, dpq and dpqc

and the rate is given by,

$$\text{Rate} = k[\text{cobalt(III) complex}][\text{Fe}^{2+}]$$

where k is the second order rate constant.

This reaction is postulated as outer sphere in comparison to such type of reactions in the literature involving ordinary lower primary amine coordinated cobalt(III) complexes similar to the surfactant cobalt(III) complexes of the present study. The complexes of the present study are inert to substitution due to the non-availability of a co-ordination site for inner-sphere precursor complex. Only a non-bridging intermediate is expected from such reactions that are inert to substitution. Already literature reports [38-41] on similar type of complexes supported only outer-sphere redox pathway. The most favorable mechanism for this outer-sphere electron transfer process consists of three elementary steps (Scheme 1): ion pair formation (k_{ip}), electron transfer (k_{et}), and product successor dissociation.

35 Influence of micelles on electron transfer

The kinetics of ETR between the surfactant cobalt(III) complexes of the present study were done in self micelles formed by surfactant cobalt(III) complex molecules themselves. The outer-sphere electron transfer proceeds with second order reaction and second order rate constants were measured on the reactions between the surfactant cobalt(III) complexes and Fe^{2+} ion at various temperatures and the rate constants are shown in Tables (Table 1 and SI Table 1 and 2) and the plots of k against various initial concentration of the surfactant cobalt(III) complex, at 298, 303, 308, 313, 318 and 323K in aqueous solution are shown in Fig. 1 and SI Fig. 1 and 2. As seen from these tables the rate constant for each reaction increases with increasing the initial concentrations of the surfactant cobalt(III) complex. As these concentrations are higher [34] than the critical micelle concentration ($3 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$) values of these surfactant complexes, all these rate constant values correspond to the rate constant values in self-micelles formed from these metal complex molecules themselves. (Attempts to perform the kinetics of the same reaction at below the CMC of the surfactant cobalt(III) complexes were unsuccessful as the reaction was so slow no change in the absorbance was observed with time). So the increase in rate constant with increase in concentration of complexes can be attributed to aggregation of this metal complex in their own self-micelles. At high initial concentration of the surfactant cobalt(III) complex presence of more number of micelles was expected.

As seen from the Tables (Table 1 and SI Table 1 and 2) the rate constant values of the surfactant cobalt(III) complexes of the present study are very much different from one another. This difference in the rate constant values between surfactant cobalt(III) complexes of the present study are explained as follows: The rate constant value of the surfactant cobalt(III)-imidazo[4,5-f][1,10]phenanthroline complex is lower than that of the corresponding surfactant cobalt(III)-dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine complex in all the initial concentrations studied. Due to high hydrophobicity of dpqc containing complexes the number of micelles formed from these complex molecules will be more compared to that of imidazo[4,5-f][1,10]phenanthroline containing complexes at the same concentration values. Hence dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine containing complexes enhance the overall rate of the reaction. Among these modified phenanthroline surfactant cobalt(III) complexes containing imidazo[4,5-f][1,10]phenanthroline, dipyrido[3,2-d:2'-3'-f]quinoxaline and dipyrido[3,2-a:2',4'-c]phenazine ligands, the rate constant values of dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine complex is the highest due to more hydrophobicity of dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine ligand. The rate constant values of surfactant cobalt(III)-modified phenanthroline complexes are higher. This is due to these extended aromaticity of modified phenanthroline ligands make the aggregation increment which increases the capacity of these complexes to form micelles than that of the previous reported [17,18,41] surfactant cobalt(III) complexes in all the initial concentrations studied.

Effect of cyclodextrin (β -CD) on electron transfer

The cyclodextrins are naturally occurring receptors which can alter the physical properties and chemical reactivities of guest molecules [42]. It is known that the binding of many simple phenyl derivatives is stronger to β -cyclodextrin [25] and these trends depend on the cavity sizes of the cyclodextrins which increase as α -CD < β -CD < γ -CD [43]. β -cyclodextrins has the ability to form complex with host molecules, that the complex forms when a suitable hydrophobic molecule displaces water from the cavity [44]. The effects of cyclodextrin inclusion on the kinetics and mechanism of ligand substitution [45,46] and electron transfer reactions of transition metal complexes in aqueous solution [47,48] have received considerable attention in recent years. The effects of the presence of cyclodextrin in the medium on the kinetics of the ETR between the surfactant cobalt(III) complexes of the present study and Fe^{2+} ion have been investigated. In cyclodextrin media also the reduction of the surfactant cobalt(III) complexes with Fe^{2+} ion proceeds with second order reaction and the resulting k value are listed in Tables (Table 2 and SI Table 3 and 4) and the plot of k against various concentrations of β -CD are shown in Fig. 2 and SI Fig. 3 and 4. As seen from these tables addition of increasing concentrations of cyclodextrin to the medium has resulted in significant decrease in the

second order rate constant. It is well-known that β -cyclodextrin is a good structure breaker of micelles. As the long aliphatic chains of surfactants can be included into the cavities of (Scheme 2) cyclodextrin the formation of micelles will be difficult leading to increase of CMC values of surfactants in the presence of cyclodextrin. So in our case the decrease of rate constant with increase in the concentration of cyclodextrin in the media can be attributed to the inclusion of long aliphatic chain present in one of the ligands into cyclodextrin. This effect of cyclodextrin in the media also supports the earlier conclusion on the effect of initial concentration of the surfactant cobalt(III) complexes on the second order rate constant.

Activation parameters and isokinetic plots

The effect of temperature on rate was studied at six different temperatures for each concentration of micelles, and β -cyclodextrin in order to obtain the activation parameters for the reaction between surfactant cobalt(III) complexes with Fe^{2+} . From the transition transition state theory, [49] making use of Eyring equation, The values of ΔS^\ddagger and ΔH^\ddagger were determined by plotting $\ln(k/T)$ versus $1/T$ and the plots are shown in Fig. 3,4 and SI Figures 5-8.

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

The ΔS^\ddagger and ΔH^\ddagger values obtained are shown in Table 3 and SI Tables 5-9. As seen from these tables the values of ΔH^\ddagger is positive for all the reactions (in micelles and β -cyclodextrin.), indicating that the formation of activated complex is endothermic. The ΔH^\ddagger values decrease with increasing initial concentration of the surfactant cobalt(III) complexes, this is due to the presence of more number of micelles at higher initial concentration of surfactant cobalt(III) complexes which facilitates the reaction. In all these media the ΔS^\ddagger values are found to be negative in direction in all the concentrations of complex used indicative of more ordered structure of the transition state; i.e a compact ion pair transition state (Scheme 1) leads to more attraction of surrounding solvent molecules around the positive and negative charges on the ion pair, resulting in the loss of freedom of movement of the solvent molecules in the transition state. In order to check for any change of mechanism occurs during the ETR isokinetic plots (ΔS^\ddagger versus ΔH^\ddagger) for the electron transfer reactions of surfactant cobalt(III) complexes were made. As seen from Fig. 5,6 and SI Figures 9-12 straight lines were obtained for all the isokinetic plots of complexes, indicating that a common mechanism exists in all the initial concentrations of each complex studied.

Conclusion

The present work explains the outer-sphere electron transfer between $\text{cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$, $\text{cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$, $\text{cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2]^{3+}$ and Fe^{2+} in micelles as well as β -CD. The kinetics of outer-sphere ETR between the complexes and Fe^{2+} ion in self micelles formed by our surfactant cobalt(III) complex molecules themselves. Rate constant increases with increasing concentrations of complexes due to this concentration range are higher than the critical micelle concentration (CMC). Increasing the concentration of complexes the number of micelles present in the medium also increases leads to higher rate and lower activation energy. β -CD is good structure- breaker of micelles. The second order rate constant decreases with increase in concentration of β -CD due to the long aliphatic chains of surfactants can be included into the cavities of cyclodextrin the formation of micelles will be difficult. This is attributed to the inclusion of long aliphatic chains present in one of the ligands into cyclodextrin. From the transition state theory activation parameters were calculated. On comparing the previous reports of surfactant complexes containing aliphatic ligand ETR is lower than that of present complexes containing modified Phenanthroline of extending aromaticity of the ligands.

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Supporting Information

Supporting Information should be attached at the end of the article or separated file.

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Scheme Captions

Scheme 1: General mechanism for the electron-transfer reaction

Scheme 2: Host-guest complex between the surfactant complexes and β -cyclodextrin

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Figure Captions

Fig. 1 Plot of k against complex ion for $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ under various temperatures; $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

Fig. 2 Plot of k against $[\beta\text{-CD}]$ for $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ at various temperatures; $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

10 Fig. 3 Eyring plot for $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ in aqueous medium. $[\text{complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$, $[\mu] = 1.0 \text{ mol dm}^{-3}$.

Fig. 4 Eyring plot for $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ in $[\beta\text{-CD}]$ medium. $[\text{complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$, $[\mu] = 1.0 \text{ mol dm}^{-3}$, $[\beta\text{-CD}] = 1.8 \times 10^{-3}$.

15 Fig. 5 Isokinetic plot of the activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ by ion(II) in aqueous solutions. $[\text{complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$, $[\mu] = 1.0 \text{ mol dm}^{-3}$.

Fig. 6 Isokinetic plot of the activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ by ion(II) in β -cyclodextrin medium. $[\text{complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$, $[\mu] = 1.0 \text{ mol dm}^{-3}$.

Table Captions

20 Table 1. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in aqueous solutions under various temperatures. $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

Table 2. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in the presence of β -cyclodextrin under various temperatures. $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

Table 3. Activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\mu = 1.0 \text{ mol dm}^{-3}$ in micelles medium

Table 4. Activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{ip})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\mu = 1.0 \text{ mol dm}^{-3}$ in β -CD medium

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Supplementary Informations

SI Figure Captions

SI Fig. 1 Plot of k against complex ion for $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ under various temperatures; $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

30 SI Fig. 2 Plot of k against complex ion for $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ under various temperatures; $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

SI Fig. 3 Plot of k against $[\beta\text{-CD}]$ for $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ at various temperatures; $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

SI Fig. 4 Plot of k against $[\beta\text{-CD}]$ for $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ at various temperatures; $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

5 SI Fig. 5 Eyring plot for $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ in aqueous medium. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$.

SI Fig. 6 Eyring plot for $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ in aqueous medium. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$.

10 SI Fig. 7 Eyring plot for $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ in $[\beta\text{-CD}]$ medium. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$, $[\beta\text{-CD}] = 1.8 \times 10^{-3}$.

SI Fig. 8 Eyring plot for $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ in $[\beta\text{-CD}]$ medium. $[\text{complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$, $[\beta\text{-CD}] = 1.8 \times 10^{-3}$.

SI Fig. 9 Isokinetic plot of the activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ by ion(II) in aqueous solutions. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$.

15 SI Fig. 10 Isokinetic plot of the activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ by ion(II) in aqueous solutions. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$.

SI Fig. 11 Isokinetic plot of the activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ by ion(II) in β -cyclodextrin medium. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$.

20 SI Fig. 12 Isokinetic plot of the activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$ by ion(II) in β -cyclodextrin medium. $[\text{Complex}] = 4 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$.

SI Table Captions

SI Table 1. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in aqueous solutions under various temperatures. $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

25 SI Table 2. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in aqueous solutions under various temperatures. $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

SI Table 3. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in the presence of β -cyclodextrin under various temperatures. $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

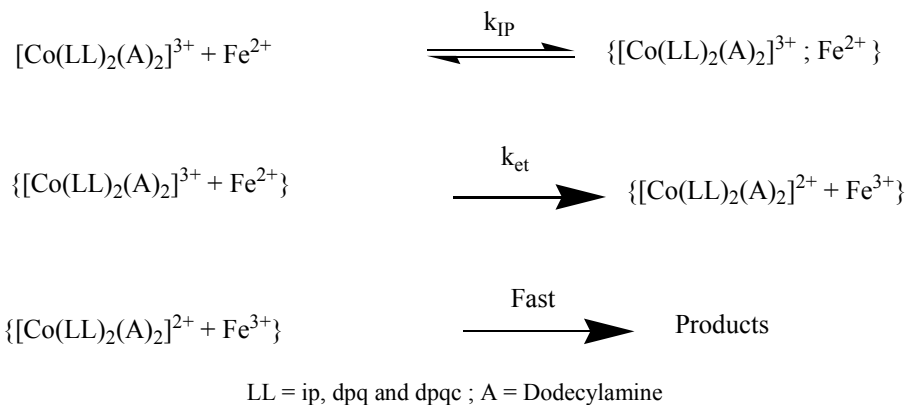
SI Table 4. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in the presence of β -cyclodextrin under various temperatures. $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3 = 4 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 1.0 \text{ mol dm}^{-3}$, $[\text{Fe}^{2+}] = 0.01 \text{ mol dm}^{-3}$

30 SI Table 5. Activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\mu = 1.0 \text{ mol dm}^{-3}$ in micelles medium

SI Table 6. Activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\mu = 1.0 \text{ mol dm}^{-3}$ in micelles medium

SI Table 7. Activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpq})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\mu = 1.0 \text{ mol dm}^{-3}$ in $\beta\text{-CD}$ medium

SI Table 8. Activation parameters for the reduction of $\text{Cis-}[\text{Co}(\text{dpqc})_2(\text{C}_{12}\text{H}_{25}\text{NH}_2)_2](\text{ClO}_4)_3$, $\mu = 1.0 \text{ mol dm}^{-3}$ in $\beta\text{-CD}$ medium

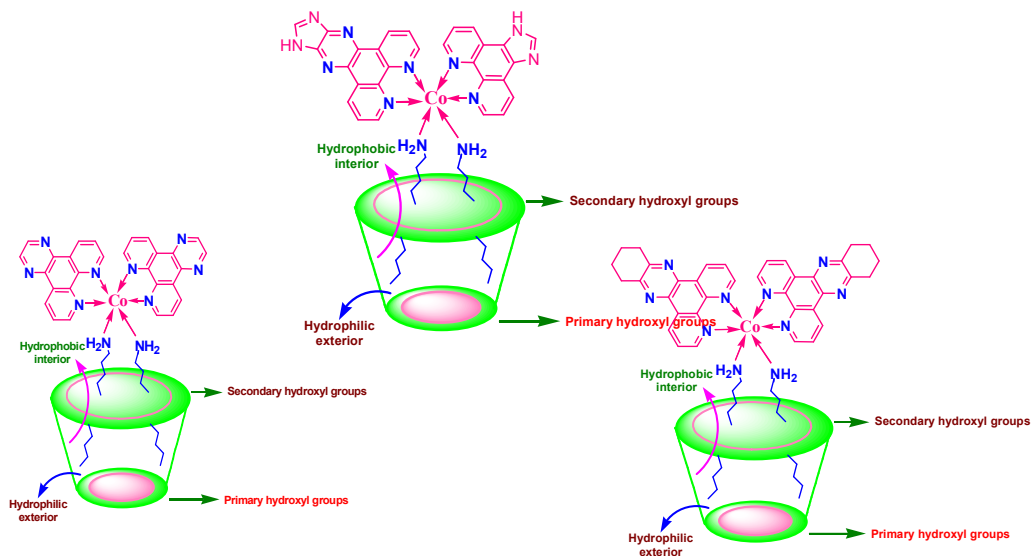


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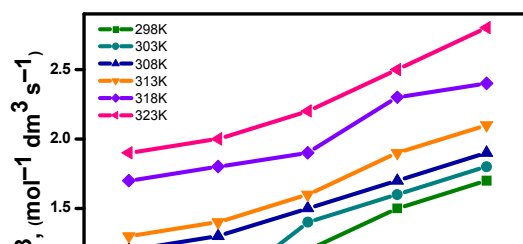
Scheme 1

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Scheme 2 Host-guest complex between the surfactant complexes and $\beta\text{-cyclodextrin}$

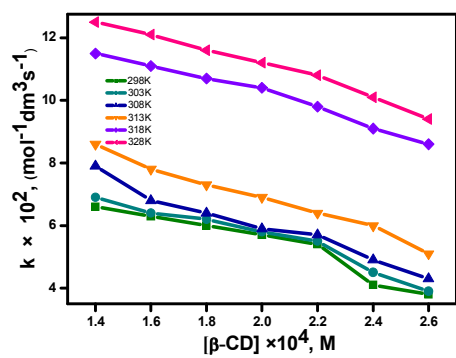
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Fig. 1

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Fig. 2

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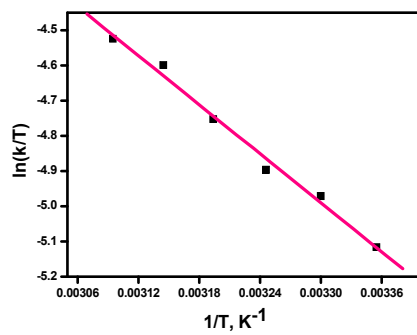


Fig. 3

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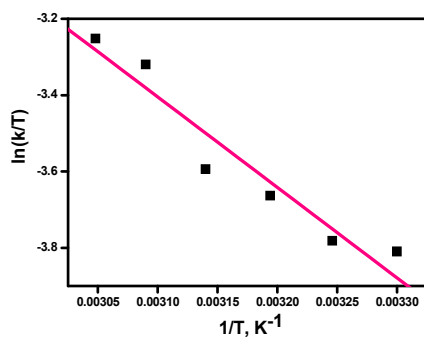


Fig. 4

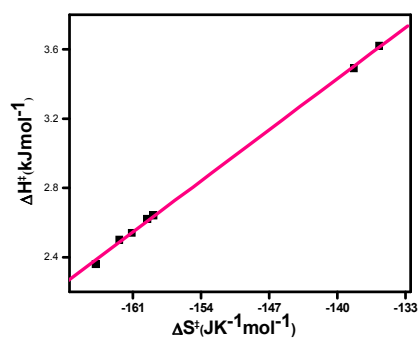
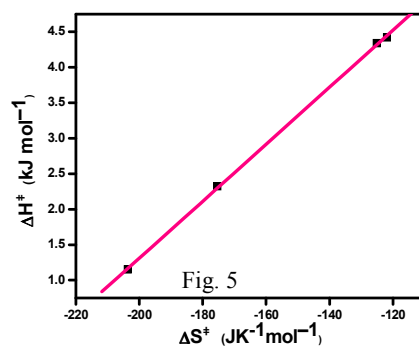


Fig. 6

Table 1

[Complex] $\times 10^4, \text{mol dm}^{-3}$	$k \times 10^2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$					
	298K	303K	308K	313K	318K	323K
3.0	0.9	1.1	1.7	2.2	2.5	2.6
4.0	1.1	1.3	1.8	2.2	2.7	3.0
5.0	1.4	2.1	2.3	2.7	2.9	3.3
6.0	2.1	3.0	3.2	3.4	3.7	4.1
7.0	3.0	3.3	3.7	4.1	4.3	4.8

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Table 2

[β -cyclodextrin] $\times 10^4, \text{mol dm}^{-3}$	$k \times 10^2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$					
	298K	303K	308K	313K	318K	323K
1.4	6.6	6.9	7.9	8.6	11.5	12.5
1.6	6.3	6.4	6.8	7.8	11.1	12.1
1.8	6.0	6.2	6.4	7.3	10.7	11.6
2.0	5.7	5.8	5.9	6.9	10.4	11.2
2.2	5.4	5.5	5.7	6.4	9.8	10.8
2.4	4.1	4.5	4.9	6.0	9.1	10.1
2.6	3.8	3.9	4.3	5.1	8.6	9.4

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Table 3

[Complex] $\times 10^4,$ mol dm^{-3}	$\Delta H^\ddagger \text{ kJmol}^{-1}$	$\Delta S^\ddagger \text{ JK}^{-1}$
3.0	1.15	-203.6
4.0	1.48	-190.8
5.0	2.32	-175.4
6.0	4.34	-125.1
7.0	4.42	-121.9

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Table 4

$[\beta\text{-cyclodextrin}] \times 10^3,$ mol dm^{-3}	ΔH^\ddagger kJmol^{-1}	ΔS^\ddagger JK^{-1}
1.4	2.36	-164.8
1.6	2.5	-162.4
1.8	2.54	-161.1
2.0	2.62	-159.5
2.2	2.64	-158.9
2.4	3.49	-138.3
2.6	3.62	-135.7

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