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Micellar catalysis on the electron transfer reactions of iron(III)-polypyridyl complexes with organic sulfides—importance of hydrophobic interactions†‡

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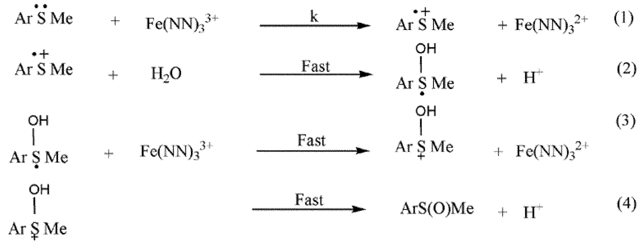
The oxidation of organic sulfides with iron(III)-polypyridyl complexes $[Fe(NN)_3]^{3+}$ proceeds through an electron transfer mechanism and an increase in the methanol content in the methanol–water mixture favors the reaction. The reaction is catalyzed by both the anionic surfactant, sodium dodecyl sulfate (SDS) and the cationic surfactant, cetyltrimethylammonium bromide (CTAB). The micellar catalysis in the presence of SDS is accounted for in terms of strong binding of the cationic oxidant with the anionic surfactant and the development of positive charge on sulfur center of substrate in the transition state. The micellar catalysis observed on the reaction involving a trication, $[Fe(NN)_3]^{3+}$, in the presence of CTAB indicates the importance of hydrophobic interaction between the micelle and hydrophobic ligand of $[Fe(NN)_3]^{3+}$. The micellar catalysis is explained in terms of a pseudophase ion exchange model.

Introduction

The chemical reactivities exhibited by molecules and ions organized around mesoscopic assemblies such as micelles are often very different from their reactivities in homogeneous solution.[1–4] The use of surfactants instead of organic solvents gains importance from a green chemistry point of view. Anionic micelles inhibit the reactions of nonionic organic substrates with anions by incorporating the substrate and (at least partially) excluding the anions.[1,2] On the contrary, cationic micelles incorporate both nonionic and anionic reagents and increase rates of anionic nucleophilic reactions. Though a broad range of organic reactions have been studied in micellar media, little attention has been paid so far to the use of organic sulfides as substrates except for the recent reports from the laboratories of Bunton[5–8] and Richardson.[9] Both the anionic and cationic surfactants inhibit the periodate (IO_4^-), peroxomonosulfate (HSO_5^-), and percarbonate (HCO_4^-) oxidation of dialkyl and aryl methyl sulfides, the inhibition being more pronounced in the presence of cationic surfactants.[5–9] The authors explained the enormous inhibition in the presence of cationic micelle with the postulation that the build-up of positive charge on the sulfur center of the substrate in the transition state leads to the electrostatic repulsion from the cationic surface of the micelle. If the charge development on the transition state has an enormous effect on the rate of the reaction then the reaction between a cationic oxidant and sulfide is expected to be favored by the negatively charged surface provided by the anionic surfactant. As far as we know, no attempt has been made so far to study the influence of micelles on the oxidation of organic sulfides with cationic oxidants. In recent reports we have established that Fe^{3+} and Ru^{3+} ions undergo efficient electron transfer reactions with organic sulfur compounds.[10–13] It is convenient to use these metal ions carrying the ligands phenanthroline and alkyl substituted 2,2′-bipyridine (NN) as the reactants, because both the electrostatic and hydrophobic interactions can be varied substantially using $M(NN)_3{}^{3+}$ complexes.[14,15] By changing the structure of the ligands in $[Ru(NN)_3]^{2+}$ (NN = 4,4′-dialkyl substituted 2,2′-bipyridine or phenyl substituted 1,10-phenanthroline) as well as the quenchers, we have proved that the photoinduced electron transfer reactions of Ru(II)-polypyridyl complexes with phenolate ions are highly influenced by the hydrophobic interactions of the reactants with the anionic and cationic surfactants.[16,17]

Based on the kinetic and spectral studies of the redox reaction between iron(III)-polypyridyl complexes, $[Fe(NN)_3]^{3+}$ and organic sulfides we have proposed a mechanism involving an electron transfer (ET) from sulfide to $[Fe(NN)_3]^{3+}$ (Scheme 1). Several reductants, particularly sulfur compounds, present in the biological system undergo an electron transfer reaction with Fe(III). Electron transfer within a protein matrix is critical to the function of a wide range of biological processes. The work carried out in a homogeneous aqueous system is far from being a realistic representation of the complexity of the heterogeneous



Scheme 1 ET from organic sulfides to $[Fe(NN)_3]^{3+}$ complex in the absence of micelles.

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‡ Abbreviations used: MPS: methyl phenyl sulfide; MPMS: *p*-methylphenyl methyl sulfide; CPMS: p-chlorophenyl methyl sulfide; EPS: ethyl phenyl sulfide; IPPS: isopropyl phenyl sulfide; DES: diethyl sulfide; DIPS: diisopropyl sulfide; DBS: dibutyl sulfide; DTBS: di-*tert*-butyl sulfide.

nature inherent to biological systems. In order to understand the efficiency of the redox reaction between Fe(III) and the thioether moiety present in biochemical systems it is useful to study the reaction in model systems. In the biological process, both electrostatic and hydrophobic interactions influence the reactivity and micelles are very good model systems to understand the role of these interactions in the biologically important process.[18–20] Now we have investigated the effect of anionic and cationic surfactants on the ET reaction between $[Fe(NN)_3]^{3+}$ and organic sulfides by spectrophotometric techniques to get an idea of the role of electrostatic and hydrophobic interactions in biological systems. Interestingly both the surfactants catalyze the ET reaction and the observed results are analyzed in terms of pseudo phase ion exchange model of micelles and presented in this report.

Results and discussion

The structure of the ligands and the abbreviations of the iron(III) complexes used in the present study are shown in Chart 1.

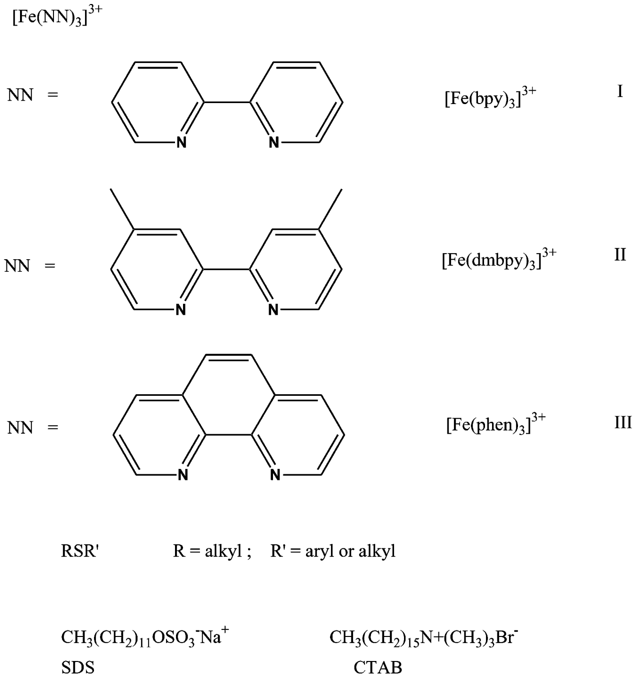


Chart 1 Structure of ligands of $[Fe(NN)_3]^{3+}$, organic sulfides and surfactants.

Kinetics of the reaction in the absence of surfactants

The reaction of $[Fe(NN)_3]^{3+}$ with aryl methyl, alkyl phenyl and dialkyl sulfides follows simple second order kinetics—first order each in the iron(III) complex and the sulfide. Based on the substituent and solvent effects on these redox reactions, and from the successful application of the Marcus theory of electron transfer to this reaction, a mechanism (Scheme 1) involving ET from sulfide to $[Fe(NN)_3]^{3+}$ in the rate determining step has been postulated.[10] This mechanism is very similar to the one proposed for the electrochemical and cytochrome P-450 oxidation of organic sulfides.[21,22]

Table 1 Effects of changing the solvent composition of the $[Fe(NN)_3]^{3+}$ oxidation of MPS and DES at 298 K

	MPS $k_1 \times 10^3/s^{-1}$		DES $k_1 \times 10^3/s^{-1}$	
CH_3OH (%)	$[Fe(bpy)_3]^{3+a}$	$[Fe(phen)_3]^{3+b}$	$[Fe(bpy)_3]^{3+a}$	$[Fe(phen)_3]^{3+b}$
10	—	—	2.96 ± 0.35	2.82 ± 0.12
20	1.61 ± 0.09	1.34 ± 0.08	3.46 ± 0.36	6.23 ± 0.23
30	2.19 ± 0.21	2.25 ± 0.12	4.40 ± 0.69	8.14 ± 0.34
40	2.06 ± 0.17	2.81 ± 0.18	5.01 ± 0.57	8.95 ± 0.42
50	2.21 ± 0.09	5.38 ± 0.38	5.73 ± 0.43	10.1 ± 1.12
60	4.18 ± 0.32	7.57 ± 1.12	5.80 ± 0.67	10.5 ± 1.26
70	6.10 ± 0.66	8.64 ± 1.04	5.82 ± 0.70	10.0 ± 0.97
80	—	—	5.85 ± 0.71	10.1 ± 1.20

[a] For $[Fe(bpy)_3]^{3+} = 1 \times 10^{-4}$ M; [MPS] = [DES] = 1.5×10^{-3} M. [b] For $[Fe(phen)_3]^{3+} = 5 \times 10^{-5}$ M;[MPS] = [DES] = 7.5×10^{-4} M.

The rate of ET from sulfide to $[Fe(NN)_3]^{3+}$ is favored with an increase in the methanol content of the medium and k_1 values at different solvent compositions (H_2O–CH_3OH) are given in Table 1. Thus, the reaction is facilitated with a decrease in the polarity of the medium. However, it should be mentioned that in the case of oxidation of DES by $[Fe(bpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ the k_1 value attains saturation at 50% CH_3OH and further increase in the CH_3OH content of the medium has no effect on the rate of the reaction.

Kinetics of the reaction in the presence of surfactants

Because of the low solubility of sulfides in aqueous media, all the reactions in the presence of anionic and cationic surfactants have been carried out in 1% CH_3OH–99% H_2O (*v*/*v*). For comparison the reaction in the micellar free medium has also been studied in a similar solvent system. Bunton and co-workers have also used similar solvent system (1% CH_3CN–99% H_2O (*v*/*v*)) to study the micellar effect on the IO_4^-, and HSO_5^- oxidation of organic sulfides. As the stability of iron(III) complexes used in the present study is more at higher acid concentration, all reactions have been carried out using either 0.5 M $HClO_4$(SDS) or 0.64 M H_2SO_4(CTAB). We have used H_2SO_4 to maintain $[H^+]$ in the presence of CTAB because addition of $HClO_4$ creates solubility problem in the presence of CTAB.

Effect of SDS on the $[Fe(NN)_3]^{3+}$ oxidation of organic sulfides

In the presence of SDS also the reaction is of total second order, first order each in $[Fe(NN)_3]^{3+}$ and sulfide (Fig. 1). The change of rate constant with the change of [SDS] at constant ionic strength for different sulfides is shown in Fig. 2 and in the ESI (Fig. S1 and S2). These results show that the reaction is catalyzed by the anionic surfactant. The k_1 value increases with the increase in [surfactant], but further increase in [surfactant] leads to saturation. These are expected results as one of the reactants is a cation and the other is a neutral molecule and hence both the reactants bind to the anionic surfactant by columbic and hydrophobic interactions, respectively. Further this reaction proceeds through an electron transfer mechanism and a positive charge develops on the S center in the transition state. It is well known that the neighboring carboxylate anion present in the organic sulfides stabilizes the sulfide cation radical in the ET reactions of organic sulfides thereby favoring the reaction.[23] Thus, in the presence of

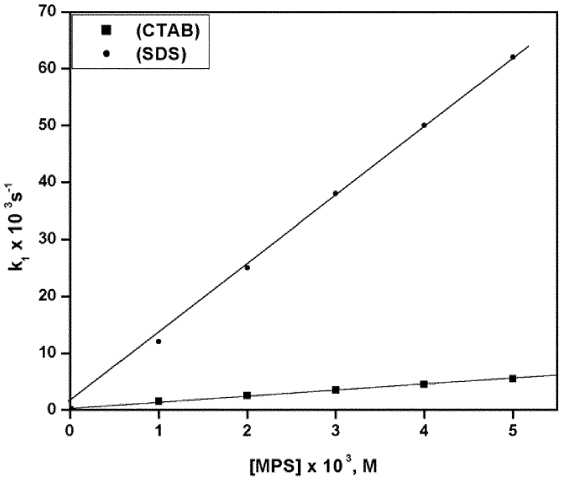


Fig. 1 Plot of k_1 *versus* [sulfide] in the presence of surfactants [● = SDS, ■ = CTAB].

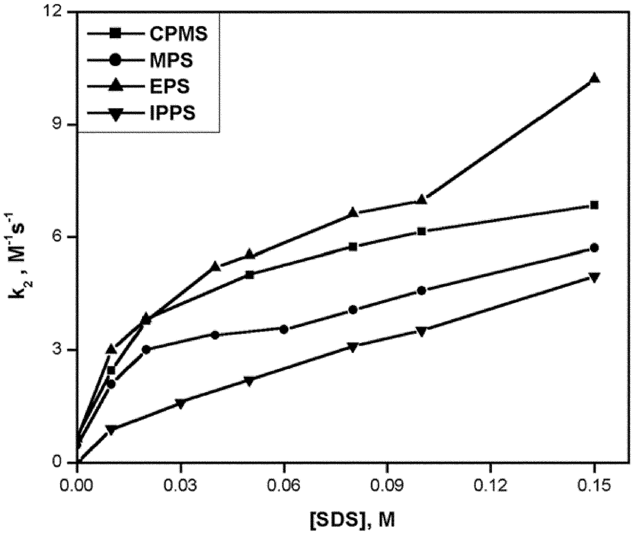


Fig. 2 Variation of rate constant with [SDS] for the reaction of $[Fe(bpy)_3]^{3+}$ with aryl sulfides.

SDS the sulfate head group can stabilize the positive charge on S in the transition state. All these favorable aspects will account for the micellar catalysis observed here in the presence of SDS. But these results observed in the presence of SDS are in striking contrast to those observed in the IO_4^-, HSO_5^- and HCO_4^- oxidation of organic sulfides wherein micellar inhibition is noticed.[5–7,9] On the other hand micellar catalysis has been observed by us on the Cr(VI) oxidation of dialkyl sulfides in the presence of SDS and the reaction proceeds through ET mechanism.[24]

Bunton and co-workers,[5–8] from the measurement of binding constants by spectral techniques, have established that organic sulfides bind efficiently with anionic as well as cationic surfactants and the binding constants are in the range of 80–340 M^{-1}. The spectral study carried out in our laboratory also provides similar values for the binding constants of the substrates with the anionic and cationic micelles. $[Fe(NN)_3]^{3+}$, the cationic reactant, will associate strongly with the anionic surfactant and the binding constants may be high. Since the reaction has been carried out in the presence of 0.5 M H^+, there will be competition between H^+ and $[Fe(NN)_3]^{3+}$ for binding with SDS. Since the concentration of H^+ is very high compared to $[Fe(NN)_3]^{3+}$, the binding constant of $[Fe(NN)_3]^{3+}$ with SDS will be less comparable to the value in the absence of H^+. When SDS is added to $[Fe(NN)_3]^{3+}$ a shift in the λ_{max} to the tune of 10 nm is observed and a substantial increase in the absorbance with the increase in [SDS] is noticed (Fig. 3). These absorbance changes with [SDS] have been used to estimate the binding constant of $[Fe(NN)_3]^{3+}$ with SDS and the K_{Fe} values for $[Fe(bpy)_3]^{3+}$, $[Fe(dmbpy)_3]^{3+}$ and $[Fe(phen)_3]^{3+}$ are 400, 450 and 1000 M^{-1} respectively (details are given in the ESI).

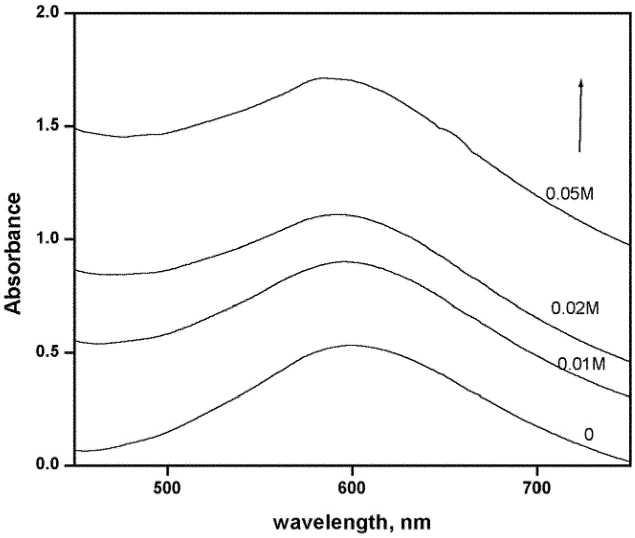
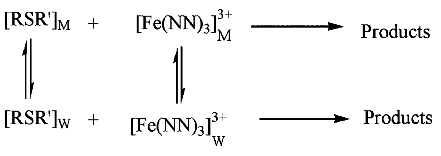


Fig. 3 The change of absorbance of $[Fe(phen)_3]^{3+}$ with [SDS].

With the reasonable assumption that $[Fe(NN)_3]^{3+}$ ion is associated with the anionic micelle and that the substrate distributes between the aqueous and micellar phases and the reaction occurs in the aqueous as well as in the micellar pseudo phases, the ET reaction in the presence of SDS can be explained by Scheme 2. The subscripts M and W stand for micellar and aqueous phases, respectively. According to Scheme 2, the Berezin expression for a second order rate constant for the micellar effect on the reaction between $[Fe(NN)_3]^{3+}$ and RSR′ can be given in the form of eqn (1).[25]

$$k = k_m\, P_s P_{Fe} C_m V + k_W\,(1 - C_m V)/ \\ [1+ (P_s - 1)C_m V]\,[1 + ((P_{Fe} - 1)\, C_m V] \quad (1)$$

In eqn (1), P_s and P_{Fe} represent the partition coefficients between micelles and water for RSR′ and $[Fe(NN)_3]^{3+}$, respectively, k_m and k_w are the rate constants in the micellar and aqueous phases, respectively, V is the partial molar volume of the micelles and C_m is the concentration of the micellized surfactant (C_m = ([surfactant] − cmc)/N) where N is the aggregation number. The volume fraction of the micelle, $C_m V$ is small at all [surfactant] under the



Scheme 2 ET from organic sulfides to $[Fe(NN)_3]^{3+}$ complex in the presence of micelle.

present experimental conditions. The partition coefficients of both reactants P_s and P_{Fe} are also much larger than unity because of large binding constants of RSR′ and $[Fe(NN)_3]^{3+}$. Hence eqn (1) can be simplified in to eqn (2).

$$k = k_m\, K_s\, K_{Fe}\, C_m + k_w\,(1 + K_S\, C_m)(1 + K_{Fe}\, C_m) \qquad (2)$$

where K_s and K_{Fe} are binding constants of sulfides and $[Fe(NN)_3]^{3+}$, respectively. The binding constants and the rate constants in the micelle (k_m) are defined by eqn (3–5).

$$K_s = V(P_s - 1) \qquad (3)$$

$$K_{Fe} = V\,(P_{Fe} - 1) \qquad (4)$$

$$k_m = k_2^m / V \qquad (5)$$

Since in eqn (2) all terms are known except k_m and K_{Fe}, they can be calculated by the best fit method. The values of k_m calculated at different [SDS] are collected in Table 2. It is interesting to point out that the binding constant of $[Fe(phen)_3]^{3+}$ with SDS from the spectral technique is 700 M^{-1} (Fig. 3) which is in fair agreement with the value obtained from the kinetic data supporting our arguments for the observed micellar catalysis.

To compare the second order rate constants in water, k_w, with the second order rate constant in the micellar phase, the volume of micellar phase must be known. Second order rate constants in the micellar phase with same units, k_2^m, $M^{-1}s^{-1}$, are given by eqn (5), where V is the molar volume of the reactive region at the micellar surface and $V = 0.37$ M^{-1} on the basis of earlier reports.[5,6,26,27] To compare the rate constants in the micellar phase (k_2^m) with the corresponding values in aqueous phase (k_w), the values of the ratio (k_2^m/k_w) are collected in Table 2. The values of k_2^m for reactions in the micellar Stern layer are close to those in water for all $[Fe(NN)_3]^{3+}$. Thus we explain the observed results based on the conclusion that k_2^m is close to k_w. There are many examples of reactions for which second order rate constants in micelles are similar to those in water and this generalization can be used to predict overall rate enhancements.[28,29] In order to assess the success of Scheme 2 to the reaction, we applied eqn (2) to calculate the rate constant of the reaction at different [SDS]. The values estimated from eqn (2) and the experimentally observed values are shown in Fig. 4. The close agreement between the experimental and calculated values proves the success of the model to the titled reaction. Therefore, it can be concluded that the rate enhancement observed in micellar solution is entirely due to an increase of the reactant concentration in the micellar pseudo phase.[1,30,31]

Table 2 Second order rate constants (k_m) in the micellar pseudo phase (SDS) and k_2^m/k_w values for the $[Fe(NN)_3]^{3+}$ oxidation of ArSMe, C_6H_5SR and R_2S at 298 K

	$[Fe(bpy)_3]^{3+}$		$[Fe(dmbpy)_3]^{3+}$		$[Fe(phen)_3]^{3+}$	
Sulfide	k_m	k_2^m/k_w	k_m	k_2^m/k_w	k_m	k_2^m/k_w
C_6H_5SMe	0.70	0.37	0.12	0.40	1.15	0.48
p-MeC_6H_4SMe	14.6	0.64	0.48	0.17	5.80	0.17
p-ClC_6H_4SMe	0.65	0.50	0.24	0.85	1.25	0.90
C_6H_5SEt	0.90	0.52	0.16	0.47	1.25	0.61
C_6H_5SPr	0.28	0.54	0.15	0.96	0.33	0.49
DES	1.05	0.35	0.39	1.00	1055	0.26
DIPS	1.05	1.20	0.04	0.56	1.55	0.81
DBS	0.42	0.22	0.17	0.47	1.07	0.37
DTBS	0.12	0.50	0.03	0.58	0.14	0.24

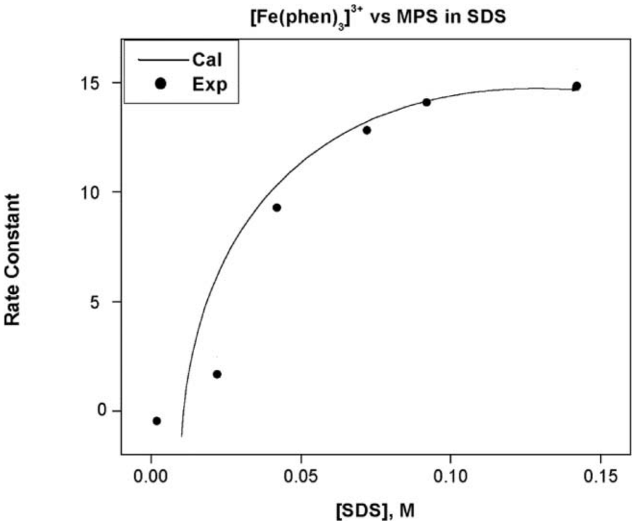


Fig. 4 Plot of calculated and experimentally observed rate constant values *versus* [SDS] for the reaction of $[Fe(phen)_3]^{3+}$ with MPS in the presence of SDS.

The data in Table 1 show that when the percentage of methanol is changed from 20 to 70 the pseudo first order rate constant increases from 1.6 to 6.1 × 10^{-3} s^{-1} with $[Fe(bpy)_3]^{3+}$ as the oxidant and the increase is from 1.4 to 8.6 × 10^{-3} s^{-1} in the case of $[Fe(phen)_3]^{3+}$ with MPS as the substrate (Table 1). This observation shows that polarity changes due to the introduction of surfactant is one of the reasons for the micellar catalysis. For the Stern layer, a polarity comparable to that of ethanol has been established.[32]

Though the observed micellar catalysis has been explained based on the Scheme 2 it is important to point out the following interesting observations:

(i) Among all aliphatic and aromatic sulfides used, DES shows enhanced catalysis. One of the explanations offered for the micellar catalysis is the stabilization of positive charge developed on the sulfur center in the transition state. With aromatic sulfides, resonance stabilization of positive charge on the sulfur center through conjugation with neighboring benzene ring is possible which is absent in dialkyl sulfides.[18] Thus, the stabilization of the positive charge on the sulfur center with the anionic head group of SDS may be more felt with dialkyl sulfides compared to aromatic sulfides. Among the dialkyl sulfides chosen for the present study, DES is less bulky. Thus the steric effect seems to play a role in the case of sulfides carrying isopropyl and *tert*-butyl groups. These two aspects favor the reaction of DES in SDS leading to enormous micellar catalysis. Interestingly, in the case of DES there is slight rate retardation at low [SDS]. (ii) The kinetic data given in the ESI (Fig. S1 and S2) show that, compared to $[Fe(bpy)_3]^{3+}$, the reaction of $[Fe(phen)_3]^{3+}$ with sulfides is favored in SDS. Though both complexes have a similar size, phen is more hydrophobic compared to bpy. Thus hydrophobicity favors more efficient binding of $[Fe(phen)_3]^{3+}$ with SDS compared to $[Fe(bpy)_3]^{3+}$ and the binding constants are 1000 and 400 M^{-1}, respectively. This is supported by the results observed on the solvent effect (*cf.* Table 1).

Reaction in the presence of the cationic surfactant, CTAB

The micellar catalysis for the reaction of a cationic reactant, $[Fe(NN)_3]^{3+}$, with organic sulfides in the presence of anionic surfactant is expected. When the same reaction is carried out in the presence of cationic surfactant, if the columbic interaction is the major factor, micellar inhibition is expected. Interestingly Blasko *et al.*[5,6] and Yao and Richardson[9] observed enormous micellar inhibition even for the reaction of anionic oxidant (IO_4^-, HSO_5^- and HCO_4^-) with organic sulfides in the presence of cationic surfactant. In order to check whether columbic repulsion (charge effect) is the major force that decides the effect of micellar system on the titled reaction we have studied the ET reaction of $[Fe(NN)_3]^{3+}$ with organic sulfides in the presence of CTAB. To our surprise micellar catalysis is observed in the presence of CTAB and the interesting results are presented in this section. The kinetic data obtained for the reaction of $[Fe(NN)_3]^{3+}$ with several sulfides in the presence of CTAB are shown in Fig. 5 and the ESI (Fig. S3 and S4). The kinetic data provided in Fig. 5, and ESI (Fig. S3 and S4) at various [CTAB] show that the ET reaction between $[Fe(NN)_3]^{3+}$ and organic sulfides is substantially catalyzed by cationic surfactant also. These results are surprising since one of the reactants carries triple positive charge and it is expected that the cationic reactant is expelled from the surface of the cationic micelle. Organic sulfides bind more efficiently with cationic micelles than anionic micelles.[5–7] The inference from this experimental observation is that some other interaction is operating between $[Fe(NN)_3]^{3+}$ and the cationic micelle which offsets the columbic repulsion between the reactant and the micelle. From a comparison of the catalytic behavior of cationic surfactants with that of anionic surfactants, a similarity in their roles can be realized. In both cases, the addition of surfactant catalyzes the ET reaction but further increase in [surfactant] leads to the maximum rate resulting in the saturation kinetics. The catalysis of the reaction between a cation and a neutral molecule by the cationic micelle indicates that here also the major part of the reaction takes place in the Stern layer. These results demonstrate the importance of hydrophobic interactions in the binding of charged metal complexes to micelles. In the positively charged CTAB micellar surface, the hydrophobic interactions of the ligands of $[Fe(NN)_3]^{3+}$ complexes with the micelles are apparently sufficient to overcome the columbic repulsion between $[Fe(NN)_3]^{3+}$ and the cationic micelle. Similar results have been observed earlier in the photochemical and electrochemical ET reactions of polypyridyl complexes Ru(II) and Co(II), respectively.[16,33] The observed micellar catalysis indicates that $[Fe(NN)_3]^{3+}$ binds with CTAB. To check this, we have recorded the absorption spectrum of $[Fe(phen)_3]^{3+}$ in the presence of different [CTAB] and the spectra are shown in the ESI (Fig. S5). The increase in absorbance of $[Fe(phen)_3]^{3+}$ with an increase in [CTAB] indicates binding of oxidant with CTAB and binding constant is 50 M^{-1} (see ESI for details).

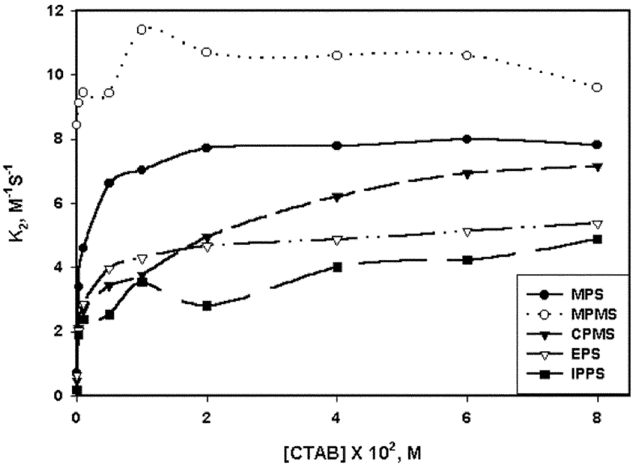


Fig. 5 The change of rate constant with [CTAB] on the rate constant for the reaction of $[Fe(bpy)_3]^{3+}$ with alkyl aryl sulfides.

The micellar catalysis observed in the presence of CTAB can be discussed in terms of Scheme 2. Thus the arguments presented for the redox reaction in the presence of SDS, can also be extended to the analysis of results observed in the presence of CTAB. Here again we applied eqn (2) to calculate the rate constant at different [CTAB] and the values are shown in Fig. 6 along with the experimentally observed values. The close agreement between the experimental and calculated values supports the arguments. The binding constants of $[Fe(NN)_3]^{3+}$ with CTAB calculated from the kinetic data are close to the values estimated from the spectral data and similar to the values reported by Pelizzetti *et al.*[32] for iron(III) complexes. The binding constant value indicates that a significant portion of the reaction takes place in the micellar phase. Thus the analysis of the kinetic data in terms of a pseudo phase model and the calculated binding constants satisfactorily account for the observed micellar catalysis of the reaction in the presence of CTAB.[34] The values of k_m and k_2^m are collected in Table 3. These data indicate that in the presence of CTAB also the rate constants in the micellar phase are similar to those in aqueous phase.

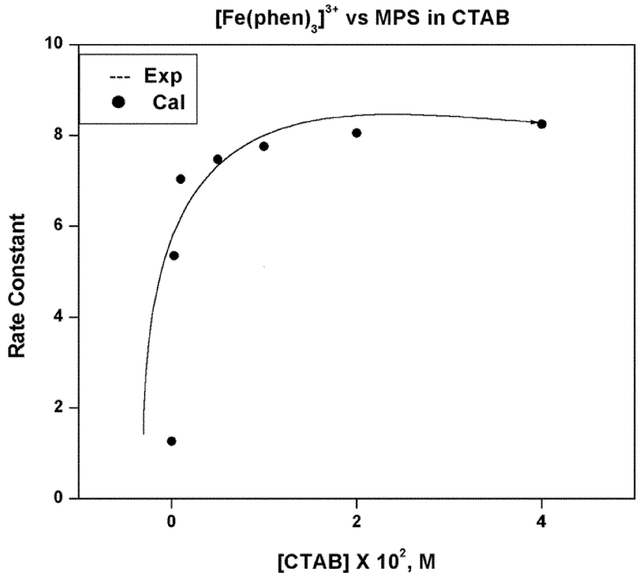


Fig. 6 Plot of calculated and experimentally observed rate constant values *versus* [CTAB] for the reaction of $[Fe(phen)_3]^{3+}$ with MPS in the presence of CTAB.

Comparison with $[Cr(V)(ehba)_2]^-$ and percarbonate ion (HCO_4^-) oxidation of organic sulfides

Recent results observed by us[35] and by Yao and Richardson[9] on the $[Cr(V)(ehba)_2]^-$ (ehba = 2-ethyl-2-hydroxy butyric acid) and percarbonate ion, HCO_4^-, oxidation of organic sulfides,

Table 3 Second order rate constants in the micellar pseudo phase (k_m) and ratio of rate constants (k_2^m/k_w) at 298 k in CTAB

	$[Fe(bpy)_3]^{3+}$		$[Fe(phen)_3]^{3+}$	
Sulfide	k_m	k_2^m/k_w	k_m	k_2^m/k_w
C_6H_5SMe	0.90	0.47	0.52	0.22
p-MeC_6H_4SMe	0.70	0.30	16.5	0.50
p-ClC_6H_4SMe	0.45	0.35	0.27	0.20
C_6H_5SEt	0.50	0.29	0.38	0.19
C_6H_5SPr	0.35	0.67	0.35	0.53
DES	0.75	0.26	1.20	0.20
DIPS	0.72	0.86	0.12	0.10
DBS	0.65	0.34	0.50	0.17
DTBS	0.18	0.74	0.18	0.31

respectively show that both reactions are inhibited by anionic micelles, but the reaction of $[Cr(V)(ehba)_2]^-$ with organic sulfides is catalyzed by cationic micelles of CTAB. On the other hand the oxidation of organic sulfides with HCO_4^- and other peroxo-oxidants IO_4^- and HSO_5^- are also enormously inhibited by cationic micelles. Thus the results observed in the present study seem to be novel as far as the oxidation of organic sulfides is concerned. It is interesting to recall that both reactants, Fe(III) and thioethers, are biologically important. As both reactants contain hydrophobic alkyl and aryl groups, one of the reasons for the micellar catalysis, particularly in the presence of cationic micelle, is the significant contribution of hydrophobic interaction. Comparison of the present results with the previous reports point out that under certain conditions, hydrophobic interaction will offset columbic repulsion and micellar catalysis will be observed even if the system involves two like charges.

Conclusion

The micellar enhancement observed for the reaction of a triply charged cation, $[Fe(NN)_3]^{3+}$, in the presence of cationic surfactant is novel and this study gives a clue on the importance of hydrophobic interaction on the ET reaction taking place within a protein matrix where Fe^{3+}/Fe^{2+} is involved as one of the redox couples. These results show that the micellar system is an excellent reaction medium and can be superior to organic co-solvents in the oxidation of organic sulfides by Fe(III). As the major product of the reaction is the organic sulfoxide, this method seems to be a good for the preparation of sulfoxides in aqueous system. Organic sulfoxides are interesting substrates and find extensive applications as starting materials for a variety of important organic molecules.

Experimental section

Materials

Tris(2,2′-bipyridine)iron(II), tris(4,4′-dimethyl-2,2′-bipyridine)-iron(II) and tris(1,10-phenanthroline)iron(II) were prepared by known procedures.[36] Iron(III) complexes were obtained by the oxidation of iron(II) complexes with PbO_2 in 1 M H_2SO_4. The iron(III) complexes were precipitated as perchlorate salts. Aryl methyl and alkyl phenyl sulfides were synthesized by published procedures and purity checked by spectral techniques.[37–39] All dialkyl sulfides used in the present study were obtained from Aldrich and used as such. The surfactants sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich and purified before use. All other reagents used were of AnalaR grade and the solvents (methanol and water) were purified by known procedures before use.[40]

Kinetic measurements

The iron(II)-polypyridyl complexes have molar extinction coefficients on the order of 1×10^4 M^{-1} cm^{-1} in the wavelength region 510–530 nm, $[Fe(bpy)_3]^{2+}$ (522 nm), $[Fe(phen)_3]^{2+}$ (510 nm) and $[Fe(dmbpy)_3]^{2+}$ (529 nm) while the corresponding Fe(III) complexes are practically transparent at this wavelength region.[41] The kinetics of $[Fe(NN)_3]^{3+}$ oxidation of organic sulfides were followed spectrophotometrically under pseudo first order conditions (a minimum of 15 fold excess of substrate over the oxidant) in the presence and absence of surfactants at 298 K by measuring the increase in absorbance of $[Fe(NN)_3]^{2+}$ with time.[41] A sample kinetic run is shown in Fig. 7. The absorption spectral studies were carried out on a JASCO model 7800 spectrophotometer. The plots of log ($A_\infty - A_t$) *versus* time were linear and the pseudo first order rate constant, k_1 values were calculated by least squares method and the details are given in our previous reports.[10,11] Duplicate kinetic runs showed that the rate constants were reproducible to within ±5%. Here, A_∞ is the final absorbance and A_t is the absorbance at time t. The second order rate constant, k_2, values were obtained from the equation, $k_2 = k_1/[\text{substrate}]$.

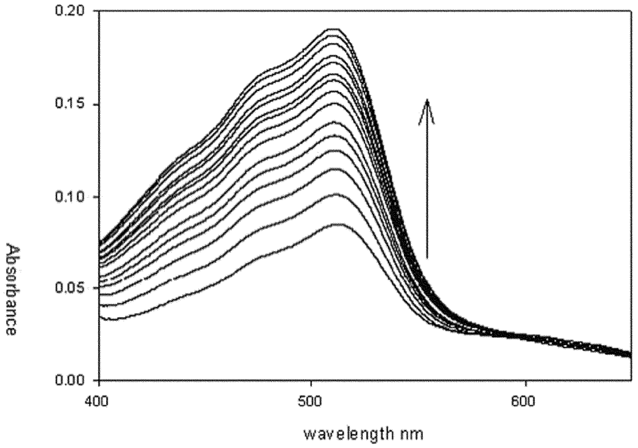


Fig. 7 Increase in the absorbance of $[Fe(phen)_3]^{2+}$ with time for the reaction of $Fe(phen)_3{}^{3+}$ with methyl phenyl sulfide.

Estimation of binding constants, *K*

The binding constants of $[Fe(NN)_3]^{3+}$ with SDS and CTAB micelles, K, were determined by spectrophotometric titration. The change in absorbance, A of the $[Fe(NN)_3]^{3+}$ with the incremental addition of surfactant was measured at the corresponding λ_{max} value (600 nm). The binding constants were then evaluated using the following eqn (6).[6]

$$(A_{obs} - A_w)/[D_n] = A_M K - A_{obs} K \tag{6}$$

where A_{obs} is the observed absorbance and subscripts W and M denote aqueous and micellar media. A sample spectrum with the increase in OD of $[Fe(phen)_3]^{3+}$ with the increase in [SDS] is shown in Fig. 3 and for CTAB the spectral changes are shown in the ESI (Fig. S5). The plot of $(A_{obs} - A_w)/[D_n]$ *versus* A_{obs} is linear and the slope gives the K value. A similar method was used by Bunton *et al.*[6] for the estimation of binding constants of organic sulfides.

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