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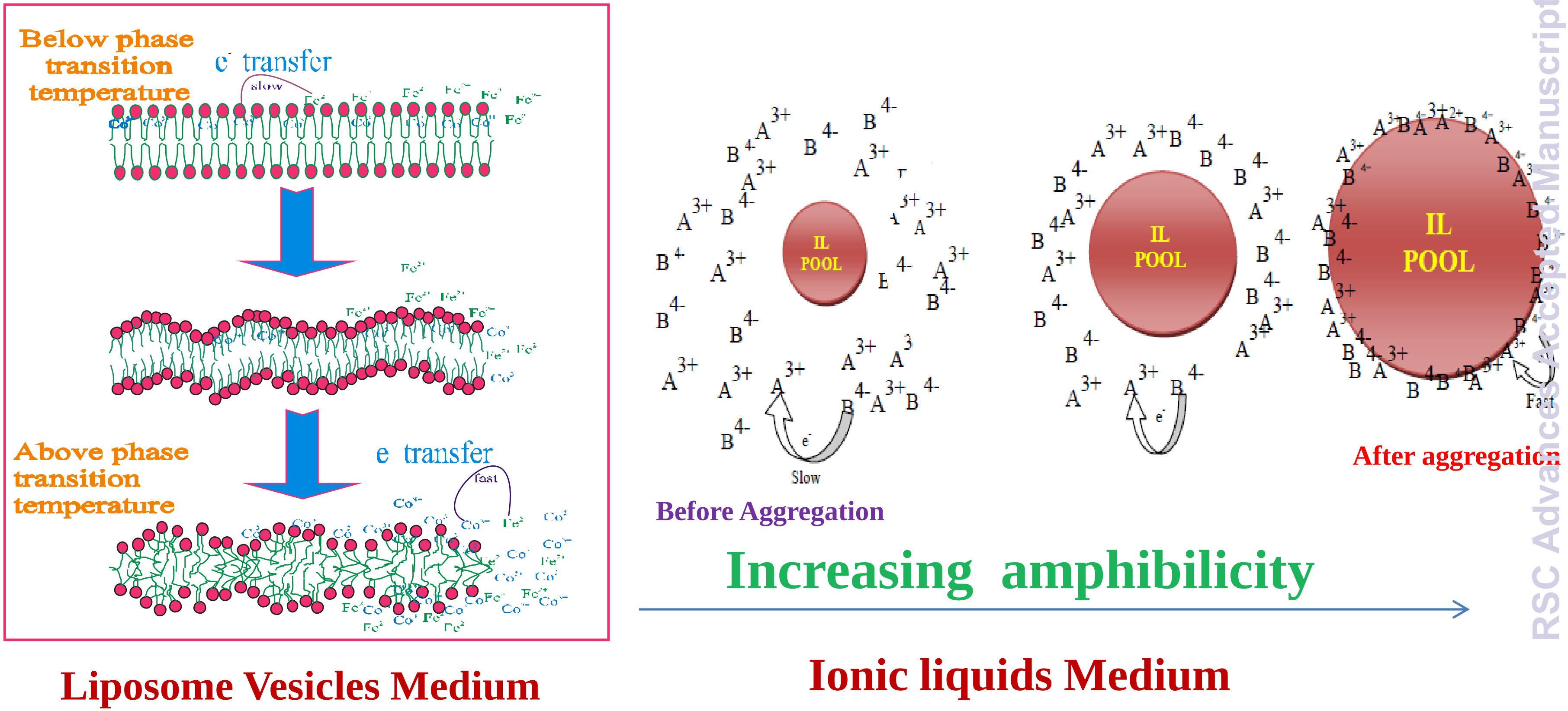
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Slow
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Before Aggregation
After aggregation
Increasing amphibilicity
Liposome Vesicles Medium
Ionic liquids Medium

Thermodynamics and kinetic investigation of Electron transfer reactions of surfactant cobalt(III) complexes containing diimine ligands with iron(II) in presence of liposome vesicles and amphiphilic salt media

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The kinetics of reductions of surfactant cobalt(III) complexes, cis-$[Co(L)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ (L = imidazo[4,5-f][1,10]phenanthroline, dipyrido[3,2-d:2'-3'-f]quinoxaline and dipyrido[3,2-a:2',4'-c](6,7,8,9-tetrahydro)phenazine, $C_{12}H_{25}NH_2$=dodecylamine) by iron(II) in liposome vesicles (DPPC) and amphiphilic salt ((BMIM)Br) were studied at different temperatures by UV-Vis absorption spectroscopy method 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. 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. It is concluded that below the phase transition temperature, there is an accumulation of surfactant cobalt(III) complexes at the interior of the vesicle membrane through hydrophobic effects, and above the phase transition temperature the surfactant cobalt(III) complexes is released from the interior to the exterior surface of the vesicle. The effects of amphiphilicity of the long aliphatic double chains of these surfactant complex ions into ionicliquids on these reactions have also been studied. The second order rate constant for the electron transfer reactions were found to increase with increasing concentrations of amphiphilic salts. The results have been interpreted in terms of the hydrophobic effect.

Introduction

Surfactants or surface-active agents are substances which have the tendency to concentrate at the surface or any interface of a system at low concentration, thereby significantly reducing the amount of work required to expand the interface. Surface-active materials are major building blocks, including chemistry (chemical kinetics or equilibria), biology (as membrane mimetics) and Pharmacy. [1a,b] 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. [2a,b] In recent times, there have been some reports on surfactant metal complexes of a different nature and their micelle forming properties. [3a,b,4a,b,5a,b,6a,b] 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.

Studies on the chemistry of electron transfer reactions involving cobalt(III) complexes are very well known because the kinetics of reduction of octahedral cobalt(III) complexes is mostly free from complications arising due to reversible electron transfer, aquation, substitution, and isomerisation reactions. Diebler and Taube [7] and other researchers [8,9] have studied the kinetics and mechanism of reduction of cobalt(III) complexes by iron(II) in aqueous and non-aqueous media. Kinetic and stoichiometric studies of the reduction of cobalt(III) ammine complexes have yielded important information regarding the mechanism of electron transfer reactions. Benson *et al.* have reported that iron(II) can reduce cobalt(III) complexes via an outer-sphere electron transfer step. [10] Y. Kurimura *et al,* have reported the iron(II) reductions of some cobalt(III) complexes to investigate the effect of non bridging ligand on the rate of electron transfer reactions [11] and other researchers have also reported the iron(II) reductions of $Co(en)_2XY^{n+}$ [12] and $Co(NH_3)_4XCl^{n+}$ [13] and electron transfer reaction between aquochromium(II) to determine the effect of non bridging ligand effect. Anbalagan *et al.* have reported [14] the mixed ligand complexes containing aryl amine ligand and a wide range of cobalt(III) complexes showing promising reactivities and physical properties, due to the presence of electron donor/acceptor groups in the aryl ligand. Linear polyamine and aryl amines are of great interest [15] from several perspectives due to systematic change in their substitution, redox reactions, and magnetic behavior, more interestingly in biological systems. Reactions in restricted geometries such as vesicles [16a,b] and DNA [17,18] have attracted growing research 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. Sanchez *et al.* [19,20] have studied many electron transfer reactions in the presence of macromolecules, in general referred to as restricted geometry conditions, as a way of modification of redox processes.

Liposomes are lipid–water systems, which have come into widespread use as a simplified model of biological membranes and delivery systems. [21] Study of the processes involved in liposome–surfactant solubilization has been of great value as this can provide useful information to better understand this complex phenomenon. [22-24] 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. Amphiphilic salts are typically composed of organic cations and organic/inorganic anions existing as liquids at ambient room temperature. They are good candidates for green solvents compared with traditional organic solvents because of their unique properties such as wide liquid state range, negligible vapor pressure, favorable solvation behavior, and high reactivity and selectivity. [25a,b,c] Their applications in chemical reactions, separation processes, and renewable batteries, and so on have been widely investigated in the past decade [26a,b,c] As a solvent, the self-assembly of some surfactants or block copolymers in amphiphilic salt has been investigated. [27] Microemulsions containing hydrophilic and hydrophobic amphiphilic salt are also prepared. [28] Some researchers have found that some amphiphilic salts behave as surfactants owing to the long hydrophobic substituent alkyl groups on the cation. The surface active characteristic of amphiphilic salts has been the cause of extensive concern recently. [29a,b]

Electron transfer reactions of many surfactant–metal complexes have been studied in our laboratory. [30-33] Recently, we have reported the outer-sphere electron transfer reactions between some surfactant cobalt(III) complexes containing aliphatic diimine ligands and iron(II) in the liposome vesicles and amphiphilic salts. [34,35] In this paper we report a further investigation on the effect of increasing amphiphilicity of the complexes on the kinetics of outer-sphere electron transfer between some surfactant–cobalt(III) complexes containing aromatic diimine ligands and iron(II).

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. Liposome (DPPC) and amphiphilic salts (BMIM)Br were purchased from Sigma-Aldrich Chemical Co.(Bangalore, India) and used as such. Buffer solutions were prepared using sodium phosphate dibasic and sodium dihydrogen orthophosphate. All solvents used were of analytical grade. Triple-distilled water was used for all the experiments.

Preparation of oxidant / Reductant

The surfactant-cobalt(III) complexes, cis-$[Co(L)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ used as oxidants were prepared as reported by us earlier. [36] The structure of complexes is shown in Scheme 2. A stock solution of $Fe(ClO_4)_2$ was prepared by dissolving pure iron powder in slight excess of perchloric acid. The concentration of iron(II) was determined by a method similar to that reported in the literature [37] the ionic strength of the solution was adjusted by the addition of sodium perchlorate solution.

Liposome preparation

For our studies, only unilamellar vesicles (ULV) were used and these were prepared by ethanol injection. [38] A solution of the lipid in ethanol was injected rapidly into the buffer with the help of a fine needle and maintained at 50^0 C under optimized conditions. The volume of ethanol injected was always <1 % v/v in order to avoid any damage to the liposome.

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 ± 0.01^0C. A solution containing the desired concentration of liposome vesicles and amphiphilic salt 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 iron(II) was added anaerobically using the syringe. The reaction was followed by measuring the absorption of the surfactant cobalt(III) complexes with time. The decrease in the absorbance was followed at 470 nm for all these complexes. All kinetic measurements were performed under pseudo-first order conditions with the iron(II) in excess over the cobalt(III) complexes. The concentration of $Fe(ClO_4)_2$ 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. The second-order rate constant, k, for the iron(II) reduction of the cobalt(III) complex defined by -d[Co(III)]/dt = k[Co(III)][iron(II)] 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[iron(II)]/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.

Stoichiometry

The stoichiometry of the reaction was determined by estimating iron(II) and cobalt(II) present in the product mixture. iron(III) was determined spectrophotometrically by Kitson's method, [39] and cobalt(II) was determined as $[CoCl_4]^{2-}$ at 690 nm in an excess of HCl. [40] The stoichiometric ratio of iron(III) and cobalt(II) concentrations was found to be 1:1 in all the reactions studied.

Electron-transfer kinetics

The reduction of the surfactant cobalt(III) complexes, cis-$[Co(L)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ by cobalt(II) proceeds to give as aqueous cobalt(II). This reaction is postulated to be outer-sphere, by comparison with similar reactions in the literature. [41-44] The present study of these complexes will be inert to substitution, due to the non-availability of a co-ordination site for an inner-sphere precursor complexes. Our previous studies as well as literature reports [45] 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 1.

Effect of liposome, dipalmitoylphosphotidylcholine (DPPC)

Because of its amphiphilic nature, DPPC (dipalmitoylphosphotidylcholine) undergoes spontaneous aggregation in aqueous solutions. This leads to the formation of a three-dimensional closed bilayer structure called vesicles. [46] When the temperature is increased, these vesicles of DPPC are known to undergo phase transitions at 40^0C, [47] from the gel phase to the liquid crystalline phase. The effect of DPPC vesicles on the kinetics of outer-sphere electron transfer between the surfactant cobalt(III) complexes and iron(II) have been investigated at different temperatures. As ethanol injection method was used, the reaction medium of these electron transfer reactions should contain only unilamellar vesicles. In the presence of these unilamellar vesicles also the outer-sphere electron transfer proceeds with second-order kinetics. The rate constants are given in Table 1 and SI Table 1 and 2, and plots of k against [DPPC] are shown in Fig. 1 and SI Fig. 1 and 2. Two trends have been observed in the behavior of the rate constants with concentration of DPPC. Below the phase transition temperature, the rate constants decrease with increasing [DPPC], whereas above this temperature the rate constants increase with [DPPC]. These trends were observed for these surfactant cobalt(III) complexes used in the present study. It is well known that when a surfactant is added to an aqueous medium containing lipid membranes, the interaction between surfactants and lipids takes place in three ways: part of the added surfactant inserts into the outer membrane leaflet; the surfactant molecules equilibrate between the outer and inner leaflets of the vesicle; and the inner leaflet equilibrates with the interior of the vesicle [48,49] Below the phase transition temperature, the lipid is very rigid, so these surfactant cobalt(III) complex molecules are tightly bound to the membrane DPPC, mostly at the inner membrane leaflet. As the concentration of DPPC is increased, more of these surfactant cobalt(III) complex molecules will be accumulated into the DPPC interior, whereas iron(II) will be at the outer surface, so the rate constant decreases. But beyond the phase transition temperature, the rigidity of the DPPC membrane is low; so when the concentration of DPPC is increased, more of these surfactant cobalt(III) complex molecules will move from the membrane interior to the outer surface where the concentration of iron(II) is also high, causing the rate constant to increase. Also the phase transition may favorably affect the reorganization energies and the free energy barrier associated with electron transfer. [50]

Effect of amphiphilic salt, [BMIM]Br

There are many reports of electron transfer or other electrochemical processes that take place in amphiphilic salts. The acceleration of electron transfer from some metal complexes in the presence of imidazolium ILs has been reported. [51] The unique advantage of amphiphilic salt is that their physical and chemical properties can be readily adjusted by suitable selection of cation, anion, and the substituents of cation. Aggregates such as micelles, liquid crystals and microemulsions formed in amphiphilic salt have been widely studied recently. [52] The effect of presence of amphiphilic salts [BMIM]Br in the medium on the kinetics of outer-sphere electron transfer between the surfactant cobalt(III) complexes of the present study with iron(II) have been investigated at different temperatures. The observed second order rate constants are given in Table 2 and SI Table 3 and 4 and the plots of k against different concentrations of amphiphilic salt, [BMIM]Br in Fig. 2 and SI Fig. 3 and 4 at 303, 308, 313, 318, 323 and 328 K. As seen from these tables the rate constant of each of the reaction goes on increasing with increase in the concentration of amphiphilic salt in the medium from 1.4×10^{-3} moldm^{-3} to 2.6×10^{-3} moldm^{-3}. As the cation of the amphiphilic salt used has an inherent amphiphilicity it can interact with the long aliphatic chain of the surfactant cobalt(III) complexes of the present study thereby the amphiphilic salt facilitates some more aggregation of the surfactant cobalt(III) complexes. 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 amphiphilic salt.

Activation parameters and isokinetic plots

The effect of temperature on rate was studied at six different temperatures for each concentration of amphiphilic salts and liposme vesicles in order to obtain the activation parameters for the reaction between surfactant cobalt(III) complexes with iron(II). From transition transition state theory, [53] it is known that

$$\ln k/T = \ln k_B/h + \Delta S^{\#}/R - \Delta H^{\#}/RT$$

The values of $\Delta S^{\#}$ and $\Delta H^{\#}$ were determined by plotting ln(k/t) versus 1/T (SI Figures 5-10). The results are shown in Tables 3,4 and SI Tables 5-8. The values of $\Delta H^{\#}$ are positive under all conditions.

The $\Delta S^{\#}$ values are negative under all conditions, indicating a more ordered transition state; as expected for a compact ion pair state (Scheme 1), leading to greater solvation, and loss of freedom of the solvent molecules in the transition state of the three different media studied, we observed the largest values of $\Delta S^{\#}$ in amphiphilic salts. This is understandable because amphiphilic salts form more aggregates compared to the liposome media, giving a larger interaction with the solvent in the transition state. and so amphiphilic salts attracts more number of surrounding solvent molecules around the positive and negative charge of the reactants resulting in the more loss of freedom 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 SI Figures 11-16 straight lines were obtained for all the isokinetic plots of complexes, indicating that a common mechanism exists in all the concentrations of each complex studied.

Conclusions

In this report, below the phase transition temperature the rate decreases with increasing concentration of DPPC through hydrophobic effects. Above the phase transition temperature, the rate increased with increasing concentration of DPPC. In amphiphilic salts media, the increase of rate constant with increase in the concentration of amphiphilic salt as additive is due to inherent amphiphilicity of (BMIM)Br which can interact with the long aliphatic chain of the surfactant cobalt(III) complexes thereby the amphiphilic salt facilitates some aggregation of the surfactant cobalt(III) complexes. An Isokinetic plot reveals that the mechanism of the reaction does not change by phase transition. Finally all these results indicate that the amphiphilicity of the complexes can modify the kinetics its redox reaction.

Acknowledgements

We are grateful to the UGC-SAP and DST-FIST programmes of the Department of Chemistry, Bharathidasan University, and UGC-SAP RFSMS Scholarship sanctioned to one of the authors, K. Nagaraj, by University Grants Commission (UGC), New Delhi. Financial assistance from the CSIR (Grant No. 01(2461)/11/EMR-II), DST (Grant No. SR/S1/IC-13/2009) and UGC (Grant No. 41-223/2012(SR) sanctioned to S. Arunachalam are also gratefully acknowledged.

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Scheme Captions

Scheme 1: General mechanism for the electron-transfer reaction

Scheme 2: The structure of surfactant cobalt(III) complexes

Figure Captions

Fig. 1 Plot of k against DPPC for cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ under different temperatures; cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

Fig. 2 Plot of k against [BMIM]Br for cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ at different temperatures; cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

Table Captions

Table 1. Second-order rate constants for the reduction of cobalt(III) complex ion by iron(II) in DPPC medium under different temperatures. cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

Table 2. Second-order rate constants for the reduction of cobalt(III) complex ion by iron(II) in the presence of [BMIM]Br under different temperatures. cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

Table 3. Activation parameters for the reduction of cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, μ = 1.0 moldm^{-3} in DPPC medium

Table 4. Activation parameters for the reduction of cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, μ = 1.0 moldm^{-3} in [BMIM]Br medium

Supplmentary Informations (SI)

SI Figure Captions

SI Fig. 1 Plot of k against DPPC for Cis-$[Co(dpq)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ under different temperatures; cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Fig. 2 Plot of k against DPPC for Cis-$[Co(dpqc)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ under different temperatures; cis-$[Co(ip)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Fig. 3 Plot of k against [BMIM]Br for Cis-[Co(dpq)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ at different temperatures; Cis-[Co(ip)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ =4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Fig. 4 Plot of k against [BMIM]Br for Cis-[Co(dpqc)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ at different temperatures; Cis-[Co(ip)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Fig. 5 Eyring plot for Cis-[Co(ip)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 6 Eyring plot for Cis-[Co(dpq)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 7 Eyring plot for Cis-[Co(dpqc)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 8 Eyring plot for Cis-[Co(ip)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 9 Eyring plot for Cis-[Co(dpq)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 10 Eyring plot for Cis-[Co(dpqc)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 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(ip)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 12 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpq)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in DPPC medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 13 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpqc)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in aqueous solutions. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 14 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(ip)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 15 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpq)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Fig. 16 Isokinetic plot of the activation parameters for the reduction of Cis-[Co(dpqc)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ by ion(II) in [BMIM]Br medium. [Complex] = 4 x 10^{-4} mol dm^{-3}; [iron(II)] = 0.01 mol dm^{-3}; [μ] = 1.0 mol dm^{-3}.

SI Table Captions

SI Table 1. Second-order rate constants for the reduction of cobalt(III) complex ion by iron(II) in DPPC under different temperatures. Cis-[Co(dpq)$_2$(C$_{12}$H$_{25}$NH$_2$)$_2$](ClO$_4$)$_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Table 2. Second-order rate constants for the reduction of cobalt(III) complex ion by iron(II) in DPPC under different temperatures. Cis-$[Co(dpqc)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, $[Fe^{2+}]$ = 0.01 mol dm^{-3}

SI Table 3. Second-order rate constants for the reduction of cobalt(III) complex ion by iron(II) in the presence of [BMIM]Br medium under different temperatures. Cis-$[Co(dpq)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Table 4. Second-order rate constants for the reduction of cobalt(III) complex ion by iron(II) in the presence of [BMIM]Br medium under different temperatures. Cis-$[Co(dpqc)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$ = 4 x 10^{-4} mol dm^{-3}, μ = 1.0 mol dm^{-3}, [iron(II)] = 0.01 mol dm^{-3}

SI Table 5. Activation parameters for the reduction of Cis-$[Co(dpq)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, μ = 1.0 $moldm^{-3}$ in DPPC medium

SI Table 6. Activation parameters for the reduction of Cis-$[Co(dpqc_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, μ = 1.0 $moldm^{-3}$ in DPPC medium

SI Table 7. Activation parameters for the reduction of Cis-$[Co(dpq)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, μ = 1.0 $moldm^{-3}$ in [BMIM]Br medium medium

SI Table 8. Activation parameters for the reduction of Cis-$[Co(dpqc)_2(C_{12}H_{25}NH_2)_2](ClO_4)_3$, μ = 1.0 $moldm^{-3}$ in [BMIM]Br medium

Schemes

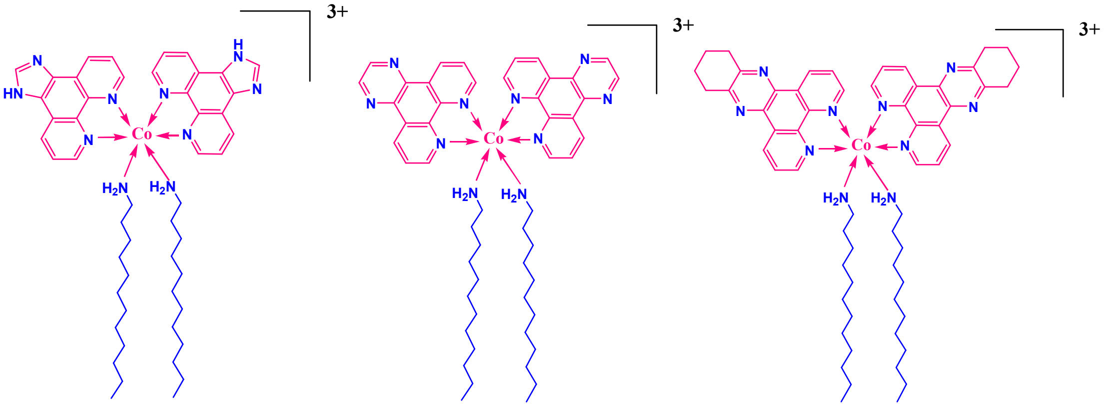
$$[Co(LL)_2(A)_2]^{3+} + Fe^{2+} \xrightleftharpoons{k_{IP}} \{[Co(LL)_2(A)_2]^{3+} ; Fe^{2+}\}$$

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

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

LL = ip, dpq and dpqc ; A = Dodecylamine

Scheme 1



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

Scheme 2

Figures

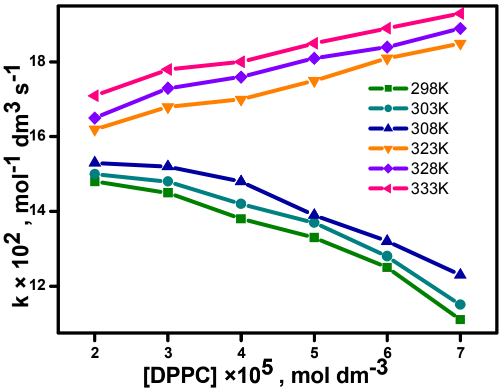


Fig. 1

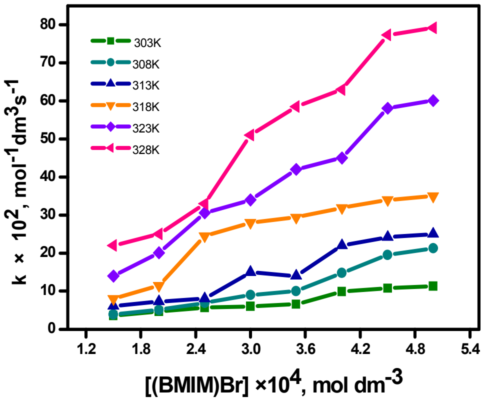


Fig. 2

Tables

Table 1

[DPPC] × 10^5 (mol dm^{-3})	k ×10^2, dm^3 mol^{-1} s^{-1}					
	298K	303K	308K	323K	328K	333K
2.0	14.8	15.0	15.3	16.2	16.5	17.1
3.0	14.5	14.8	15.2	16.8	17.3	17.8
4.0	13.8	14.2	14.8	17.0	17.6	18.0
5.0	13.3	13.7	13.9	17.5	18.1	18.5
6.0	12.5	12.8	13.2	18.1	18.4	18.9
7.0	11.1	11.5	12.3	18.5	18.9	19.3

Table 2

[(BMIM)Br] × 10^4, mol dm^{-3}	k ×10^2, dm^3 mol^{-1} s^{-1}					
	303K	308K	313K	318K	323K	328K
1.5	3.9	4.1	6.4	8.7	14.5	22.8
2.0	5.1	5.4	7.6	11.8	20.4	27.2
2.5	5.9	7.2	8.3	25.4	31.4	33.6
3.0	6.4	9.3	15.4	28.5	34.7	55.3
3.5	10.4	15.1	21.3	32.0	45.1	59.8
4.0	11.2	21.3	24.1	35.0	58.1	66.9
4.5	11.4	24.1	25.4	36.1	59.4	71.3
5.0	11.8	25.4	28.9	43.5	62.4	79.2

Table 3

[DPPC]×10^5	ΔH‡ $kJmol^{-1}$	ΔS‡ JK^{-1}

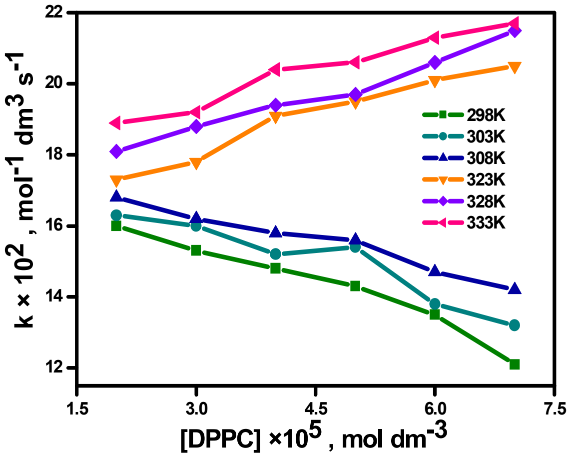
(mol dm^{-3})		
2.0	6.39	-64.2
3.0	6.54	-58.0
4.0	6.64	-49.9
5.0	6.57	-49.6
6.0	6.71	-34.9
7.0	6.78	-25.9
8.0	6.81	-7.6

Table 4

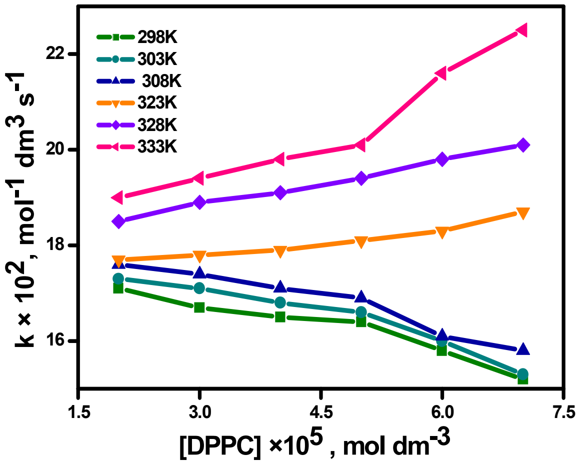
[(BMIM)Br] × 10^{3}, mol dm^{-3}	ΔH‡ kJmol^{-1}	ΔS‡ JK^{-1}
1.5	6.39	-64.2
2.0	6.54	-58.0
2.5	6.64	-49.9
3.0	6.57	-49.6
3.5	6.71	-34.9
4.0	6.78	-25.9
4.5	6.81	-7.6

Supplementary Informations

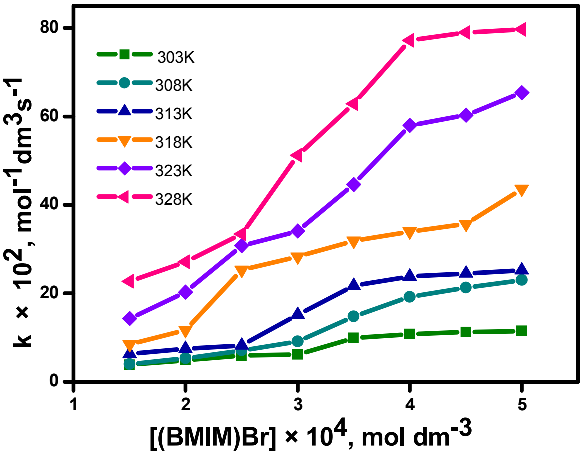
Figures



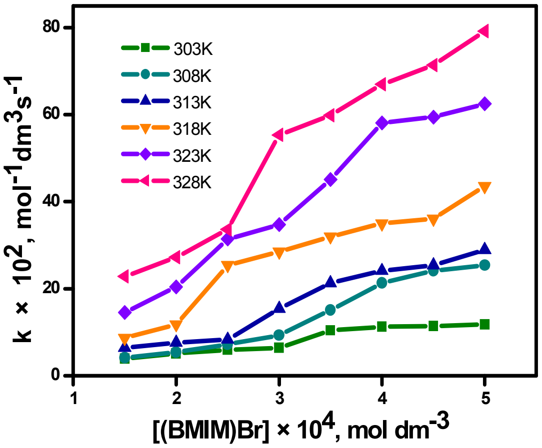
SI Fig. 1



SI Fig. 2



SI Fig. 3



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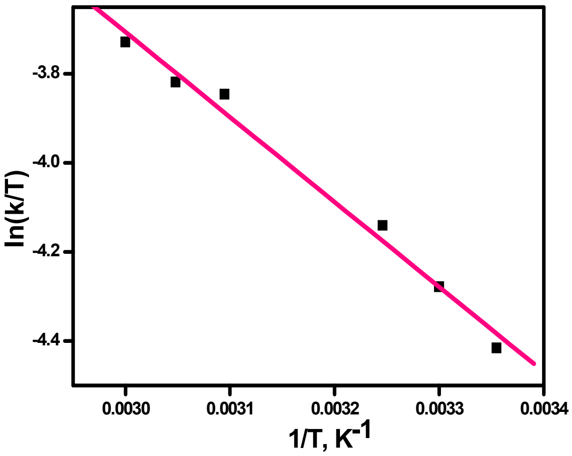

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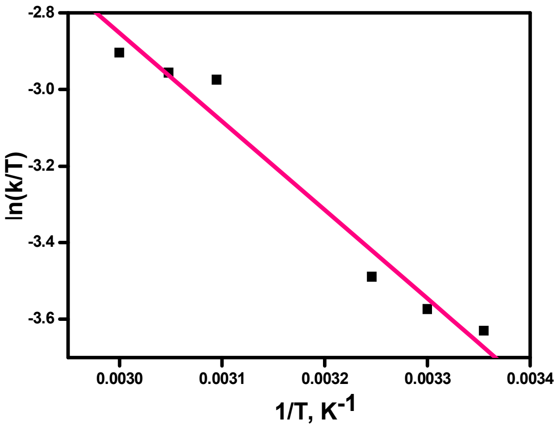

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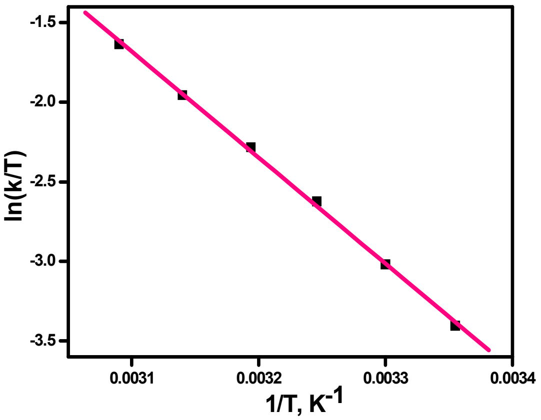

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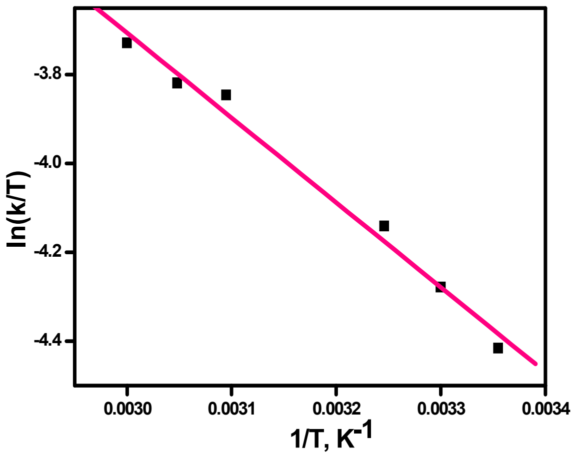
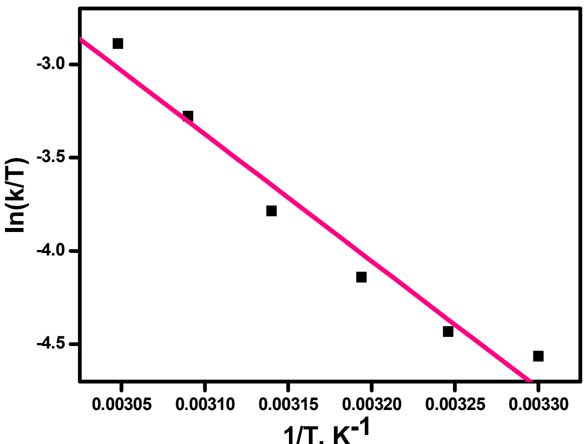


SI Fig. 8



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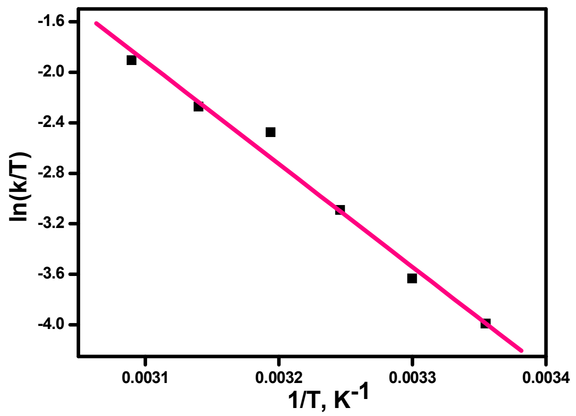

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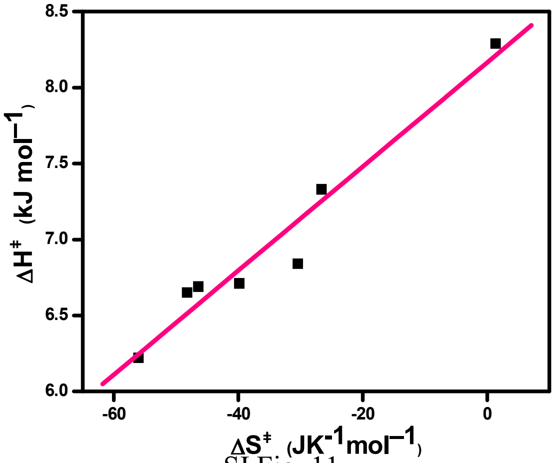

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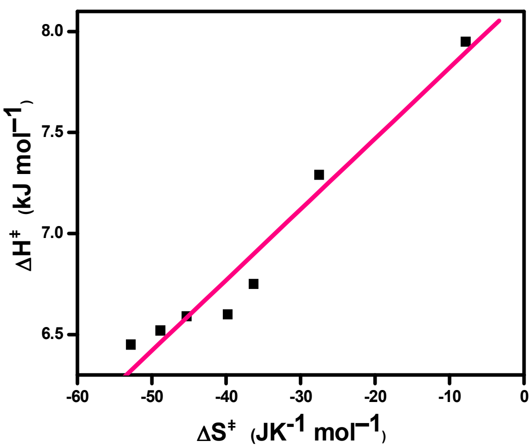
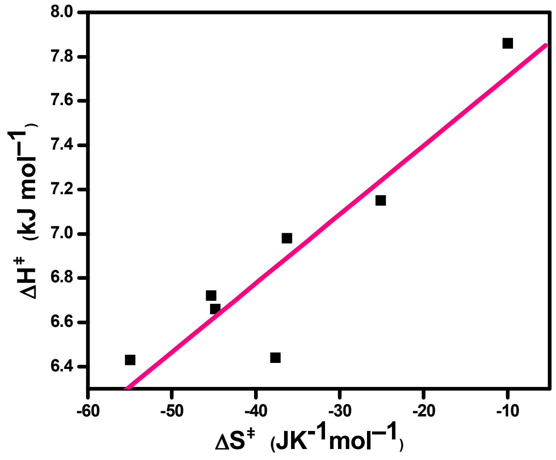


S Fig. 12



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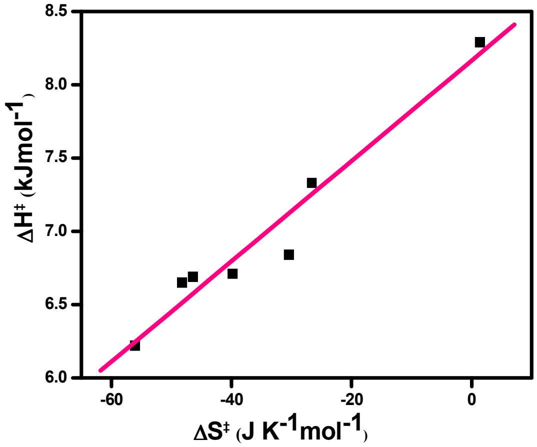

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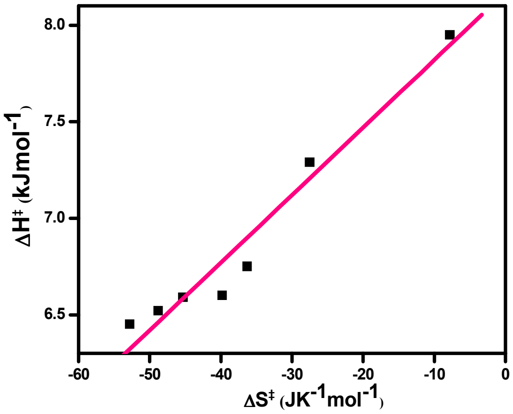

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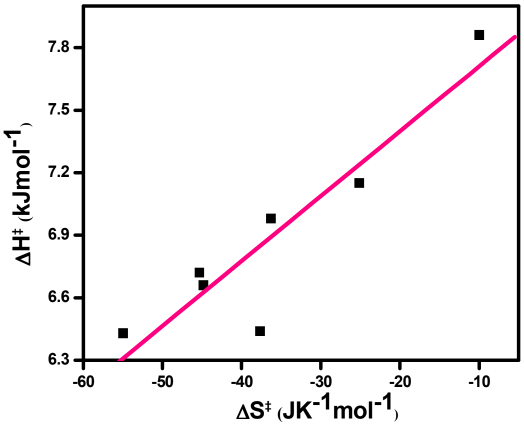

SI Fig. 16

Tables

SI Table 1

[DPPC] × 10^5 (mol dm^{-3})	k ×10^2, dm^3 mol^{-1} s^{-1}					
	298K	303K	308K	323K	328K	333K
2.0	16.0	16.3	16.8	17.3	18.1	18.9
3.0	15.3	16.0	16.2	17.8	18.8	19.2
4.0	14.8	15.2	15.8	19.1	19.4	20.4
5.0	14.3	15.4	15.6	19.5	19.7	20.6
6.0	13.5	13.8	14.7	20.1	20.6	21.3
7.0	12.1	13.2	14.2	20.5	21.5	21.7

SI Table 2

$[DPPC] \times 10^5$ (mol dm^{-3})	$k \times 10^2$, $dm^3\ mol^{-1}\ s^{-1}$					
	298K	303K	308K	323K	328K	333K
2.0	17.1	17.3	17.6	17.7	18.5	19.0
3.0	16.7	17.1	17.4	17.8	18.9	19.4
4.0	16.5	16.8	17.1	17.9	19.1	19.8
5.0	16.4	16.6	16.9	18.1	19.4	20.1
6.0	15.8	16.0	16.1	18.3	19.8	21.6
7.0	15.2	15.3	15.8	18.7	20.1	22.5

SI Table 3

$[(BMIM)Br] \times 10^4$, mol dm^{-3}	$k \times 10^2$, $dm^3\ mol^{-1}\ s^{-1}$					
	303K	308K	313K	318K	323K	328K
1.5	4.1	4.3	6.7	9.1	15.0	23.1
2.0	5.2	5.5	7.8	11.5	21.2	28.1
2.5	6.0	7.3	8.5	25.6	31.4	33.8
3.0	6.5	9.4	15.5	28.9	34.8	56.1
3.5	10.8	15.3	21.4	32.1	45.4	63.8
4.0	11.5	21.0	24.7	35.3	59.4	78.2
4.5	11.9	22.4	25.8	37.1	60.0	79.4

SI Table 4

[(BMIM)Br] × 10^4, mol dm^{-3}	k ×10^2, dm^3 mol^{-1} s^{-1}					
	303K	308K	313K	318K	323K	328K
1.5	4.2	4.4	6.8	9.2	15.1	23.2
2.0	5.3	5.6	7.9	17.6	23.0	29.1
2.5	6.3	7.4	8.1	25.7	31.6	33.9
3.0	6.6	9.8	15.7	28.9	34.9	56.6
3.5	10.9	15.4	21.6	32.7	45.8	64.1
4.0	11.6	21.1	25.2	35.8	60.1	71.6
4.5	12.1	22.6	27.9	38.4	64.5	80.1

SI Table 5

[DPPC]×10^5 (mol dm^{-3})	ΔH‡ $kJmol^{-1}$	ΔS‡ JK^{-1}
2.0	6.45	-52.8
3.0	6.52	-48.8
4.0	6.59	-45.3
5.0	6.60	-39.8
6.0	6.75	-36.3
7.0	7.29	-27.5
8.0	7.95	-7.8

SI Table 6

$[DPPC]\times10^5$ (mol dm^{-3})	$\Delta H^\ddagger$ $kJmol^{-1}$	$\Delta S^\ddagger$ JK^{-1}
2.0	6.43	-54.9
3.0	6.44	-37.6
4.0	6.66	-44.8
5.0	6.72	-45.3
6.0	6.98	-36.2
7.0	7.15	-25.1
8.0	7.86	-9.97

SI Table 7

$[(BMIM)Br] \times 10^3$, mol dm^{-3}	$\Delta H^\ddagger$ $kJmol^{-1}$	$\Delta S^\ddagger$ JK^{-1}
1.5	6.45	-52.8
2.0	6.52	-48.8
2.5	6.59	-45.3
3.0	6.60	-39.8
3.5	6.75	-36.3
4.0	7.29	-27.5
4.5	7.95	-7.8

SI Table 8

[(BMIM)Br] × 10^3, mol dm^{-3}	ΔH‡ $kJmol^{-1}$	ΔS‡ JK^{-1}
1.5	6.43	-54.9
2.0	6.44	-37.7
2.5	6.66	-44.8
3.0	6.72	-45.3
3.5	6.98	-36.3
4.0	7.15	-25.1
4.5	7.86	-9.9