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RESEARCH ARTICLE

Kinetic study of surfactant cobalt (III) complexes by [Fe(CN)6 4-]: Outer-Sphere Electron-Transfer in Ionic liquids and Liposome Vesicle

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Abstract: UV-Vis., absorption spectroscopy are used to monitor the electron transfer reaction between the surfactant cobalt(III) complexes, cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2]^{3+}$, cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2]^{3+}$ and cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2]^{3+}$ (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, $C_{14}H_{29}NH_2$=Tetradecylamine) and $[Fe(CN)_6]^{4-}$ ion in liposome vesicles (DPPC) and ionic liquids ((BMIM)Br) were investigated at different temperatures under pseudo first order conditions using an excess of the reductant. The reactions were found to be second order and the electron transfer is postulated as outer-sphere. The rate constant for the electron transfer reactions were found to increase with increasing concentrations of ionic liquids. The effects of hydrophobicity of the long aliphatic double chains of these surfactant complex ions into liposome vesicles on these reactions have also been studied. Below the phase transition temperature of DPPC, the rate decreased with increasing concentration of DPPC, while above the phase transition temperature the rate increased with increasing concentration of DPPC. Kinetic data and activation parameters are interpreted in terms of an outer-sphere electron transfer mechanism. In all these media the $\Delta S^{\#}$ values are found to be negative in direction in all the concentrations of complexes used indicative of more ordered structure of the transition state. This is consistent with a model in which the surfactant cobalt(III) complexes and $Fe(CN)_6^{4-}$ ions bind to the DPPC in the transition state. Thus, the results have been explained based on the self-aggregation, hydrophobic effect, and the reactants with opposite charge.

Keywords: Phase transition; vesicles; ionic liquids; surfactant complex; hydrophobicity; electron transfer

1. INTRODUCTION

During the last few decades, quick advances in the understanding of surface phenomenon have taken place. However, the significance of surface science has been recognized for more than a century. A class of compounds called surface-active compounds (or surfactants) (M.J. Rosen *et al.* 1978) that decrease prominently the interfacial tension or interfacial free energy of the interfaces (J.W. McBain *et al.* 1950). Surfactant molecules are amphiphilic in character, i.e., they possess hydrophilic and hydrophobic regions (C. Tanford *et al.* 1973) having a long hydrocarbon tail and a relatively small ionic or polar head group. Surface-active materials are major building blocks, including chemistry (chemical kinetics or equilibria), biology (as membrane mimetics) and Pharmacy (J.H. Fendler *et al.* 1975). 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 (O.A. Babich *et al.* 2002). In recent times, there have been some reports on surfactant metal complexes of a various nature and their micelle forming properties (G.W. Walker et al. 2003).

The outer-sphere electron transfer between transition metal complexes plays an essential role both in vivo[5] and in operation of molecular scale devices, such as molecular wires and logic gates (K. Szacilowski *et al.* 2004). The alteration of the outer-sphere environment of metal complex caused by the variation of concentration of the counter ions (J. Pfeiffer *et al.* 2001) has an influence on electron transfer reactions. Gaswick *et al.* have reported that the hexacyanoferrate(II) anion can reduce some pentamminecobalt(III) complexes to cobalt(II) via an outer-sphere electron transfer step (D. Gaswick et al. 1971) and also they have reported that the substituted pentamminecobalt(III) complexes could be reduced by hexacyanoferrate(II) with the formation of an ion pair (A.J. Miralles *et al.* 1982). There are many reports available on electron transfer between metal complexes and $[Fe(CN)_6]^{4-}$ (P. Rillema *et al.* 1972, R. Van Eldik *et al.* 1982, (K. Kustin *et al.* 1921, R. Larrson 1967). A.R.Mustafina *et al.* have studied the outer-sphere association of p-sulfanotothiacalix[4]arene with some cobalt(III) complexes. The ion pairing of the complexes with macrocycle STCA accelerates the $[Fe(CN)_6]^{4-}$-cobalt(III) electron transfer reactions. A.J.Miralles *et al.* have reported the outer-sphere reductions of pyridinepentamminecobalt(III) and pyridinepentammineruthenium(III) by hexacyanoferrate(II) (A.R. Mustafina *et al.* 2007, A.J.miralles *et al.* 1977). They have discussed the mechanisms of these reactions on the basis of Marcus' equation, electrostatic effects and orbital considerations (A.A. Holder *et al.* 2022). A.A.Holder has done work on the kinetics and mechanism of the reduction of the molybdatopentamminecobalt(III) ion by aqueous sulfite and aqueous potassium hexacyanoferrate(II). The mechanism of the reaction has been confirmed as outer-sphere mechanism. A.P.Szecsy, A.Haim (A. P.Szecsy *et al.* 1981) have studied the intramolecular electron transfer between pentacyanoferrate(II) and pentammine cobalt(III) complexes containing imidazole and its conjugate base. They have proposed that the mechanism of the reaction have gone through the imidazolate bridges. Jing-Jer Jwo *et al.* (J.J. Jwo *et al.* 1979) have worked on the intramolecular electron transfer between pentammine cobalt(III) mediated by various 4,4′-bipyridines and pentacyanoferrate(II). It has been suggested that the conjugation between the two pyridine rings is essential for electron transfer mediated by the ligand.

When the two rings are separated by each other by insulating methylene groups, electron transfer through the ligand is precluded but ligands that permit close approach of the metal centres lead to intramolecular, outer-sphere electron transfer reaction. M. Martinez *et al.* have studied the outer-sphere reactions of $(N)_5$ -macrocyclic cobalt(III) complexes (M. Martinez *et al.* 1977).

A reaction in restricted geometries such as micelles (H.L. Tavernier *et al.* 1998), vesicles (L. Hammarstrom *et al.* 1977) and DNAs (X.L. Wang *et al.* 2004, L.N. Ji et al. 2001, S. Srinivasan *et al.* 2005) have attracts great deal of interest for several decades. 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. A number of studies have been devoted to the understanding of the principles governing the interaction of surfactants with simplified membrane models such as phospholipid vesicles (R. Predo-Gotor *et al.* 1998). The action of surfactants on the phospholipid bilayer leads to the incorporation of surfactant molecules into these structures. Due to the partition equilibrium between the bilayers and the aqueous phase, this incorporation involves complex perturbations in the physical properties of vesicle membranes, which depend upon the type and amount of surfactant. It is well known that amphiphilic molecules are characterized by their dual nature. On the same molecule two differentiated parts, the hydrocarbon (hydrophobic) and the ionic (hydrophilic), are found. This general structure, characteristic of surfactants, is responsible for the self-assembly process in solution. Electron transfer in these restricted geometry systems attracts great deal of interest because of their potential to prolong lifetime of charge transfer states, a goal of electron transfer studies aiming to utilize solar energy (P.J. Cameron *et al.* 2004).

Liposomes have also proved to be useful carriers for the delivery of genes to cultured cells and for gene therapy in preclinical and clinical trials (A. Chonn *et al.* 1995). Surfactant-liposome systems represent good models for studying solubilization of cell membranes (R. Pignatello *et al.* 2011) and surfactant interactions with such biosystems such as skin. In recent years, ionic liquids (ILs) have attracted considerable interest as potential new media for organic synthesis, electrochemistry, catalyst support, and nanostructure construction materials (M.T. Paternostre *et al.* 1988, S. Almog *et al.* 1990) from a fundamental perspective, ionic liquid solutions present extraordinary features. The impressive solvation ability of ionic liquids facilitates their interaction with surfactants (S. Javadian *et al*. 2013, M. Blesic *et al*. 2007) It was shown that solvatophobic interactions are present between ionic liquids and the hydrocarbon portion of the surfactant, thus leading to the formation of surfactant micelles in ionic liquids and enhancing the solvation characteristics of the ionic liquid-surfactant system (A. Kristin *et al*. 2004) Electron transfer reactions of many surfactant–metal complexes have been studied in our laboratory (Karuppiah Nagaraj *et al*. 2012-2014). Recently we have reported some studies on the outer-sphere electron transfer reaction between some single and double chain surfactant complexes with Fe^{2+} ion in vesicles (Karuppiah Nagaraj *et al*. 2012-2014) where both the oxidant and reductant are cations. The present study reports the influence of ionic liquids and phase transition behavior of liposome vesicles on the outer-sphere electron transfer reaction between double chain surfactant cobalt(III) complexes containing aromatic diimine ligands and $[Fe(CN)_6]^{4-}$.

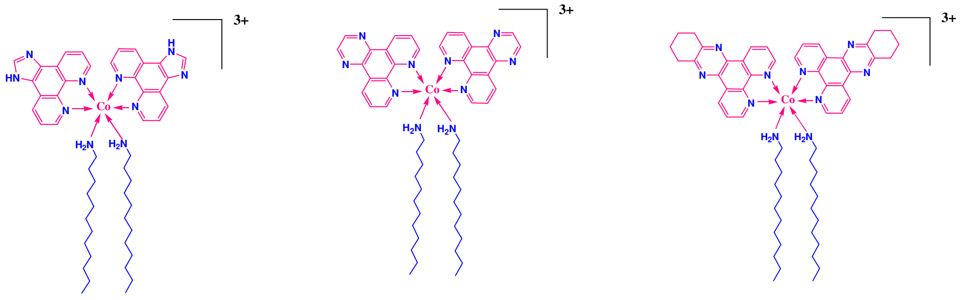
2. Experimental

2.1. Materials and methods

Potassium ferrocyanide, sodium nitrate, and disodium ethylenediamine tetraacetate (Na_2H_2EDTA) were obtained from Fluka located in seize, Germany and were used as received. To prepare buffer solutions, sodium phosphate and sodium dihydrogen orthophosphate were used. All solvents used were of analytical grade. The ionic liquids BMIM-Br(1-butyl-3-methyl imidazolium bromide) and liposome vesicles (DPPC) were purchased from Sigma-Aldrich Chemical Co.(Bangalore, India) and were used as such. To prepare buffer solutions sodium phosphate and sodium dihydrogen orthophosphate were used. All solvents used were of analytical grade.

2.2. Preparation of Reductant/Oxidant

The surfactant cobalt(III) complexes, cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2]^{3+}$, cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2]^{3+}$ and cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2]^{3+}$ used as oxidants were prepared as reported by us earlier. (Karuppiah Nagaraj *et al*. 2014) The structure of complexes is shown in Scheme 1.



***Cis*-[Co(ip)$_2$(TA)** ***Cis*-[Co(dpq)$_2$(TA)$_2$]$^{3+}$** ***Cis*-[Co(dpqc)$_2$(TA)$_2$]$^{3+}$**

Scheme 1: The structure of surfactant cobalt(III) complexes

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2.3. Nature of Reaction

On mixing $Fe(CN)_6{}^{4-}$ and our surfactant cobalt(III) complexes in the aqueous solution, a precipitate was formed and, therefore, homogeneous kinetic measurements were precluded. However, when Na_2H_2EDTA was present in the solution, no precipitate was formed during the reaction and therefore all the experiments were carried out in the presence of Na_2H_2EDTA. A disodium salt of ethylenediamine tetraacetic acid acted as a sequestering agent to remove cobalt(II) and prevented the precipitation of the cobalt(II) ion as a hexacyanoferrate salt.

2.4. Liposome preparation

In this study, unilamellar vesicles (ULV) were used and these were prepared by ethanol injection (E.B. Kipp *et al.* 1969). A solution of the lipid in ethanol was injected quickly into the buffer with the help of a fine needle and maintained at 50^0C under optimized conditions. The volume of ethanol injected was always <1 % v/v in order to avoid any devastation to the liposome. This method gives rise to small unilamellar vesicles (SUV) in the size range of ~15–25 nm (M.L. Morris *et al.* 1969).

2.5. Kinetic measurements

The rate of the reaction was evaluated spectrophotometrically using a Shimadzu-1800 UV-Vis., spectrophotometer equipped with a water Peltier system (PCB 150). The temperature was controlled within ± 0.01^0C. A solution containing the desired concentration of potassium ferrocyanide, sodium nitrate, disodium ethylenediamine tetraacetate (Na_2H_2EDTA), liposome/ ionic liquids 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 surfactant cobalt(III) complexes were added anaerobically using the syringe, and then increase in the absorbance of the oxidant followed at 470 nm were recorded as a function of time. The ionic strength was preserve at 1.0 mol dm^{-3} in all runs using $NaNO_3$. The second-order rate constant, k, for the $Fe(CN)_6{}^{4-}$reduction of the cobalt(III) complex defined by $-d[Co(III)]/dt = k[Co(III)][Fe(CN)_6{}^{4-}]$ was calculated from the concentration of $Fe(CN)_6{}^{4-}$ and the slope of the pseudo first order plot of $\log(A_t - A_\infty)$ versus time plot, which is equal to $-k[Fe(CN)_6{}^{4-}]/2.303$, where A_t is the absorbance at time t, A_∞ is the absorbance after all the cobalt(III) complexes 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 consecutive half-life values within a single run agreed to within ± 5%.

3. Results and discussion

3.1. Electron-transfer kinetics

On mixing $Fe(CN_6)^{4-}$ and our surfactantcobalt(III) complex in aqueous solution a precipitate was formed and therefore homogeneous kinetic measurements were precluded. When $EDTA^{2-}$ was present in the solution to sequester the cobalt(II), no precipitate was formed during the reaction and therefore all the experiments were carried out in the presence of $EDTA^{2-}$ (O. Miyashita et al. 2005). $EDTA^{2-}$ acted as a sequestering agent to remove cobalt(II) and prevent its precipitation as a hexacyanoferrate salt. The reduction of the surfactant cobalt(III) complexes, cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2]^{3+}$, cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2]^{3+}$ and cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2]^{3+}$ (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, $C_{14}H_{29}NH_2$=dodecylamine) by $Fe(CN_6)^{4-}$ ion proceeds to give as aqueous cobalt(II). This reaction is postulated to be outer-sphere, by comparison with similar reactions in the literature (H. Yamamura *et al.* 1999, A.J. Miralles *et al.* 1982, S.C. Hak et al. 2003). The present study of these complexes will be inert to substitution, due to the non-availability of a co-ordination site for inner-sphere precursor complexes. Our previous studies as well as literature reports (Karuppiah Nagaraj *et al.* 2014) on similar types of complexes revealed only outer-sphere redox pathways. The most favorable mechanism for the second-order reaction is an outer-sphere electron transfer process which consists of three elementary steps; ion pair formation (k_{ip}), electron transfer (k_{et}), and product dissociation. Accordingly the mechanism is delineated in Scheme 2.

$$[Co(LL)_2(A)_2]^{3+} + Fe^{2+} \xrightleftharpoons{k_{IP}} \{[Co(LL)_2(A)_2]^{3+} ; Fe^{2+}\}$$

$$\{[Co(LL)_2(A)_2]^{3+} + Fe^{2+}\} \xrightarrow{k_{et}} \{[Co(LL)_2(A)_2]^{2+} + Fe^{3+}\}$$

$$\{[Co(LL)_2(A)_2]^{2+} + Fe^{3+}\} \xrightarrow{\text{Fast}} \text{Products}$$

LL = ip, dpq and dpqc ; A = Dodecylamine

Scheme 2: Mechanism for the electron-transfer reaction of Surfactant cobalt(III) complexes

3.1. Effect of DPPC on electron transfer

The effect of DPPC vesicles on the kinetics of outer-sphere electron transfer between the surfactant cobalt(III) complexes, cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2]^{3+}$, cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2]^{3+}$ and cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2]^{3+}$ (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, and $Fe(CN)_6^{4-}$ ion has been investigated at various temperatures. As we have used the ethanol injection method for the preparation of solution of DPPC, the reaction medium of these electron transfer reactions should contain only unilamellar vesicles. The rate constants are given in Table 1 and SI Table 1 and 2 and the plots of k against various concentrations of DPPC are shown in Fig. 1 and SI Fig. 1 and 2. In presence of liposome vesicles the behavior of electron transfer is quite different from our previous studies where both reactants were cations. In the present system containing both reductant and oxidant have opposite charges we have observed two trends in the behavior of kinetics of the reaction with increase in the concentration of DPPC. As seen from the Table 1 and SI Table 1 and 2 up to the phase transition temperature (i.e. 40°C) the rate constant decreases with increase in the concentration of DPPC in the medium; above that temperature the rate constant increases with the increase in the concentration of DPPC in the medium. In this medium we have observed two extreme lipid phases that occur both below (gel phase) and above (liquid phase) phase transition. i.e. the temperature that is required for inducing the lipid melting from a solid-ordered to a liquid-disordered phase, is depending on the nature of its hydrophobic moiety. Below the phase transition temperature the lipid is very rigid**.** When DPPC concentration is increased in the medium we expect more number of surfactant cobalt(III) complexes will be accumulated into the interior of DPPC due to the hydrophobic nature of our surfactant complex and $Fe(CN)_6{}^{4-}$ will be at the outer surface. In this case formation of precursor complex and dissociation of successor complex are fast due to far apart distance between surfactant cobalt(III) complex and $Fe(CN)_6^{4-}$ metal centers where the freedom of movement of individual molecule is low so the rate constant decreased. But beyond the phase transition temperature lipid membrane passes from tightly ordered gel phase to liquid crystal phase where freedom of movement of the individual molecule is higher. Above the phase transition temperature the rigidity of the DPPC membrane is low so when the concentration of DPPC is increased, more number of the surfactant cobalt(III) complex molecules will move from the membrane interior to the outer surface where the concentration of $Fe(CN)_6{}^{4-}$ is also high. As a result the more hydrophobicity of complex, cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2]^{3+}$ is higher second order rate constant compared cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2]^{3+}$ which in tune higher than that of cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2]^{3+}$. Also the phase transition may change favorably the reorganization energies and the free energy barrier associated with the electron transfer (S. Ghosh *et al.* 2006, O. Miyashita *et al.* 2005)

3.2. Effect of ionic liquid, [BMIM]Br

There are many reports of electron transfer or other electrochemical processes that take place in ionic liquid. The acceleration of electron transfer from some metal complexes in the presence of imidazolium ILs has been reported. (S. Batzri *et al.* 1973) Aggregates such as micelles, liquid crystals and micro emulsions formed in ionic liquids have been widely studied recently (P. Benson et al. 1965). The effect of presence of ionic liquids as additive in the medium on the kinetics of outer-sphere electron transfer between the surfactant cobalt(III) complexes with $[Fe(CN)_6]^{4-}$ ion has been investigated at various temperatures. The observed second order rate constants are given in Table 2 and SI Table 3 and 4 and the plot of k against various concentration of [BMIM]Br in Fig. 2 and SI Fig. 3 and 4 for the above reaction, at different temperatures. As seen from these tables the rate constant of the reaction goes on increasing with increase in the concentration of ionic liquids from 1.4×10^{-3} moldm^{-3} to 2.8×10^{-3} moldm^{-3}. As the cation of the ionic liquid used has an inherent amphiphilicity it can interact with the long aliphatic double chain of the surfactant cobalt(III) complexes leading to specific structures before and after aggregation consisting of well aligned cation–anion aggregates. This is similar to the observation of surfactant cobalt(III) complex *cis*-$[Co(en)_2(4AMP)(DA)](ClO_4)_3$-$Fe^{2+}$ reactions. In initial aggregation the surfactant cobalt(III) complexes and $[Fe(CN)_6]^{4-}$ were far apart distance from the ionic liquids pool so rate constant increased not much. After aggregation the surfactant complex and $[Fe(CN)_6]^{4-}$ moved towards the ''ionic liquids pool'' surface. As a result of charge neutralization or charge creation and thus marginal contribution to the activation volume is expected. Since dpqc is larger in size than ip and dpq (Scheme. 1), the dpqc complexes are also larger than the ip and dpq complexes, i.e. the charge densities of dpqc complexes are lower than those of the ip and dpq complexes. Thus, it is possible to elucidate the coulombic interaction between the redox couples and the ions composing ionic liquids using the similar complexes with different charge densities. Thus the ionic liquids consisting of charged ions should be energetically favored which could leads to a increase in the reaction rate with increasing concentration of ionic liquids reactants are encountered in a small volume leading to higher rate and lower activation energy. This aggregation leads to higher local concentration of reactants leading to increase in the rate of the reaction. Hence the rate of the outer-sphere electron transfer reaction of the present study increases with increase in the concentration of the ionic liquid. As changes in amphiphilicity of the transition state can cause large effects in terms of electrostriction/solvation in ionic liquids, thereby the ionic liquid medium facilitates more aggregation of the surfactant cobalt(III) complex increases with increase in the concentration of the ionic liquid. In our previous reports of the electron transfer reaction in this media with Fe^{2+} established that amphiphilicity influenced the reaction rates. On comparing the previous reports second order rate constant of the present study reaction rate is higher due to increase in size of the amine ligand which increases amphiphilicity of the complexes which facilitates more aggregation leads to increasing the rate of electron transfer reaction.

3.3. Self-aggregation (critical micelle concentration) forming capacity between various surfactant cobalt(III) complexes

The self-aggregation of each complex indicates its respective self aggregation forming capacity. Lower CMC value indicates higher aggregation forming capacity and vice versa. The difference in the self aggregation between various surfactant cobalt(III) complexes of the present study (Table 2 and SI Table 3 and 4) are explained as follows: For all types of complexes it has been observed that the CMC value of each double chain surfactant cobalt(III) complex is lower than the respective single chain surfactant complex. This is due to the presence of higher aggregation of the former type of complexes due to the presence of two aliphatic chains compared to their respective single chain surfactant complexes. Increase in the self aggregation of the surfactant will always facilitate micelle formation. The critical micelle concentration value of each of the modified phenanthroline complex is lower compared to that of the corresponding phenanthroline complex. Because these extended aromaticity of modified phenanthroline ligands make the complexes more aggregation in character which increases the capacity of these complexes to form self aggregation. The order of self aggregation forming capacity of the surfactant cobalt(III) complexes is as follows: Complex **1** < Complex **2** < Complex **3.** This trend in critical micelle concentration is in tune with the aggregation strength of the surfactant cobalt(III) complexes.

3.4. Activation parameters and Isokinetic plots

3.4.1. Effect of Temperature

The effect of temperature on the rate was studied at six different temperatures (298, 303, 308, 313, 318, and 323 K; all rate constant tables) in ionic liquids and liposome vesicles medium in order to obtain the activation parameters for the reaction between cobalt(III) surfactant complexes with $Fe(CN)_6^{4-}$. Fig. 2 and SI Fig. 3 and 4 shows that on increasing temperature rate constant increased in ionic liquids and Fig. 1 and SI Fig. 1 and 2 shows that increasing the temperature increases the rate of the electron transfer (above phase transition) and decrease the rate of electron transfer (below phase transition) reactions in liposome vesicles.

3.4.2. Isokinetic plots

From the transition state theory (N. Arulsamy *et al.* 2001), making use of Eyring equation, $\ln k/T = \ln k_B/h + \Delta S^{\#}/R - \Delta H^{\#}/RT$, the values of $\Delta S^{\#}$ and $\Delta H^{\#}$ were determined by plotting ln(k/T) versus 1/T and the plots are shown in Fig. 3,4 and SI Figures 5-8. The $\Delta S^{\#}$ and $\Delta H^{\#}$ values obtained are shown in Table 3 and SI Tables 5-9. As seen from these tables the values of $\Delta H^{\#}$ is positive for all the reactions (ionic liquids and liposome vesicles), indicating that the formation of activated complex is endothermic. In all these media the $\Delta S^{\#}$ 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**)** This is consistent with a model in which the surfactant cobalt(III) complexes and $Fe(CN)_6^{4-}$ ions bind to the DPPC in the transition state. Though we expected an increase of entropy in the transition state due to charge neutralization process (union of a positive charged oxidant and negatively charged reductant), our $\Delta S^{\ddagger}$ values reveal that the entropy has decreased. In such a case 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 electron transfer reaction isokinetic plots ($\Delta S^{\#}$ versus $\Delta H^{\#}$) for the electron transfer reactions of surfactant cobalt(III) complexes were made. As seen from Fig. 4 and SI Figures 10-14 straight lines were obtained for all the isokinetic plots of complexes, indicating that a common mechanism exists in all these media.

4. Conclusion

The kinetics of outer-sphere electron transfer reaction between the surfactant cobalt(III) complex with $[Fe(CN)_6]^{4-}$ in presence of ionic liquids and unilamellar liposome vesicles were also studied. In ionic liquids media the rate constant increase with increase in concentration of ionic liquid which shows that self aggregation of surfactant complexes and ionic liquids interaction enhance the rate with increasing concentration of ionic liquids. Since dpqc is larger in size than ip and dpq, the dpqc complexes are also larger than the ip and dpq complexes, i.e. the charge densities of dpqc complexes are lower than those of the ip and dpq complexes. Thus, it is possible to elucidate the coulombic interaction between the redox couples and the ions composing ionic liquids using the similar complexes with different charge densities. The electron transfer reaction of the surfactant cobalt(III) complexes with $[Fe(CN)_6]^{4-}$ ion in liposome vesicles media reveal that below the phase transition temperature the rate decreases with increasing concentration of DPPC, which is explained by the accumulation of these surfactant cobalt(III) complex inside the vesicles through hydrophobic effects. Above the phase transition temperature, the rate increased with increasing concentration of DPPC, which may be due to release of the cobalt(III) complex from the interior to the exterior surface of the DPPC membrane. On comparing electron transfer reactions involving $Fe(CN)_6^{4-}$ and Fe^{2+} ions as oxidants with the same surfactant cobalt(III) complexes the rate constants involving $Fe(CN)_6^{4-}$ as oxidant is higher for each surfactant cobalt(III) complex due to good π-accepting character of $Fe(CN)_6^{4-}$ compared to Fe^{2+} ion. Finally the isokinetic plots of all these complexes give straight lines indicating that a common mechanism exists in all the concentrations of ionic liquids and liposome vesicles.

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Fig. 1 Plot of k against DPPC for cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ under various temperatures; cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}

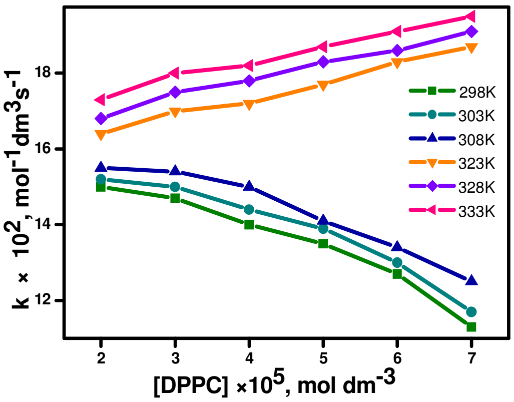


Fig. 2 Plot of k against [BMIM]Br for cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ at various temperatures; cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}

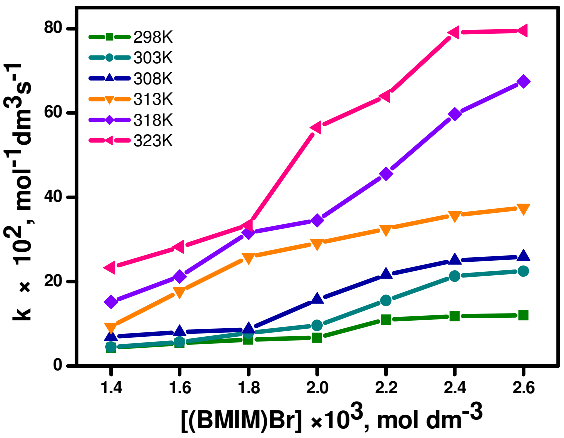


Fig. 3 Eyring plot for Cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [[Fe(CN)$_6$]$^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

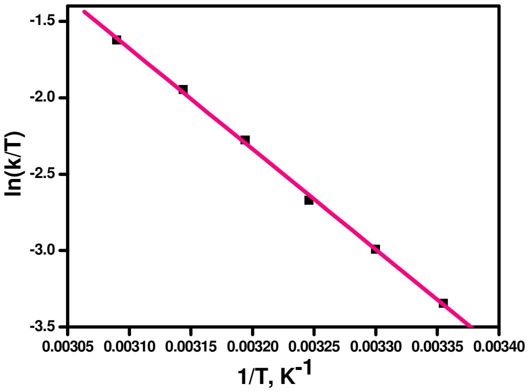


Fig. 4 Eyring plot for Cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

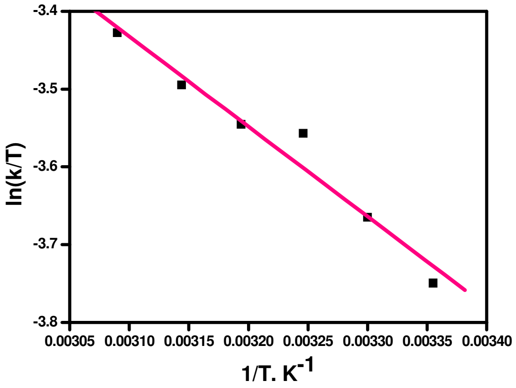


Fig. 5 Isokinetic plot of the activation parameters for the reduction of Cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ by ion(II) in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

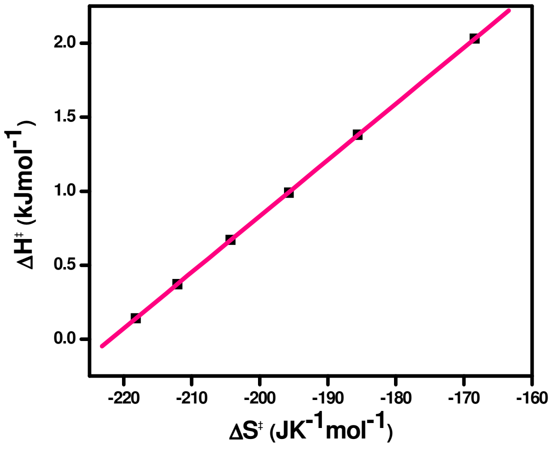


Fig. 6 Isokinetic plot of the activation parameters for the reduction of Cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ by ion(II) in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

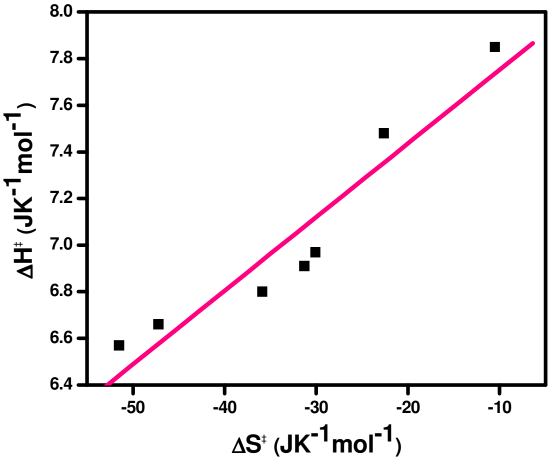


Table 1. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in DPPC medium under various temperatures. cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}

[DPPC] × 10^5 (mol dm^{-3})	k ×10^2, dm^3 mol^{-1} s^{-1}					
	298K	303K	308K	323K	328K	333K
2.0	15.0	15.2	15.5	16.4	16.8	17.3
3.0	14.7	15.0	15.4	17.0	17.5	18.0
4.0	14.0	14.4	15.0	17.2	17.8	18.2
5.0	13.5	13.9	14.1	17.7	18.3	18.7
6.0	12.7	13.0	13.4	18.3	18.6	19.1
7.0	11.3	11.7	12.5	18.7	19.1	19.5

Table 2. Second-order rate constants for the reduction of cobalt(III) complex ion by Fe^{2+} in the presence of [BMIM]Br under various temperatures. cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}

[(BMIM)Br] × 10^3, mol dm^{-3}	k ×10^2, dm^{-3} mol^{-1} s^{-1}					
	298K	303K	308K	313K	318K	323K
1.4	4.0	4.2	6.5	8.9	14.7	23.0
1.6	5.2	5.5	7.7	12.0	20.6	27.4
1.8	6.1	7.4	8.5	25.5	31.5	33.7
2.0	6.5	9.4	15.5	28.6	34.8	55.4
2.2	10.5	15.2	21.3	32.1	45.3	63.7
2.4	11.4	20.2	24.2	35.2	58.2	77.2
2.6	11.6	21.2	25.6	36.2	59.6	80.4

Table 3. Activation parameters for the reduction of cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$, μ = 1.0 $moldm^{-3}$ in DPPC medium

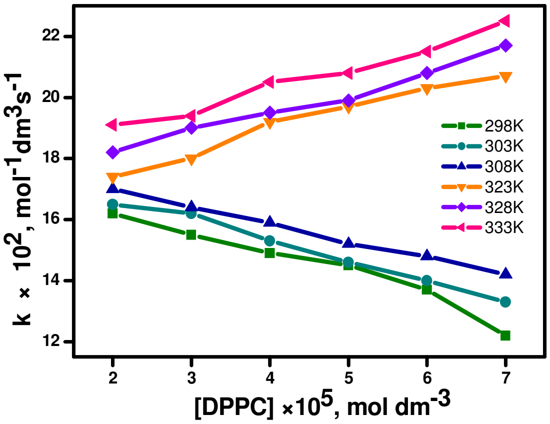
[DPPC]×10^5 (mol dm^{-3})	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$
2.0	0.14	218.2
3.0	0.37	212.1
4.0	0.67	204.3
5.0	0.99	195.7
6.0	1.38	185.6
7.0	2.03	168.4

Table 4. Activation parameters for the reduction of cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$, μ = 1.0 moldm^{-3} in [BMIM]Br medium

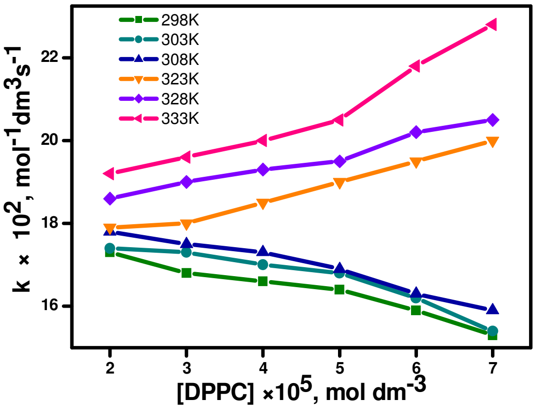
[(BMIM)Br]× 10^3, mol dm^{-3}	$\Delta H^‡$	$-\Delta S^‡$
1.4	6.62	50.2
1.6	6.56	49.7
1.8	6.57	42.1
2.0	6.67	35.0
2.2	6.79	34.7
2.4	7.26	24.2
2.6	7.96	7.3

Supplmentary Informations Figures (SI Figures)

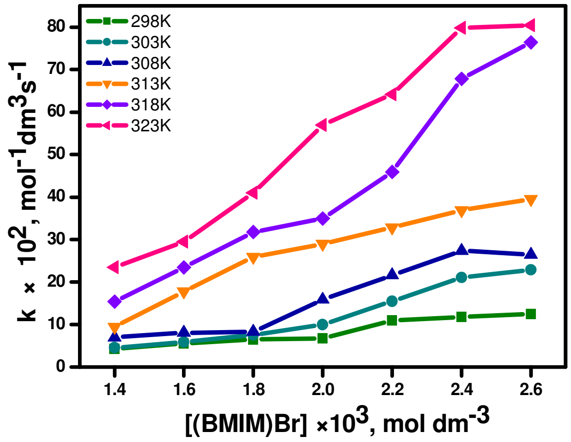
SI Fig. 1 Plot of k against DPPC for Cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ under various temperatures; cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}



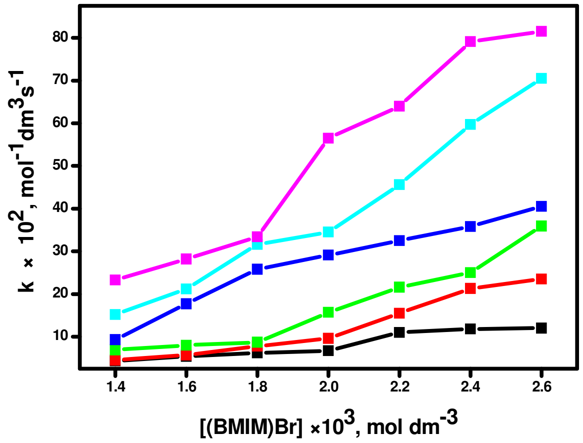
SI Fig. 2 Plot of k against DPPC for Cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ under various temperatures; cis-$[Co(ip)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}



SI Fig. 3 Plot of k against [BMIM]Br for Cis-[Co(dpq)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ at various temperatures; Cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ =4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}



SI Fig. 4 Plot of k against [BMIM]Br for Cis-[Co(dpqc)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ at various temperatures; Cis-[Co(ip)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}



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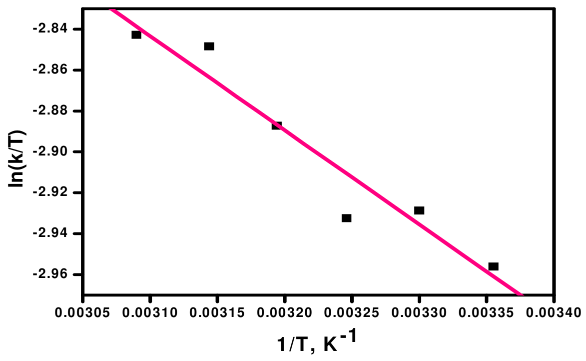
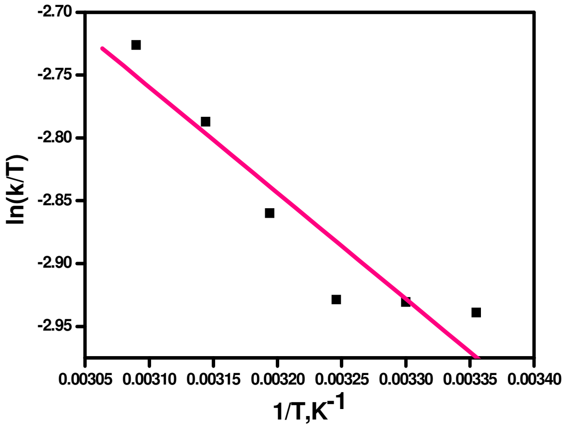
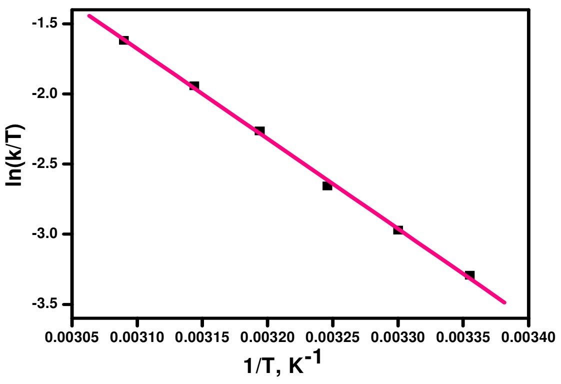
SI Fig. 5 Eyring plot for Cis-[Co(dpq)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ in DPPC medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



SI Fig. 6 Eyring plot for Cis-[Co(dpqc)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ in DPPC medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



SI Fig. 7 Eyring plot for Cis-[Co(dpq)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ in [BMIM]Br medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



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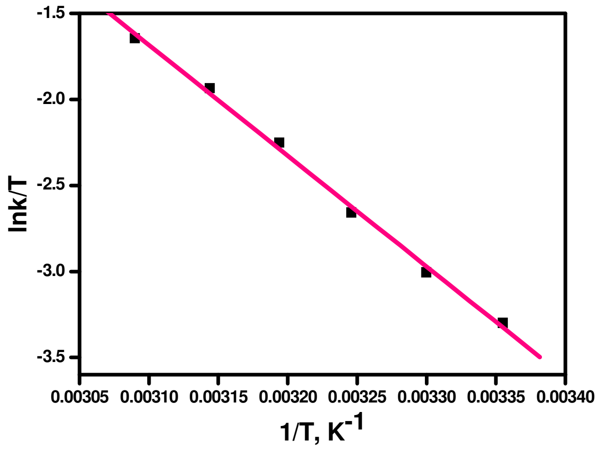
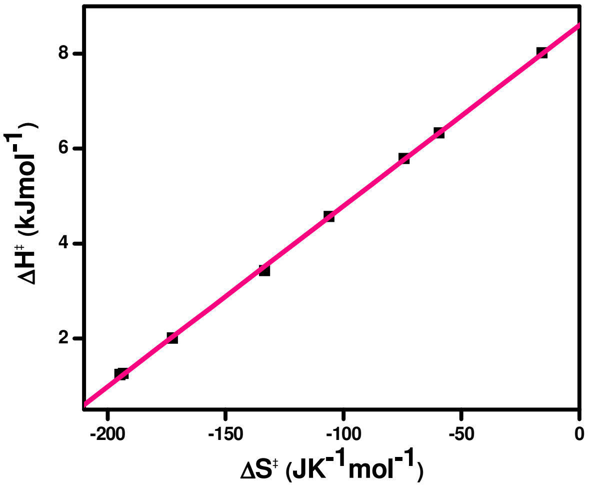
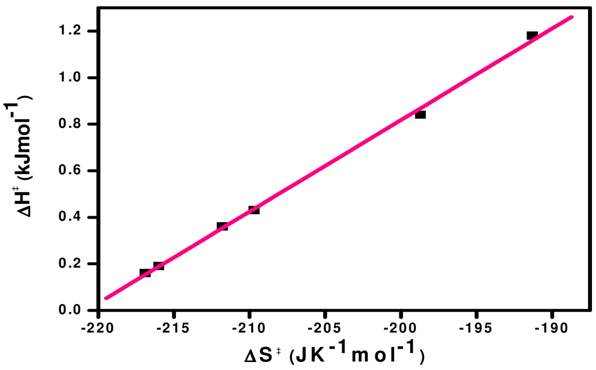
SI Fig. 8 Eyring plot for Cis-[Co(dpqc)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ in [BMIM]Br medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



SI Fig. 9 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpq)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in DPPC medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



SI Fig. 10 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpqc)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in aqueous solutions. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



SI Fig. 11 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpq)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in [BMIM]Br medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

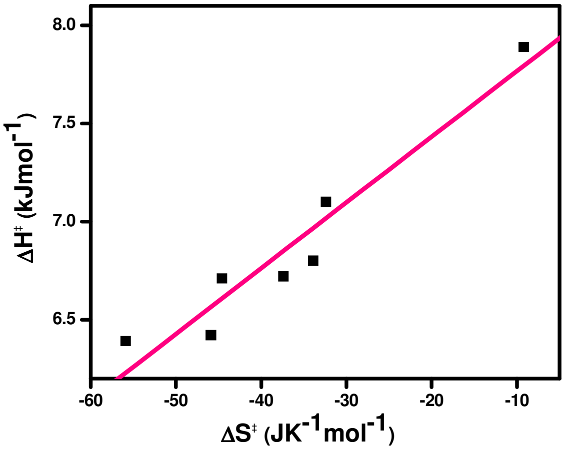
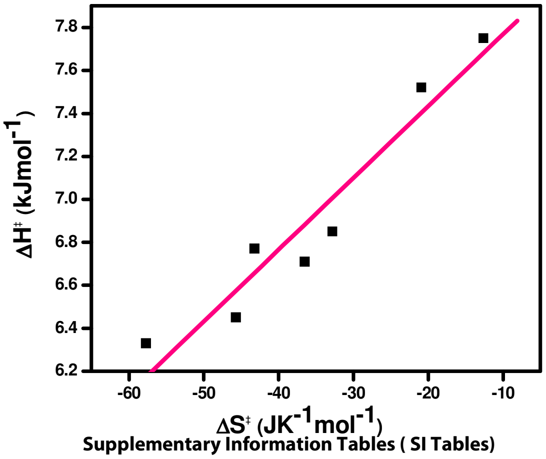


Fig. 12 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpqc)$_2$(C$_{14}$H$_{29}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in [BMIM]Br medium. [complex] = 4 x 10^{-4} mol dm^{-3}; [Fe(CN)$_6$ $^{4-}$] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.



Supplementary Information Tables (SI Tables)

SI Table 1. Second-order rate constants for the reduction of cobalt(III) complex ion by $[Fe(CN)_6{}^{4-}]$ in DPPC under various temperatures. Cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}

[DPPC] × 10^5 (mol dm^{-3})	k ×10^2, dm^3 mol^{-1} s^{-1}					
	298K	303K	308K	323K	328K	333K
2.0	16.2	16.5	17.0	17.4	18.2	19.1
3.0	15.5	16.2	16.4	18.0	19.0	19.4
4.0	14.9	15.3	15.9	19.2	19.5	20.5
5.0	14.5	14.6	15.2	19.7	19.9	20.8
6.0	13.7	14.0	14.8	20.3	20.8	21.5
7.0	12.2	13.3	14.2	20.7	21.7	22.5

SI Table 2. Second-order rate constants for the reduction of cobalt(III) complex ion by $[Fe(CN)_6{}^{4-}]$ in DPPC under various temperatures. Cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}

[DPPC] × 10^5 (mol dm^{-3})	k ×10^2, dm^3 mol^{-1} s^{-1}					
	298K	303K	308K	323K	328K	333K
2.0	17.3	17.4	17.8	17.9	18.6	19.2
3.0	16.8	17.3	17.5	18.0	19.0	19.6
4.0	16.6	17.0	17.3	18.5	19.3	20.0
5.0	16.4	16.8	16.9	19.0	19.5	20.5
6.0	15.9	16.2	16.3	19.5	20.2	21.8
7.0	15.3	15.4	15.9	20.0	20.5	22.8

SI Table 3. Second-order rate constants for the reduction of cobalt(III) complex ion by $[Fe(CN)_6{}^{4-}]$ in the presence of [BMIM]Br medium under various temperatures. Cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}

[(BMIM)Br] × 10^3, mol dm^{-3}	k ×10^2, dm^3 mol^{-1} s^{-1}					
	298K	303K	308K	313K	318K	323K
1.4	4.0	4.2	6.5	8.9	14.7	23.0
1.6	5.2	5.5	7.7	12.0	20.6	27.4
1.8	6.1	7.4	8.5	25.5	31.5	33.7
2.0	6.5	9.4	15.5	28.6	34.8	55.4
2.2	10.5	15.2	21.3	32.1	45.3	63.7
2.4	11.4	20.2	24.2	35.2	58.2	77.2
2.6	11.6	21.2	25.6	36.2	59.6	80.4

SI Table 4. Second-order rate constants for the reduction of cobalt(III) complex ion by $[Fe(CN)_6{}^{4-}]$ in the presence of [BMIM]Br medium under various temperatures. Cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe(CN)_6{}^{4-}]$ = 0.01 mol dm^{-3}

[(BMIM)Br] ×10^3, mol dm^{-3}	k ×10^2, dm^{-3} mol^{-1} s^{-1}					
	298K	303K	308K	313K	318K	323K
1.4	4.3	4.6	7.0	9.5	15.4	23.5
1.6	5.6	5.9	8.1	17.8	23.5	29.5
1.8	6.5	7.6	8.3	25.9	31.8	41.0
2.0	6.8	10.0	15.9	29	35.0	57.0
2.2	11.0	15.5	21.6	32.9	45.9	64.2
2.4	11.8	21.1	27.4	36.9	67.8	80.8
2.6	12.5	22.9	26.5	39.5	76.4	82.4

SI Table 5. Activation parameters for the reduction of Cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$, $\mu = 1.0$ moldm^{-3} in DPPC medium

[DPPC]×10^5 (mol dm^{-3})	ΔH‡	-ΔS‡
2.0	1.26	193.3
3.0	2.01	172.5
4.0	3.43	133.4
5.0	4.57	106.0
6.0	5.79	74.20
7.0	6.33	59.40
8.0	8.02	15.80

SI Table 6. Activation parameters for the reduction of Cis-$[Co(dpqc_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$, $\mu = 1.0$ moldm^{-3} in DPPC medium

[DPPC]×10^5 (mol dm^{-3})	ΔH‡	-ΔS‡
2.0	0.16	216.9
3.0	0.19	216.0
4.0	0.36	211.8
5.0	0.43	209.7
6.0	0.84	198.7
7.0	1.18	191.3

SI Table 7. Activation parameters for the reduction of Cis-$[Co(dpq)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$, $\mu = 1.0$ moldm^{-3} in [BMIM]Br medium medium

[(BMIM)Br]× 10^3, mol dm^{-3}	ΔH‡	-ΔS‡
1.4	6.39	55.9
1.6	6.42	45.9
1.8	6.71	44.6
2.0	6.72	37.4
2.2	6.80	33.9
2.4	7.10	32.4
2.6	7.89	-9.2

SI Table 8. Activation parameters for the reduction of Cis-$[Co(dpqc)_2(C_{14}H_{29}NH_2)_2](ClO_4)_3$, $\mu = 1.0$ moldm^{-3} in [BMIM]Br medium

[(BMIM)Br]× 10^3, mol dm^{-3}	ΔH‡	-ΔS‡
1.4	6.33	57.7
1.6	6.45	45.7
1.8	6.77	43.2
2.0	6.71	36.5
2.2	6.85	32.8
2.4	7.52	20.9
2.6	7.75	12.6

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CONFLICTS OF INTEREST

"The authors declare no conflict of interest".