



# A MECHANISTIC STUDY OF THE ELECTRON TRANSFER REACTIONS IN THE OXIDATION OF PHENYLSULFINYLACETIC ACIDS BY IRON(III) POLYPYRIDYL COMPLEXES IN THE SDS MICELLAR MEDIA

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## ABSTRACT

Electron transfer reactions in the oxidation of phenylsulfinylacetic acids (PSAAs) by iron(III) polypyridyl complexes in anionic surfactant sodium dodecyl sulphate (SDS) medium has been investigated spectrophotometrically. An initial intermediate formation between PSAA and  $[\text{Fe}(\text{NN})_3]^{3+}$  is confirmed from the observed Michaelis–Menten kinetics and fractional order dependence on PSAA. On applying the Hammett substituent constants to the overall rate constants obtained in SDS medium gives non-linear concave upward Hammett plots. A suitable mechanism involving the formation of Diphenyl sulphone as the product has been proposed. The observed increase in rate with increase in concentration of SDS at low concentrations clearly shows that the reaction takes place in micellar medium and both the reactants are associated or incorporated into micellar phase.

**Keywords:** Electron transfer reaction; Iron(III) polypyridyl complex; Phenylsulfinylacetic acid; Non-linear Hammett

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## 1. INTRODUCTION

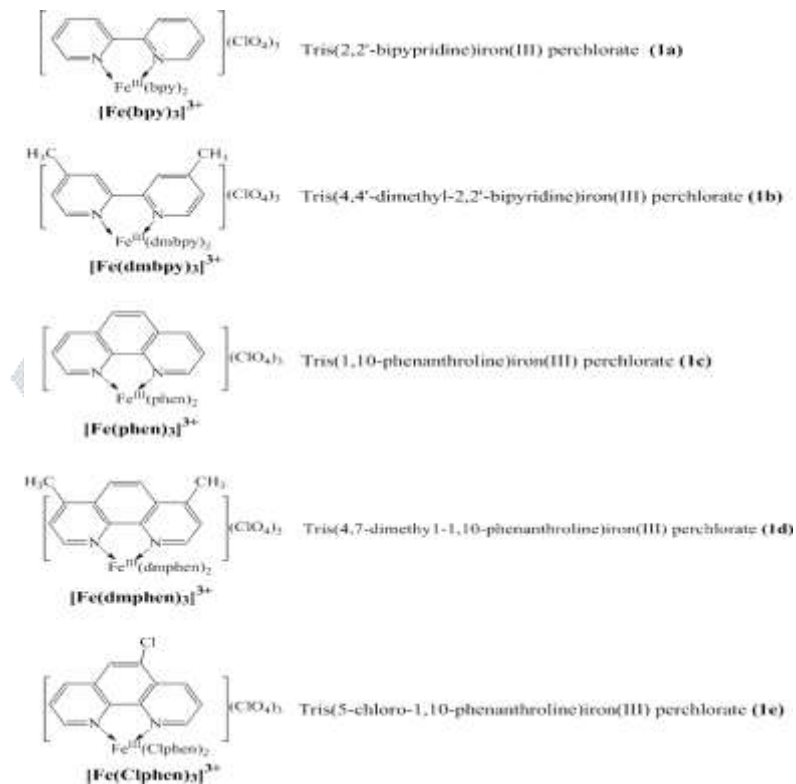
Electron transfer (ET) is a key process in redox reactions in (bio)chemistry (Migliore et al 2014) from photosynthesis to cellular respiration to electricity storage and conversion technologies (Hemmati et al 2016, Salimijazi et al 2019, Shapiguzov et al 2020 and Cao et al 2020). Surfactants are a various collection of chemicals that are directed to have properties of solubilization or cleaning. Surfactants combine the properties of hydrophilic and hydrophobic in one molecule (Najim et al 2022). Further, in recent years much attention has been devoted to the effect of organized structures like micelles and vesicles on the rate of ET reactions involving metal complexes. The interest in this subject arises due to their diverse applications in biological processes. Iron(III) polypyridyl complexes are versatile oxidizing agents and synthetic model owing to a variety of advantages like mild oxidant in nature, abstracting only one electron from the electron rich centre, forms a stable product and the reactions can be conveniently followed spectrophotometrically in the visible region. Realizing the importance of organic sulphur compounds as reductants and the vital role of Fe(III) in biological systems, an attempt was made to find the mechanism of the ET reaction between phenylsulfinylacetic acid and iron(III) polypyridyl complexes in presence of SDS.

## 2. EXPERIMENTAL

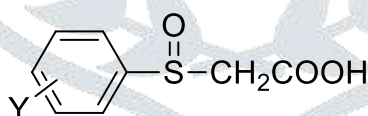
### 2.1 Synthesis of Fe(III) polypyridyl $[\text{Fe}(\text{NN})_3]^{3+}$ complexes and preparation of Phenylsulfinylacetic acids

The ligands 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 1,10-phenanthroline (phen), 4,7-dimethyl-1,10-phenanthroline (dmphen) and 5-chloro-1,10-phenanthroline (Clphen) were obtained from Sigma-Aldrich and used as such. Fe(III) polypyridyl complexes  $[\text{Fe}(\text{NN})_3]^{3+}$  were prepared by the oxidation of corresponding Fe(II) tris(pyridyl) complexes with lead dioxide in sulphuric acid medium (Adaikalasamy et al 2003). The preparation of  $[\text{Fe}(\text{NN})_3]^{3+}$  must be done in highly acidic medium in order to get better yield. Finally Fe(III) complexes were precipitated as perchlorate salts. The purity of the complexes was checked from their IR and absorption spectra. The tris(pyridyl) complexes of Fe(II) were obtained by known procedure (Balakumar et al 1995). The structure and the abbreviation of iron(III) polypyridyl complexes used in the present study are shown in Figure 1. Stock Solutions of Fe(III) complexes were made up in concentrated perchloric acid and were diluted with aqueous acetonitrile just before initiating the kinetic run. In order to avoid the decomposition of complexes, stock solutions were kept in refrigerator. PSAA, meta- and para-substituted PSAAs were prepared from the corresponding phenylthioacetic acid (PTAA) by the controlled oxidation with hydrogen peroxide

(Deepalakshmi et al 2014). PSAAs were purified by recrystallization from ethyl acetate–benzene mixture and their purities were checked by melting point and LC-MS. The recrystallized samples were stored in vacuum desiccator in order to avoid the decomposition with moist air. The structure of substituted phenylsulfinyl acetic acids used in this work is shown in Figure 2.



**Figure 1.** Structure of iron(III) polypyridyl complexes.



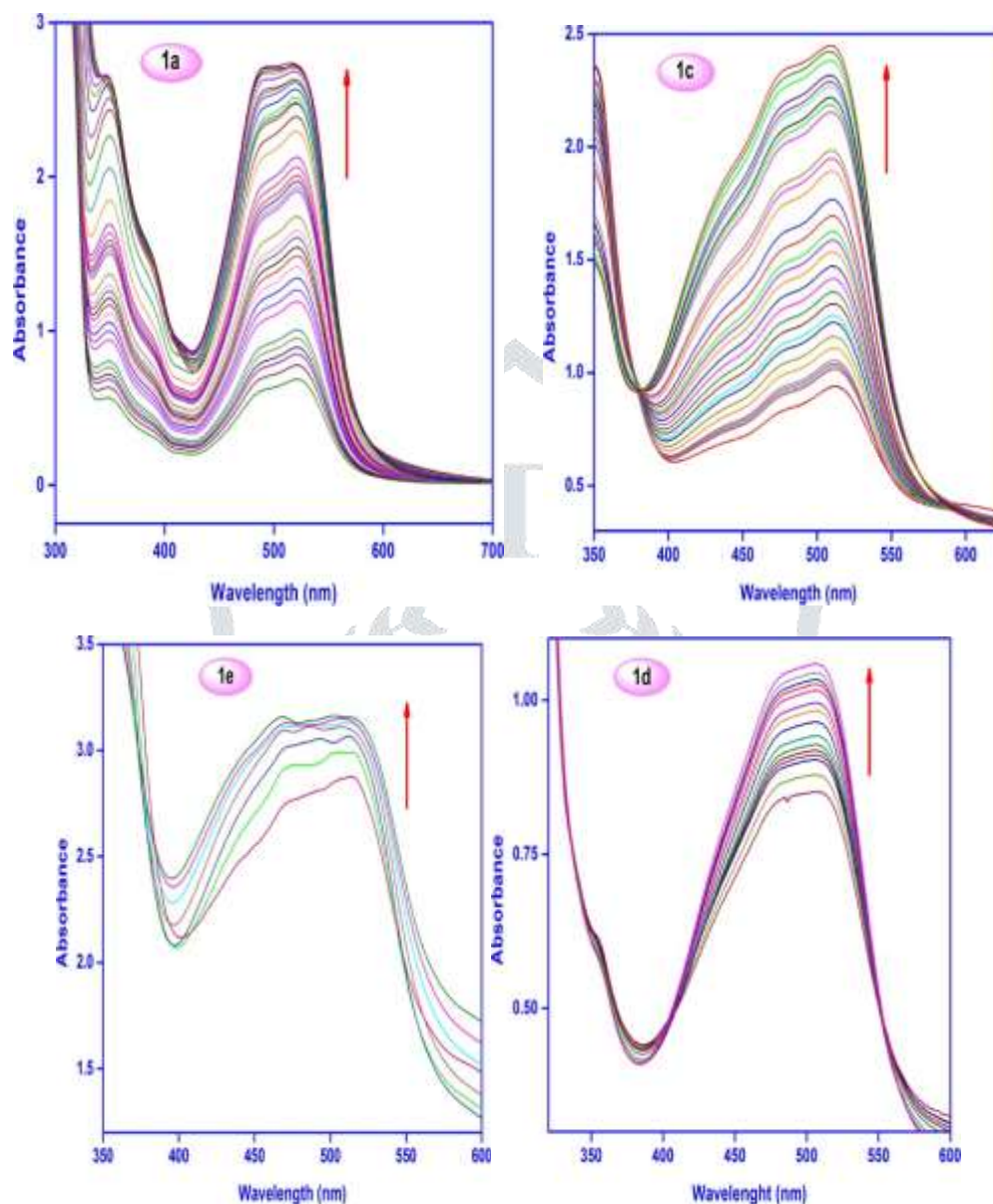
Where Y = *p*-F, *p*-Cl, *p*-Br, *m*-F, *m*-Cl, *m*-Br, H, *m*-Me, *p*-Et, *p*-Me, *p*-*t*.Bu, *p*-OEt, *p*-OMe

**Figure 2.** Structure of substituted phenylsulfinylacetic acids.

## 2.2. Kinetics in SDS micelles

The kinetics of electron transfer reaction between phenylsulfinylacetic acids and  $[\text{Fe}(\text{NN})_3]^{3+}$  was followed spectrophotometrically under pseudo-first-order conditions with PSAAs at least 10 fold in excess over the iron(III) polypyridyl complex in the presence of SDS at 303 K. As the iron(II) polypyridyl complexes have high molar extinction coefficient of the order of  $1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$  in the wavelength region 510–530 nm and the corresponding iron(III) polypyridyl complexes are practically transparent at this wavelength region (Ishikawa et al 1990, Rollick et al 1982 & Fukuzumi et al 1980), the reactions were followed by measuring the increase in the absorbance of  $[\text{Fe}(\text{NN})_3]^{2+}$  with time. As the reported CMC of SDS is  $8 \times 10^{-3} \text{ M}$  (Van Os et al 1993 & Frescura et al 1995), the reactions were carried out in the concentration range of  $0.8 \times 10^{-2} \text{ M}$  to  $15 \times 10^{-2} \text{ M}$ , i.e. above the CMC value. Due to low solubility problem of reactants in aqueous medium, all the reactions in the presence of SDS were carried out in 97%  $\text{H}_2\text{O}$ -3%  $\text{CH}_3\text{CN}$  (v/v) medium. Many researchers have also used similar solvent systems to study micellar effect on the oxidation of organic sulphides (Bosco Bharathy et al 2005 & Subramaniam et al 2015). Since iron(III) polypyridyl complexes are stable in high acid concentration and the reactions are very slow at low acid concentration, 0.5 - 1.5 M  $\text{HClO}_4$  was maintained during the kinetic study. The ionic strength was maintained in all the reactions using  $\text{NaClO}_4$ .

In SDS micellar medium a blue shift to the tune of 6 - 10 nm in the  $\lambda_{\text{max}}$  of Fe(II) and Fe(III) is observed for bipyridine complexes (**Ia** and **Ib**) while no shift is noted in phenanthroline complexes. Similar shift is already reported by Balakumar et al. (2006) in SDS medium. The shift in  $\lambda_{\text{max}}$  indicates strong binding of iron bipyridine complexes with SDS micelle. In SDS medium all the reactions were followed at the wavelength of 516nm for  $[\text{Fe}(\text{bpy})_3]^{2+}$ , 519nm for  $[\text{Fe}(\text{dmbpy})_3]^{2+}$ , 510nm for  $[\text{Fe}(\text{phen})_3]^{2+}$ , 512nm for  $[\text{Fe}(\text{dmphen})_3]^{2+}$  and 510nm for  $[\text{Fe}(\text{Clphen})_3]^{2+}$ . Representative kinetic plots between absorbance and wavelength at different time intervals are shown in Figure 3. The plot of  $\log(A_\infty - A_t)$  vs. time is linear and the pseudo-first order rate constant,  $k_1$  values were calculated by least square analysis.



**Figure 3.** Increase in absorbance of  $[\text{Fe}(\text{NN})_3]^{2+}$  at different time interval

### 2.3. Product analysis

The reaction mixtures containing PSAA and  $[\text{Fe}(\text{bpy})_3]^{3+}$  /  $[\text{Fe}(\text{phen})_3]^{3+}$  in 1:1 molar ratio under the experimental conditions were kept aside for two days. After the completion of the reaction, the organic solvent was removed under reduced pressure, extracted with chloroform and dried over anhydrous sodium sulfate. The product obtained after the removal of chloroform was identified as diphenyl disulfone which was characterized by FT-IR and GC-MS spectral studies.

The FT-IR spectrum of the product (Figure 4) shows strong characteristic bands at  $1143\text{ cm}^{-1}$  and  $1294\text{ cm}^{-1}$  confirming the existence of  $\text{SO}_2$  group in the product and the absorption bands are assigned to symmetric and asymmetric stretching vibrations of  $\text{SO}_2$  respectively. The absorption band at  $2924\text{ cm}^{-1}$  shows aromaticity,  $1570\text{ cm}^{-1}$  shows C=C stretching,  $737\text{ cm}^{-1}$ ,  $685\text{ cm}^{-1}$  and  $630\text{ cm}^{-1}$  show C-H bending vibrations of phenyl rings. GC-MS spectral analysis (Figure 5) was done using Thermo GC-Trace ultra ver: 5.0, Thermo MS DSQ II mass spectrometer using DB 35-MS capillary standard non-polar column of length 30 m and internal diameter of 0.25 mm. The sample was dissolved in benzene and  $1\text{ }\mu\text{L}$  of the solution was injected into the column. Helium gas was used as the carrier gas. The parent peak eluted at a retention time of 11.79 min at  $m/z = 282.3$  in GC-MS confirms the formation of diphenyl disulfone as the product. The other product was confirmed as  $[\text{Fe}(\text{NN})_3]^{2+}$  from the formation of new peak in the absorption spectra where the characteristic absorption increases with time during the course of the reaction.

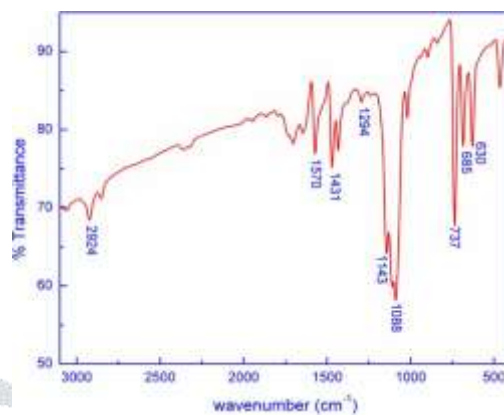


Figure 4. FT-IR spectrum of the product, diphenyl disulfone.

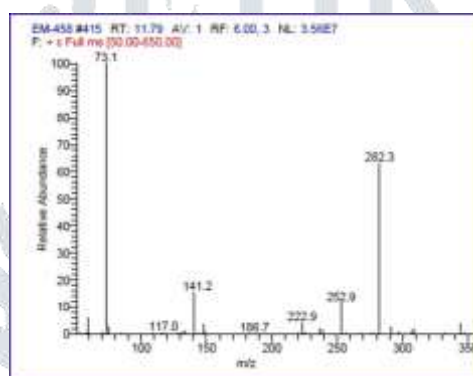


Figure 5. GC-MS spectrum of the product, diphenyl disulfone.

### 3. Results and discussion

#### 3.1 Effect of [PSAA], $[\text{Fe}(\text{NN})_3]^{3+}$ and $[\text{H}^+]$ on the reaction rate

The kinetics of electron transfer reactions in SDS medium was carried out at different initial concentrations of reactants, PSAA, **1a** and **1c** at fixed concentration of  $[\text{H}^+]$ , ionic strength and at constant temperature. The results clearly demonstrate the fractional order dependence on PSAA as observed in the absence of SDS (Subramaniam et al 2016) (Table-1). The order with respect to PSAA is determined from the slope value of  $\log k_1$  vs.  $\log [\text{PSAA}]$ . The non-integral, fractional slope values of 0.861 and 0.601 respectively for the complexes **1a** and **1c** support the fractional order dependence of PSAA. The operation of Michaelis-Menten kinetics is inferred from the linear double reciprocal plots of  $k_1$  vs.  $[\text{PSAA}]$  with finite intercept on the rate axis. This confirms the binding among the reactants to form an intermediate before the rate determining step in the reaction mechanism. The Michaelis-Menten constants ( $K_M$ ) were evaluated from the slope and intercept of these plots. The observed low  $K_M$  value of  $4.95 \times 10^{-2}$  for **1a** and  $1.16 \times 10^{-2}$  for **1c** ensure strong binding of PSAA with iron(III) polypyridyl complexes in SDS medium.

The linearity of the plots of  $\log (A_\infty - A_t)$  vs. time for the reactions at various concentrations of  $[\text{Fe}(\text{NN})_3]^{3+}$  suggest that electron transfer reaction is clear first order with respect to  $[\text{Fe}(\text{NN})_3]^{3+}$ . However, the pseudo-first-order rate constant is found to decrease appreciably with increase in  $[\text{Fe}(\text{NN})_3]^{3+}$  for both complexes (Table-1). Similar rate retardation is observed in the absence of SDS medium also. But in SDS medium, the observed retardation is less than in the absence of SDS. The possible explanations for the decrease in rate with increase in  $[\text{Fe}(\text{NN})_3]^{3+}$  would be coordination of a water molecule by nucleophilic attack at the carbon atom adjacent to the ring nitrogen of the metal polypyridyl complexes (Gillard, 1975) as proposed by Burchett and Meloan (1972) and Schmid and Han (1983) and the conversion of active complex into inactive oxo-bridged diiron complex as proposed by Hey (1982) at higher concentrations of  $[\text{Fe}(\text{NN})_3]^{3+}$  in a parallel reaction.

The overall rate constants recorded in Table 2 with **1a** and **1c** reveal that the rate constant increases with increase in  $[\text{H}^+]$ . The acid catalytic activity in the present case can be attributed by the formation of more reactive oxidizing species with  $\text{H}^+$ . As the effect of ionic strength show positive effect, ionic strength is maintained as constant in all the kinetic runs.

**Table 1.** Effect of [PSAA] and  $[\text{Fe}(\text{NN})_3]^{3+}$  on the rate of SDS mediated reactions.

PSAA](M)	$10^4$ [Fe(NN) <sub>3</sub> <sup>3+</sup> ](M)	$10^4$ k <sub>1</sub> (s <sup>-1</sup> )	$10^2$ k <sub>ov</sub> (M <sup>-1</sup> ) <sup>n</sup> (s <sup>-1</sup> )
<b>1a</b>			
3.0	4.0	6.89 ± 0.10	10.2 ± 0.15
5.0	4.0	11.0 ± 0.01	10.5 ± 0.01
10	4.0	19.6 ± 0.01	10.3 ± 0.01
20	4.0	34.7 ± 0.07	10.1 ± 0.02
30	4.0	50.9 ± 0.03	10.4 ± 0.01
10	2.0	23.5 ± 0.04	13.0 ± 0.02
10	8.0	14.6 ± 0.03	8.10 ± 0.02
<b>1c</b>			
3.0	4.0	7.03 ± 0.01	2.31 ± 0.01
5.0	4.0	10.2 ± 0.02	2.46 ± 0.01
10	4.0	15.6 ± 0.08	2.48 ± 0.01
20	4.0	22.3 ± 0.04	2.34 ± 0.01
30	4.0	28.7 ± 0.09	2.36 ± 0.01
10	2.0	18.7 ± 0.04	3.16 ± 0.01
10	8.0	10.2 ± 0.01	1.72 ± 0.01

$[\text{H}^+] = 0.5 \text{ M}$ ;  $\mu = 0.6 \text{ M}$ ;  $[\text{SDS}] = 5 \times 10^{-2} \text{ M}$ ; solvent = 97 % H<sub>2</sub>O-3 % CH<sub>3</sub>CN (v/v);  
n = order with respect to PSAA.

**Table 2.** Effect of  $[\text{H}^+]$  on the overall rate constant for the reaction of PSAA with **1a** and **1c** in SDS.

$[\text{H}^+]$ (M)	$10^2$ k <sub>ov</sub> (M <sup>-1</sup> ) <sup>n</sup> (s <sup>-1</sup> )	
	<b>1a</b>	<b>1c</b>
0.5	10.5 ± 0.06	2.48 ± 0.07
0.7	10.9 ± 0.04	3.03 ± 0.02
0.9	11.7 ± 0.08	3.71 ± 0.06
1.0	12.4 ± 0.01	4.85 ± 0.02
1.1	13.6 ± 0.01	6.42 ± 0.01
1.2	14.4 ± 0.01	8.14 ± 0.01

$[\text{PSAA}] = 1 \times 10^{-2} \text{ M}$ ;  $[\mathbf{1a}] = [\mathbf{1c}] = 4 \times 10^{-4} \text{ M}$ ;  $\mu = 1.2 \text{ M}$ ;  $[\text{SDS}] = 5 \times 10^{-2} \text{ M}$ ;  
solvent = 97 % H<sub>2</sub>O-3 % CH<sub>3</sub>CN (v/v); n = order with respect to PSAA.

### 3.2 Substituent effects and Thermodynamic parameters

The study of influence of substituents on the rate of a reaction often provides an insight into the nature of the transition state and mechanism. The effect of substituents on the reaction rate is studied with several *meta*- and *para*-substituted PSAAs at three different temperatures, viz. 293 K, 303 K and 313 K. The observed overall rate constants are given in Tables 3 and 4. From the study of substituent effect it is clear that both electron releasing groups (ERG) and electron withdrawing groups (EWG) accelerate the reaction rate. This indicates that both ERG and EWG facilitate the electron transfer from PSAA to  $[\text{Fe}(\text{NN})_3]^{3+}$ . As the reaction is

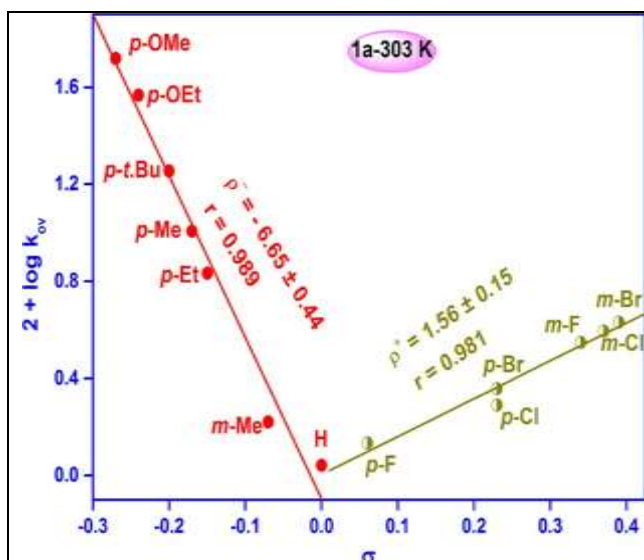
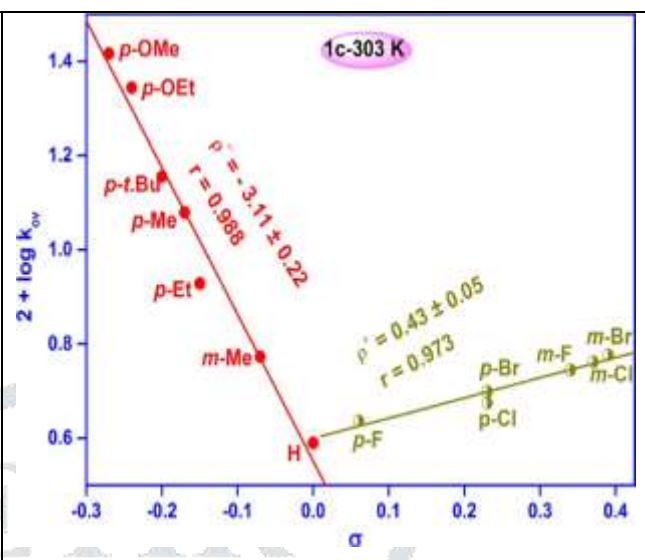
fractional order with respect to PSAA, overall rate constants can be used to evaluate the reaction constant,  $\rho$  from Hammett correlation.

On applying Hammett correlation between substituent constant  $\sigma$  and  $\log k_{ov}$  of *meta*- and *para*- substituted PSAAs, a non-linear Hammett plot similar to the one observed in the absence of SDS micelle was obtained (Subramaniam et al 2016). The non-linear Hammett plots exhibit concave-upward curves with ERG falling on one side of the curve having negative  $\rho$  value and the EWG on the other side, with positive  $\rho$  values. The Hammett plots of  $\log k_{ov}$  vs.  $\sigma$  for the complexes **1a** and **1c** are shown in Figures 6 and 7. The values of  $\rho^+$  and  $\rho^-$  obtained from Hammett plots for the complexes **1a** and **1c** are tabulated in Tables 3 and 4. The observed non-linear Hammett behaviour with upward curvature in the present series of reactions can be visualized to a change in the rate determining step on changing the substituents in PSAA from ERG to EWG.

**Table 3.** Overall rate constants and thermodynamic parameters for the oxidation of *para*- and *meta*-substituted PSAAs by **1a** in SDS medium.

No.	X	$10^2 k_{ov} (M^{-1})^n (s^{-1})$			$\Delta^\ddagger H$ kJ mol <sup>-1</sup>	$-\Delta^\ddagger S$ J K <sup>-1</sup> mol <sup>-1</sup>
		293 K	303 K	313 K		
1.	<i>p</i> -F	8.72 ± 0.08	13.6 ± 0.02	20.6 ± 0.02	30.2 ± 0.30	85.4 ± 1.04
2.	<i>p</i> -Cl	12.7 ± 0.02	19.5 ± 0.06	26.5 ± 0.06	25.6 ± 0.18	98.1 ± 0.62
3.	<i>p</i> -Br	14.9 ± 0.06	22.8 ± 0.02	29.8 ± 0.02	23.9 ± 0.14	102 ± 0.50
4.	<i>m</i> -F	17.1 ± 0.02	35.3 ± 0.06	42.3 ± 0.06	32.1 ± 0.11	72.8 ± 0.38
5.	<i>m</i> -Cl	21.0 ± 0.04	39.3 ± 0.08	46.3 ± 0.08	27.7 ± 0.14	85.9 ± 0.51
6.	<i>m</i> -Br	25.1 ± 0.06	42.8 ± 0.12	49.8 ± 0.11	23.7 ± 0.19	98.5 ± 0.66
7.	H	6.96 ± 0.08	10.5 ± 0.02	18.0 ± 0.02	33.7 ± 0.37	75.5 ± 1.29
8.	<i>m</i> -Me	9.32 ± 0.04	16.6 ± 0.04	23.6 ± 0.04	33.0 ± 0.21	75.3 ± 0.75
9.	<i>p</i> -Et	34.2 ± 0.02	68.1 ± 0.12	75.2 ± 0.04	27.7 ± 0.07	81.9 ± 0.26
10.	<i>p</i> -Me	58.4 ± 0.06	102 ± 0.08	109 ± 0.02	21.3 ± 0.05	99.5 ± 0.18
11.	<i>p</i> -t.Bu	90.6 ± 0.16	179 ± 0.16	187 ± 0.14	25.7 ± 0.09	80.5 ± 0.31
12.	<i>p</i> -OEt	191 ± 0.14	369 ± 0.37	376 ± 0.32	23.5 ± 0.07	81.8 ± 0.23
13.	<i>p</i> -OMe	270 ± 0.04	523 ± 0.09	530 ± 0.02	23.5 ± 0.01	78.9 ± 0.03
	$\rho^+$	1.28 ± 0.16	1.56 ± 0.15	1.20 ± 0.14		
	<b>r</b>	0.970	0.981	0.975		
	$\rho^-$	-6.34 ± 0.50	-6.65 ± 0.44	-5.82 ± 0.48		
	<b>r</b>	0.984	0.989	0.983		

[PSAA] =  $5 \times 10^{-3}$  M; [**1a**] =  $4 \times 10^{-4}$  M; [H<sup>+</sup>] = 0.5 M,  $\mu$  = 0.6 M, [SDS] =  $5 \times 10^{-2}$  M; solvent = 97 % H<sub>2</sub>O-3 % CH<sub>3</sub>CN (v/v); n = order with respect to PSAA.

Figure 6. Non-linear Hammett plot for **1a**.Figure 7. Non-linear Hammett plot for **1c**

**Table 4.** Overall rate constants and thermodynamic parameters for the oxidation of *para*- and *meta*-substituted PSAAs by **1c** in SDS medium.

No.X	$10^2 k_{ov} (M^{-1})^n (s^{-1})$			$\Delta^\ddagger H$ kJ mol <sup>-1</sup>	$-\Delta^\ddagger S$ J K <sup>-1</sup> mol <sup>-1</sup>
	293 K	303 K	313 K		
1.p-F	3.13 ± 0.14	4.33 ± 0.03	6.93 ± 0.02	27.7 ± 1.39	83.6 ± 4.88
2.p-Cl	3.53 ± 0.08	4.73 ± 0.11	7.16 ± 0.06	24.4 ± 1.38	93.8 ± 4.86
3.p-Br	3.79 ± 0.12	4.99 ± 0.12	7.59 ± 0.02	23.8 ± 1.48	95.3 ± 5.22
4.m-F	4.36 ± 0.22	5.56 ± 0.05	8.15 ± 0.03	21.3 ± 1.60	103 ± 5.65
5.m-Cl	4.58 ± 0.06	5.78 ± 0.07	8.38 ± 0.08	20.5 ± 0.88	105 ± 3.11
6.m-Br	4.78 ± 0.04	5.98 ± 0.05	8.68 ± 0.01	20.2 ± 0.45	106 ± 1.60
7.H	2.69 ± 0.02	3.16 ± 0.06	5.91 ± 0.02	27.5 ± 0.67	85.5 ± 2.35
8.m-Me	4.73 ± 0.04	5.93 ± 0.06	8.53 ± 0.04	19.9 ± 0.59	107 ± 2.08
9.p-Et	5.87 ± 0.06	8.48 ± 0.12	14.1 ± 0.04	30.8 ± 0.69	67.8 ± 2.44
10.p-Me	8.84 ± 0.02	12.0 ± 0.08	17.9 ± 0.02	24.4 ± 0.26	86.4 ± 0.90
11.p-t.Bu	11.2 ± 0.16	14.3 ± 0.06	21.2 ± 0.14	21.8 ± 0.64	93.4 ± 2.25
12.p-OEt	14.9 ± 0.18	22.1 ± 0.02	27.3 ± 0.12	20.7 ± 0.44	94.3 ± 1.56
13.p-OMe	18.5 ± 0.06	26.1 ± 0.09	32.0 ± 0.02	18.4 ± 0.98	100 ± 3.45
$\rho^+$	0.56 ± 0.06	0.43 ± 0.05	0.297 ± 0.05		
<b>r</b>	0.974	0.973	0.941		
$\rho^-$	-3.07 ± 0.24	-3.11 ± 0.22	-2.80 ± 0.09		
<b>r</b>	0.986	0.988	0.998		

[PSAA] =  $5 \times 10^{-3}$  M; [**1c**] =  $4 \times 10^{-4}$  M; [H<sup>+</sup>] = 0.5 M,  $\mu$  = 0.6 M, [SDS] =  $5 \times 10^{-2}$  M; solvent = 97 % H<sub>2</sub>O-3 % CH<sub>3</sub>CN (v/v); n = order with respect to PSAA.

From the  $\rho$  values it is observed that the accelerating effect due to ERG is significantly greater than EWG. Such high  $\rho$  values are also obtained in many electron transfer reactions reported in the literature (Arias 2001 et al & Alhaji et al 2011). Further, from the observed  $\rho$  values, it is concluded that the electronic transition between the substituent and the reaction centre is significantly high in bipyridyl complex (**1a**) than in phenanthroline complex (**1c**).

The reactions of all substituted PSAAs with **1a** and **1c** were carried out at three different temperatures in order to calculate the thermodynamic parameters. The thermodynamic parameters,  $\Delta^\ddagger H$  and  $\Delta^\ddagger S$  are evaluated respectively from the intercept and slope of the Eyring's plot of  $\log(k_{ov}/T)$  vs.  $1/T$ . The calculated thermodynamic parameters are given in Table 3 and 4. The almost constant  $\Delta^\ddagger H$  values for both complexes and for all substituted PSAAs proves that in this reaction series,  $\Delta^\ddagger H$  value is independent of nature of complex and the type of substituents present in the PSAA. The negative values of the entropy of activation ( $\Delta^\ddagger S$ ) for **1a** and for **1c** suggest the extensive solvation of the products over the reactants in the rate determining step. Though the  $\Delta^\ddagger S$  value is almost constant in all the reactions, it is worthwhile to mention that the observed magnitude of entropy of activation for the SDS mediated reactions are appreciably higher than the values calculated for the reactions in the absence of SDS. This follows the trend expected for the catalysis reactions. Further, the higher value of negative entropy of activation in the presence of SDS shows loss of degrees of freedom in the reaction by the accumulation of more reactant molecules in the SDS micelle. It appears that the potential energy barrier is lowered in the presence of SDS. Thus comparison of  $\Delta^\ddagger S$  values in aqueous medium and SDS micellar medium shows that the reactant molecules tend to associate in a regular fashion in micellar phase.

### 3.3. Effect of SDS on rate

In order to get an insight on the interaction between the micelles and the reactants, the kinetic study has been carried out between PSAA and five  $[\text{Fe}(\text{NN})_3]^{3+}$  complexes (**1a-1e**) at different concentrations of SDS keeping other conditions as constant. In all these cases, the pseudo-first-order rate constants are found to be higher than those observed in the absence of SDS. For  $[\text{Fe}(\text{bpy})_3]^{3+}$ , the rate constant values increases from  $7.94 \times 10^{-4}$  to  $23.4 \times 10^{-4}$  when we increase the concentration of SDS from  $0.8 \times 10^{-2}$  M to  $15 \times 10^{-2}$  M. The observed pseudo-first-order rate constants without and with SDS at different concentrations are reported in Table 5.

The rate data in Table 4.5 clearly show that the rate acceleration with an increase in [SDS] is up to a certain concentration of SDS for all complexes. Beyond these concentrations, a little rate retardation or saturation is observed with [SDS]. Many researchers observed such type of retardation (Sen et al 2013) or saturation (Balakumar et al 2006 & Pandey, S. and Upadhyay 2005) of rate at higher concentration of micelle. Similar trend in rate acceleration at lower concentration of micelle and decrease in rate after reaching a maximum value is noticed in the Cr(V) oxidation of organic sulphides in micellar media (Bosco Bharathy et al 2005). The variation in rate constants with increase in [SDS] is shown in Figure 8.

**Table 5.** Effect of [SDS] on the rate of reaction between PSAA and the complexes **1a-1e**.

SDS]M	$10^4 k_1$ (s <sup>-1</sup> )				
	<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>	<b>1e</b>
0	7.14 ± 0.04	3.63 ± 0.08	8.33 ± 0.02	1.69 ± 0.01	13.3 ± 0.06
0.8	7.94 ± 0.01	3.64 ± 0.11	9.80 ± 0.12	3.43 ± 0.01	35.2 ± 0.01
0.9	8.15 ± 0.02	4.91 ± 0.02	10.1 ± 0.01	3.60 ± 0.02	37.4 ± 0.02
1.0	8.43 ± 0.04	5.03 ± 0.01	11.3 ± 0.02	3.72 ± 0.01	39.3 ± 0.05
2.0	11.1 ± 0.06	6.04 ± 0.04	12.3 ± 0.11	4.56 ± 0.04	51.3 ± 0.24
3.0	14.0 ± 0.05	6.70 ± 0.06	13.7 ± 0.05	4.95 ± 0.01	54.8 ± 0.21
4.0	16.4 ± 0.01	7.04 ± 0.08	14.8 ± 0.07	5.20 ± 0.03	55.9 ± 0.01
5.0	19.6 ± 0.02	7.29 ± 0.01	15.6 ± 0.02	5.37 ± 0.02	56.6 ± 0.12
7.0	21.2 ± 0.01	7.66 ± 0.02	18.9 ± 0.06	5.57 ± 0.05	57.3 ± 0.11
9.0	23.0 ± 0.12	7.86 ± 0.04	21.7 ± 0.03	5.67 ± 0.03	57.6 ± 0.04
10	23.4 ± 0.08	7.95 ± 0.01	20.2 ± 0.02	5.66 ± 0.02	57.6 ± 0.05
12	22.3 ± 0.04	7.53 ± 0.05	18.0 ± 0.01	5.43 ± 0.04	57.1 ± 0.01



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 $21.5 \pm 0.05$  $7.12 \pm 0.02$  $17.8 \pm 0.07$  $5.02 \pm 0.01$  $56.7 \pm 0.09$ 

[PSAA] =  $3 \times 10^{-3}$  M; [1a-1e] =  $4 \times 10^{-4}$  M; [H<sup>+</sup>] =  $5 \times 10^{-1}$ M;  $\mu = 0.6$  M;  
solvent = 97 % H<sub>2</sub>O-3% CH<sub>3</sub>CN.

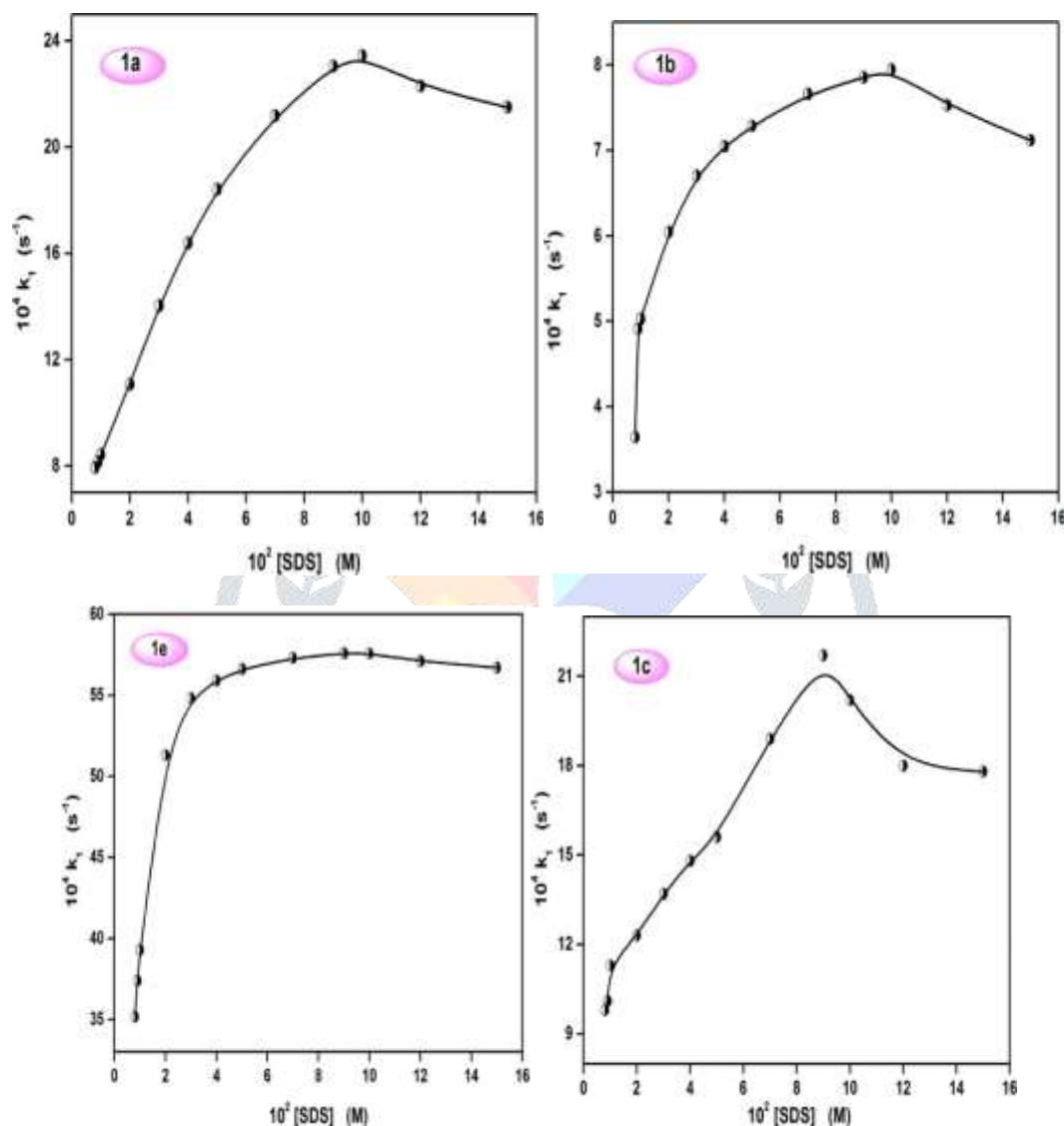


Figure 8. Effect of SDS on rate constants.

### 3.4 Mechanism

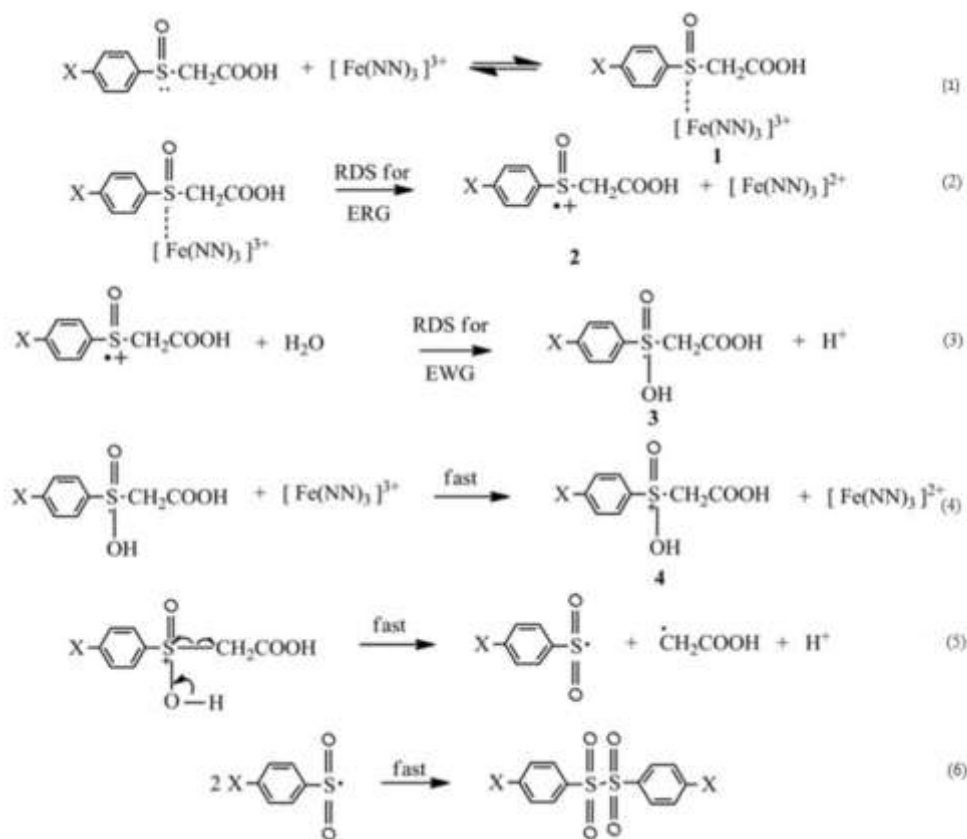
From the kinetic evidences, it is clear that the reaction in SDS medium shows the same kinetic effects with respect to PSAA, [Fe(NN)<sub>3</sub>]<sup>3+</sup> and H<sup>+</sup> as observed in the absence of SDS (Subramaniam et al 2016). On the basis of kinetic studies, substituent effects, temperature effect and the formation of diphenyl disulfone as product, it is concluded that the reaction mechanism for the electron transfer between PSAA and [Fe(NN)<sub>3</sub>]<sup>3+</sup> in SDS medium is similar to the mechanism that operates in the absence of SDS.

The reaction between [Fe(NN)<sub>3</sub>]<sup>3+</sup> and PSAA in presence of SDS follows Michaelis-Menten kinetics. This observation is a kinetic evidence for the formation of an adduct between PSAA and [Fe(NN)<sub>3</sub>]<sup>3+</sup> (1). Since [Fe(NN)<sub>3</sub>]<sup>3+</sup> is a strong one electron oxidant, it accepts an electron from PSAA and gets converted into [Fe(NN)<sub>3</sub>]<sup>2+</sup>. The formation of [Fe(NN)<sub>3</sub>]<sup>2+</sup> is evident from the increase in the characteristic  $\lambda_{max}$  value. During this single electron transfer, sulfoxide radical cation is formed as the intermediate species (2). Many authors have reported such sulfur radical cation formation (Bosch & Kochi 1995) in their oxidation studies on sulfur compounds.

The formation of sulfoxide radical cation has been considered as the rate determining step in the proposed mechanism of electron transfer reaction between PSAA and [Fe(NN)<sub>3</sub>]<sup>3+</sup>. The rate of the electron transfer reaction is accelerated to a greater extent by the electron releasing groups substituted in the phenyl ring of PSAA. The sulfoxide radical cation formation by the transfer of electron from PSAA to [Fe(NN)<sub>3</sub>]<sup>3+</sup> in the adduct (2) is strongly favoured by the electron releasing groups. It has been shown in the literature that higher concentration of H<sup>+</sup> stabilizes the sulfur radical cation (Gawandi et al 2000).

The nucleophilic attack of water on the sulfoxide radical cation leads to the formation of sulfoxide radical (3). The sulfoxide radical then transfers its electron to [Fe(NN)<sub>3</sub>]<sup>3+</sup> and is converted into sulfoxide cation (4). This cation undergoes C-S cleavage and rearrangement to form phenyl sulfonyl free radical. Such type of water attack followed by second electron transfer is already reported by Adaikalasamy et al (2003). Dimerization of phenylsulfonyl radical leading to the formation of the final product

diphenyl disulfone is evident from FT-IR and GC-MS studies. Based on the above facts the following scheme of mechanism is proposed.

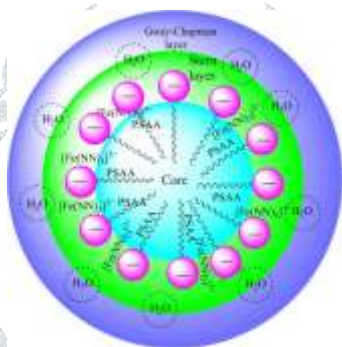


Scheme 1. Mechanism of the reaction in SDS micellar medium.

### 3.5. Interpretation of micellar effect

In micellar reactions, the reaction rate in micellar medium is different from that in aqueous medium if any reactant is interacting with the micelle. The reactant may interact with the micelle by hydrophobic or electrostatic interaction. Depending upon the relative concentration of reactants in micellar and aqueous phases, rate acceleration or retardation may occur. It has been shown that accumulation of both reactants in a single pseudo phase leads to micellar catalysis while partitioning of reactants in two phases causes retardation in rate. The micellar catalysis observed here, is as expected, as one of the reactants is a cation  $[\text{Fe}(\text{NN})_3]^{3+}$  and the other is a neutral PSAA. Hence, they can bind with the anionic micelle by electrostatic and hydrophobic interactions respectively. The substrate, PSAA contains hydrophobic aryl moiety. As both the reactants bind with micelles strongly, the overall rate benefit observed is a result of enhanced stoichiometric concentration of the reactants in the micellar phase. With the increase in  $[\text{SDS}]$ , the extent of partitioning of reactants in the micellar phase increases followed by increase in the rate constant.

The electron acceptors,  $[\text{Fe}(\text{NN})_3]^{3+}$  will associate strongly with the anionic surfactant and the binding constant is expected to be high. Moreover, as the reaction between PSAA and iron(III) polypyridyl complex proceeds through electron transfer mechanism, sulfoxide radical cation is formed as an intermediate during the course of the reaction. The formation of sulfoxide radical cation is also favoured by SDS medium due to its stabilization by the anionic sulfate head group. Thus, the increase in rate of reaction between PSAA and  $[\text{Fe}(\text{NN})_3]^{3+}$  may also be partially due to the stabilization of the intermediate formed. All these favourable aspects account for the micellar catalysis observed in the presence of SDS. A schematic representation of location of reactants in SDS micelle is shown in figure 9.



**Figure 9.** Schematic representation of location of reactants in SDS micelle.

Such type of micellar catalytic effect is observed in the oxidation of aryl methyl, alkyl phenyl and dialkyl sulfides by  $[\text{Fe}(\text{NN})_3]^{3+}$  complexes (Balakumar et al 2006), Cr(VI) oxidation of dialkyl sulfides in the presence of SDS (Sankararaj et al 1995) and in the oxidation of diphenyl sulfide by iron(III) bipyridyl complex in SDS medium (Balakumar et al 2012). They have explained the rate acceleration observed in SDS medium by preferential partitioning of the positively charged oxidizing species by electrostatic attraction and the neutral substrate by hydrophobic attraction by SDS.

### 4. CONCLUSION

The kinetics of the electron transfer reactions between PSAA and  $[\text{Fe}(\text{NN})_3]^{3+}$  were studied in the presence of anionic surfactant, SDS in order to gain a better understanding of their oxidizing properties. The calculated low values of Michaelis-Menten constant ( $K_m$ ) ensures that strong binding of PSAA to the iron(III) polypyridyl complexes during intermediate formation in SDS medium. The observed non-linear Hammett behavior with upward curvature in the present series of reactions can be visualized to a change in the rate determining step on changing the substituents in PSAA from ERG to EWG. As both the reactants bind with micelles strongly, the overall rate benefit observed is a result of enhanced stoichiometric concentration of the reactants in the micellar phase. With the increase in  $[\text{SDS}]$ , the extent of partitioning of reactants in the micellar phase increases followed by increase in the rate constant. A suitable mechanism has been proposed.

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