



# NON-LINEAR HAMMETT IN THE SDS MEDIATED ELECTRON TRANSFER REACTIONS IN THE OXIDATION OF PHENYLSULFINYLACETIC ACID BY IRON(III) POLYPYRIDYL COMPLEXES

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## ABSTRACT

Micelles are treated as enzyme-like particles and micellar catalysis was used to mimic enzyme catalysed reactions. In order to get in-depth knowledge of enzymatic reactions, the electron transfer reactions were carried out in the presence of Sodium- dodecylsulfate (SDS) micelles. The micellar kinetic data shows fractional order dependence on Phenylsulfinylacetic acid, PSAA and the operation of Michaelis-Menten kinetics is inferred from the linear double reciprocal plots of  $k_1$  versus [PSAA] with finite intercept on the rate axis. The kinetic data shows first order dependence with respect to Iron (III) polypyridyl complex,  $[\text{Fe}(\text{NN})_3]^{3+}$  and the rate constant is found to increase with increase in  $[\text{H}^+]$ . From the study of substituent effect it is clear that both ERG and EWG accelerate the reaction rate. On applying Hammett correlation between substituent constant  $\sigma$  and  $k_{ov}$  of meta- and para-substituted PSAAs, a nonlinear Hammett plot was obtained. The micellar catalysis observed here is as expected since one of the reactants is a cation  $[\text{Fe}(\text{NN})_3]^{3+}$  and the other one is neutral PSAA. Hence, both can bind with the anionic micelle by electrostatic and hydrophobic interactions respectively.

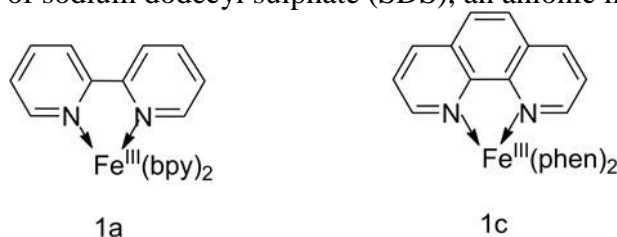
**Keywords :** Electron transfer reaction ; Iron (III) polypyridyl complex ; Phenylsulfinylacetic acid ; Non-linear Hammett

## 1. INTRODUCTION

Surfactants play an important role in many technological applications such as dispersion stabilization, enhanced oil recovery and lubrication. Surfactant molecules are biphilic in nature which contain a hydrophilic head and a hydrophobic tail. This makes the surfactants to adsorb preferably on interfaces. They are soluble both in oil and aqueous phases and their solubility depends on their hydrophile-lipophile balance (Kruglyakov, 2000). At low concentrations, surfactant molecules are believed to exist in the solution mainly as single molecule. If the concentration increases and reaches some critical value called critical micelle concentration, (CMC) the surfactant molecules form micelles (Tsuji, 1998, Jönsson, 1998, Rusanov 1998). In aqueous solutions hydrophobic tails are collected inside the micelle and only hydrophilic heads are exposed to the aqueous phase.

In 1959, Duynstee and Grunwald found that anionic surfactants inhibit while cationic surfactants enhance the rate of alkaline fading of several dyes. This discovery marked the beginning of the study of micellar-catalyzed reactions. A full kinetic treatment was presented for first-order reactions by Menger and Portnoy in 1967. Later micelles are treated as enzyme-like particles, not surprisingly, micellar catalysis was used to mimic enzyme-catalyzed reactions (Romsted, 1984). For a bimolecular reaction, the concentrations of both reactants in the micellar medium are important in deciding the rate of the reaction in addition to their differences in solvation in aqueous and micellar phases. Many organic substrates having high affinity towards the micellar phase over the aqueous phase concentrate in the micelles that make up only a relatively small part of the total volume of the system. This results in enhancement of rate for bimolecular reactions. The effect diminishes at higher surfactant concentrations because both reactants are diluted.

In this paper, the results of the electron transfer reactions between thirteen PSAAs and two iron(III) polypyridyl complexes, tris(2,2'-bipyridine)iron(III) perchlorate **1a** and tris(1,10-phenanthroline)iron(III) perchlorate **1c** in the presence of sodium dodecyl sulphate (SDS), an anionic micelle are discussed.

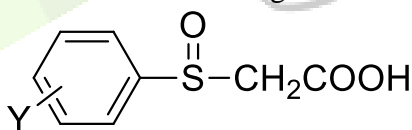


**Figure 1.** Structure of the Fe(III) complexes, **1a** and **1c**.

## 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) and 1,10-phenanthroline (phen) 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 per-chlorate salts. The purity of the complexes was checked from their IR and absorption spectra. The structure and the abbreviation of iron(III) polypyridyl complexes used in the present study are shown in Figure 1. In order to avoid the decomposition of complexes, stock solutions of Fe(III) complexes 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.



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 Micellar kinetics

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 PSAA at least 10 fold in excess over the iron(III) polypyridyl complex in the presence of SDS at 303 K. 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  $8 \times 10^{-3}$  M (Frescura et al 1995, Van Os et al 1993) the reactions were carried out in the concentration range of  $0.8 \times 10^{-2}$  M to  $15 \times 10^{-2}$  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% H<sub>2</sub>O-3% CH<sub>3</sub>CN (v/v) medium. Many researchers have also used similar solvent systems to study micellar effect on the oxidation of organic sulphides (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 HClO<sub>4</sub> was maintained during the kinetic study. The ionic strength was maintained in all the reactions using NaClO<sub>4</sub>.

In SDS micellar medium a blue shift to the tune of 6-10 nm is observed for bipyridine complex

while no shift is noted in phenanthroline complex. Similar shift is already reported by Balakumar et al. (2006) in SDS medium. The shift in  $\lambda_{\max}$  indicates strong binding of iron bipyridine complex with SDS micelle. In SDS medium the reactions were followed at the wavelength of 516 nm for  $[\text{Fe}(\text{bpy})_3]^{2+}$  and 510 nm for  $[\text{Fe}(\text{phen})_3]^{2+}$ . 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.

### 3. Results and discussion

#### 3.1 Effect of [PSAA] 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 dependence of PSAA on the rate of the reaction was investigated by varying the concentration of PSAA from  $3 \times 10^{-3}$  M to  $3 \times 10^{-2}$  M. The plots of decrease in  $[\text{Fe}(\text{NN})_3^{3+}]$  with time at different concentrations of PSAA in SDS medium are shown in the Figure 4.

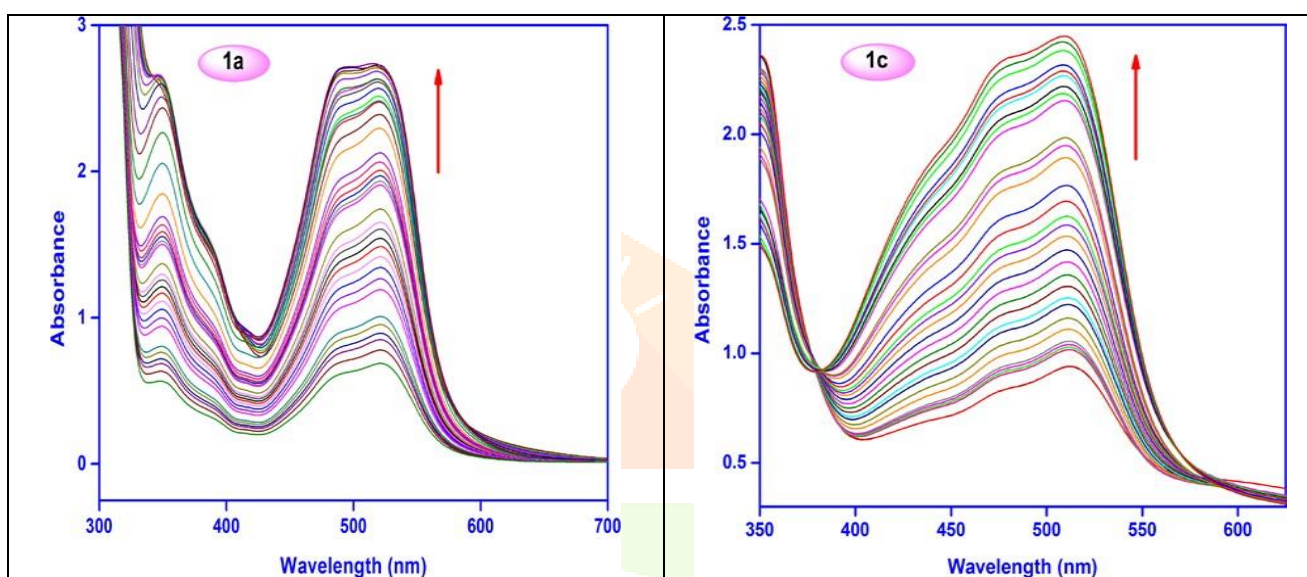


Figure 3. Increase in absorbance of  $[\text{Fe}(\text{NN})_3]^{2+}$  at different time intervals.

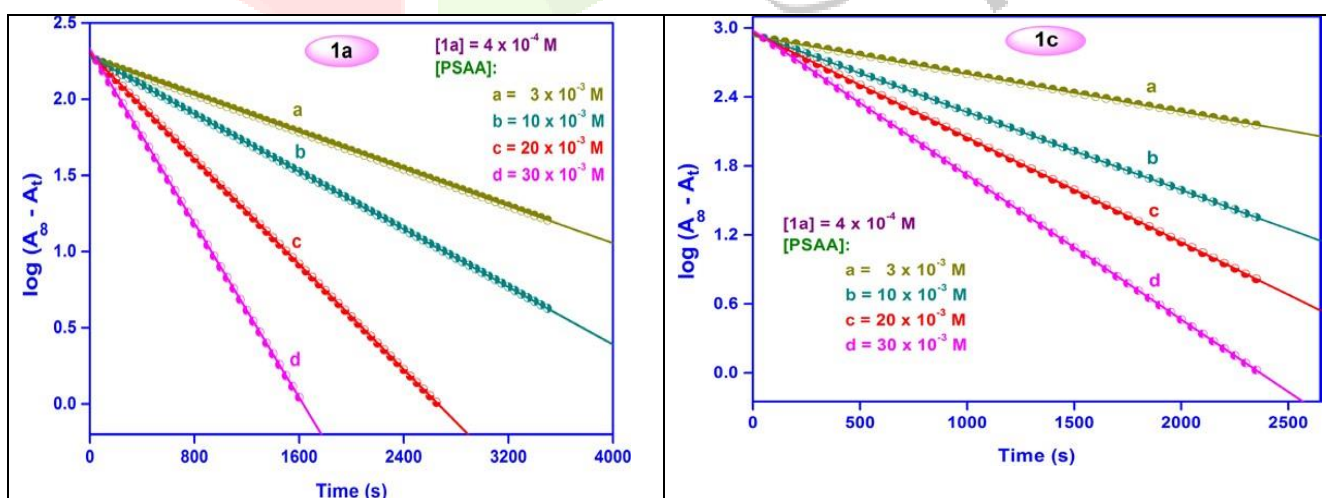


Figure 4. Progress of the reaction at different [PSAA] in SDS mediated reactions.

The pseudo-first-order and overall rate constants calculated from these plots are consolidated in Table 1. The data presented in Table 1 show that the pseudo-first-order rate constant increases with increase in [PSAA] while the overall rate constant calculated using the relation  $k_{\text{ov}} = k_1 / [\text{PSAA}]^{\text{order}}$  remain constant with **1a** and **1c**. Further, the plots of  $k_1$  against [PSAA] show linear dependence without passing through the origin (Figure 5). These results clearly demonstrate the fractional order dependence on PSAA as

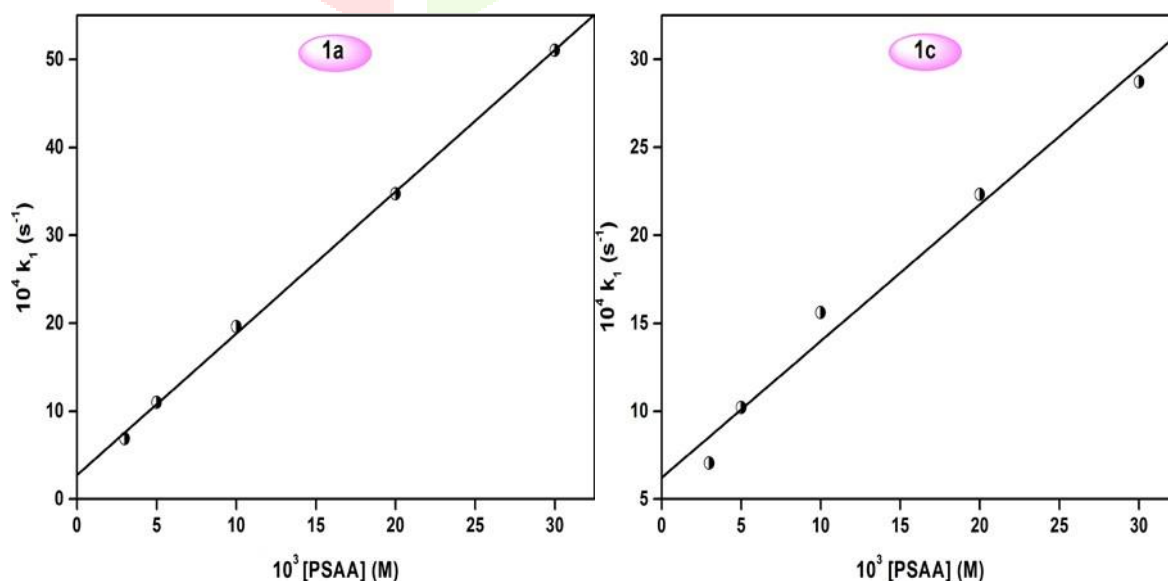
observed in the absence of SDS (Subramaniam et al 2016).

The order with respect to PSAA is determined from the slope value of  $\log k_1$  vs.  $\log [\text{PSAA}]$  (Figure 6). 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 (Figure 7).

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

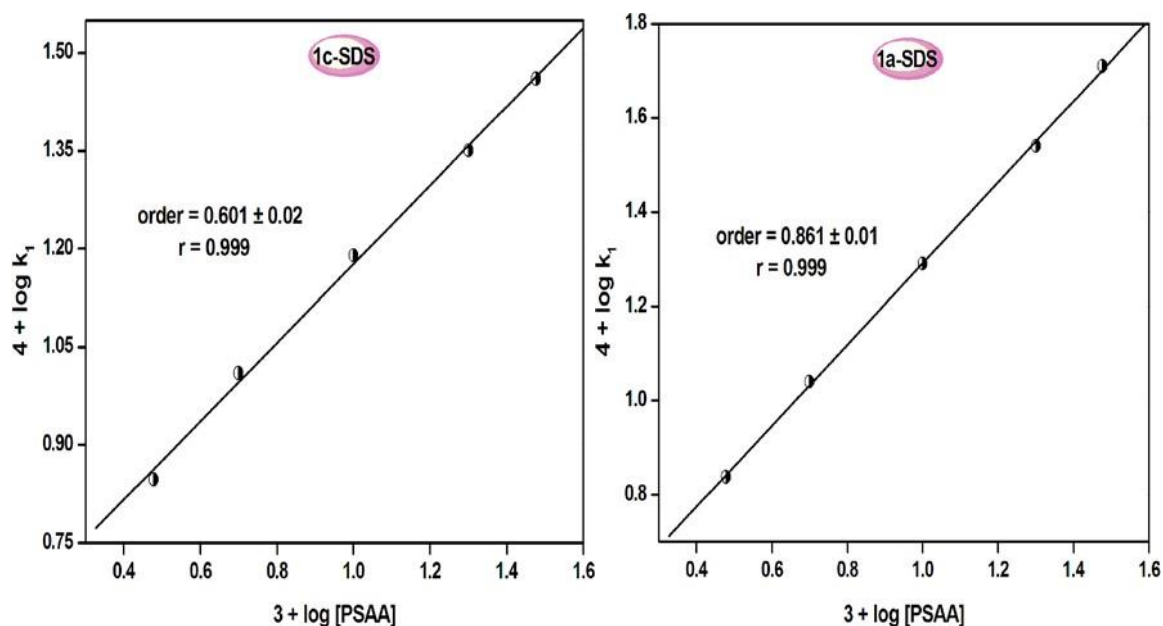
$[\text{PSAA}] (\text{M})$	$10^4 [\text{Fe}(\text{NN})_3^{3+}] (\text{M})$	$10^4 k_1$ ( $\text{s}^{-1}$ )	$10^2 k_{\text{ov}}$ ( $\text{M}^{-1}$ ) <sup>n</sup> ( $\text{s}^{-1}$ )
<b>1a</b>			
3.0	4.0	$6.89 \pm 0.10$	$10.2 \pm 0.15$
5.0	4.0	$11.0 \pm 0.01$	$10.5 \pm 0.01$
10	4.0	$19.6 \pm 0.01$	$10.3 \pm 0.01$
20	4.0	$34.7 \pm 0.07$	$10.1 \pm 0.02$
30	4.0	$50.9 \pm 0.03$	$10.4 \pm 0.01$
10	2.0	$23.5 \pm 0.04$	$13.0 \pm 0.02$
10	8.0	$14.6 \pm 0.03$	$8.10 \pm 0.02$
<b>1c</b>			
3.0	4.0	$7.03 \pm 0.01$	$2.31 \pm 0.01$
5.0	4.0	$10.2 \pm 0.02$	$2.46 \pm 0.01$
10	4.0	$15.6 \pm 0.08$	$2.48 \pm 0.01$
20	4.0	$22.3 \pm 0.04$	$2.34 \pm 0.01$
30	4.0	$28.7 \pm 0.09$	$2.36 \pm 0.01$
10	2.0	$18.7 \pm 0.04$	$3.16 \pm 0.01$
10	8.0	$10.2 \pm 0.01$	$1.72 \pm 0.01$

$[\text{H}^+] = 0.5 \text{ M}$ ;  $\mu = 0.6 \text{ M}$ ;  $[\text{SDS}] = 5 \times 10^{-2} \text{ M}$ ; solvent = 97 %  $\text{H}_2\text{O}$ -3 %  $\text{CH}_3\text{CN}$  (v/v);  
n = order with respect to PSAA.

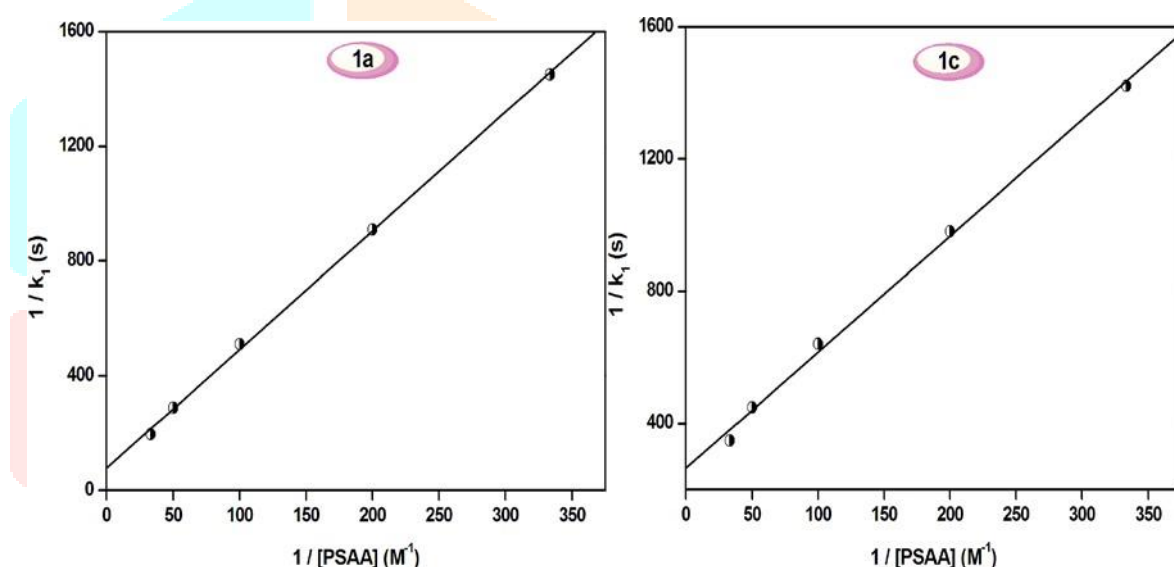


**Figure 5.** Plots of  $k_1$  vs.  $[\text{PSAA}]$  for **1a** and **1c** in SDS.





**Figure 6.** Order plots for PSAA with **1a** and **1c** in SDS medium.

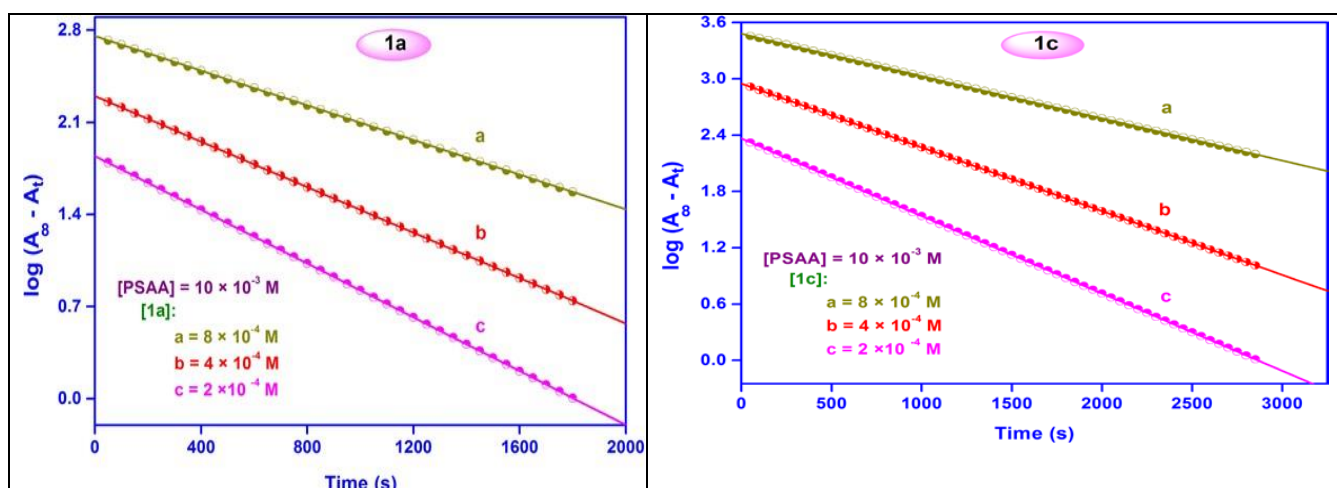


**Figure 7.** Michaelis-Menten plot for PSAA with **1a** and **1c** in SDS medium.

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.

### 3.2 Effect of $[\text{Fe}(\text{NN})_3]^{3+}$ on rate

Under pseudo-first order conditions, the linearity of the plots of  $\log(A_\infty - A_t)$  vs. time for the reactions at various concentrations of  $[\text{Fe}(\text{NN})_3]^{3+}$  (Figure 8) suggest that electron transfer reaction is clear first order with respect to  $[\text{Fe}(\text{NN})_3]^{3+}$ .



**Figure 8.** Progress of the reactions at different [1a] and [1c] with PSAA in SDS.

However, the pseudo-first-order rate constant is found to decrease appreciably with increase in  $[\text{Fe}(\text{NN})_3]^{3+}$  for both complexes. Similar rate retardation is observed in the absence of SDS medium also [(Subramaniam et al 2016). 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 as proposed by 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.

### 3.3 Effect of $[\text{H}^+]$ on rate

The effect of  $[\text{H}^+]$  on the rate of reaction is studied by varying the concentration of  $\text{HClO}_4$  in the reaction mixture. 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  $\text{H}^+$ . This is similar to the effect reported in the oxidative decarboxylation of PSAA by  $[\text{Fe}(\text{NN})_3]^{3+}$  in the absence of SDS [(Subramaniam et al 2016). As the effect of ionic strength show positive effect, ionic strength is maintained as constant in all the kinetic runs.

**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)	$10^2 k_{ov} (\text{M}^{-1})^n (\text{s}^{-1})$	
	1a	1c
0.5	$10.5 \pm 0.06$	$2.48 \pm 0.07$
0.7	$10.9 \pm 0.04$	$3.03 \pm 0.02$
0.9	$11.7 \pm 0.08$	$3.71 \pm 0.06$
1.0	$12.4 \pm 0.01$	$4.85 \pm 0.02$
1.1	$13.6 \pm 0.01$	$6.42 \pm 0.01$
1.2	$14.4 \pm 0.01$	$8.14 \pm 0.01$

[PSAA] =  $1 \times 10^{-2}$  M; [1a] = [1c] =  $4 \times 10^{-4}$  M;  $\mu$  = 1.2 M; [SDS] =  $5 \times 10^{-2}$  M; solvent = 97 %  $\text{H}_2\text{O}$ -3 %  $\text{CH}_3\text{CN}$  (v/v); n = order with respect to PSAA

### 3.4. Effect of substituent on PSAAs

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  $\log k_{\text{ov}}$  of *meta*- and *para*-substituted PSAAs, a non-linear Hammett plot similar to the one observed in the absence of SDS micelle was obtained[14] The non-linear Hammett plots exhibit concave-upward curves with ERG falling on one side of the curve having negative  $\rho$  value (ranging from -2.80 to -6.65) and the EWG on the other side, with positive  $\rho$  values (ranging from 0.297 to 1.56). The Hammett plots of  $\log k_{\text{ov}}$  vs.  $\sigma$  at three different temperatures are shown in Figures 9 and 10. The values of  $\rho^+$  and  $\rho^-$  obtained from Hammett plots for the complexes **1a** and **1c** are tabulated in Tables 3 and 4.

The data in Tables 3 and 4 reveal that the  $\rho$  values for the SDS catalyzed reactions are lower than the corresponding  $\rho$  values for the reactions in the absence of SDS. This is in accordance with the reactivity selectivity principle. In the absence of SDS, the electron releasing substituents fall on one side of the curve with a large reaction constant values ( $\rho = -3.28$  to  $-7.47$ ) and the electron withdrawing substituents fall on the other side of the curve with a small positive reaction constant values ( $\rho = +0.351$  to  $+0.836$ ). As the rate of reaction in SDS medium is higher than in aqueous phase, the reaction in aqueous phase will be more sensitive to substituent effect and hence  $\rho$  value in aqueous phase is higher than in SDS micellar phase.

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

No.	X	$10^2 k_{\text{ov}} (\text{M}^{-1})^n (\text{s}^{-1})$			$\Delta^\ddagger\text{H}$ kJ mol <sup>-1</sup>	$-\Delta^\ddagger\text{S}$ 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		
	$\rho^-$	0.970	0.981	0.975		

[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.

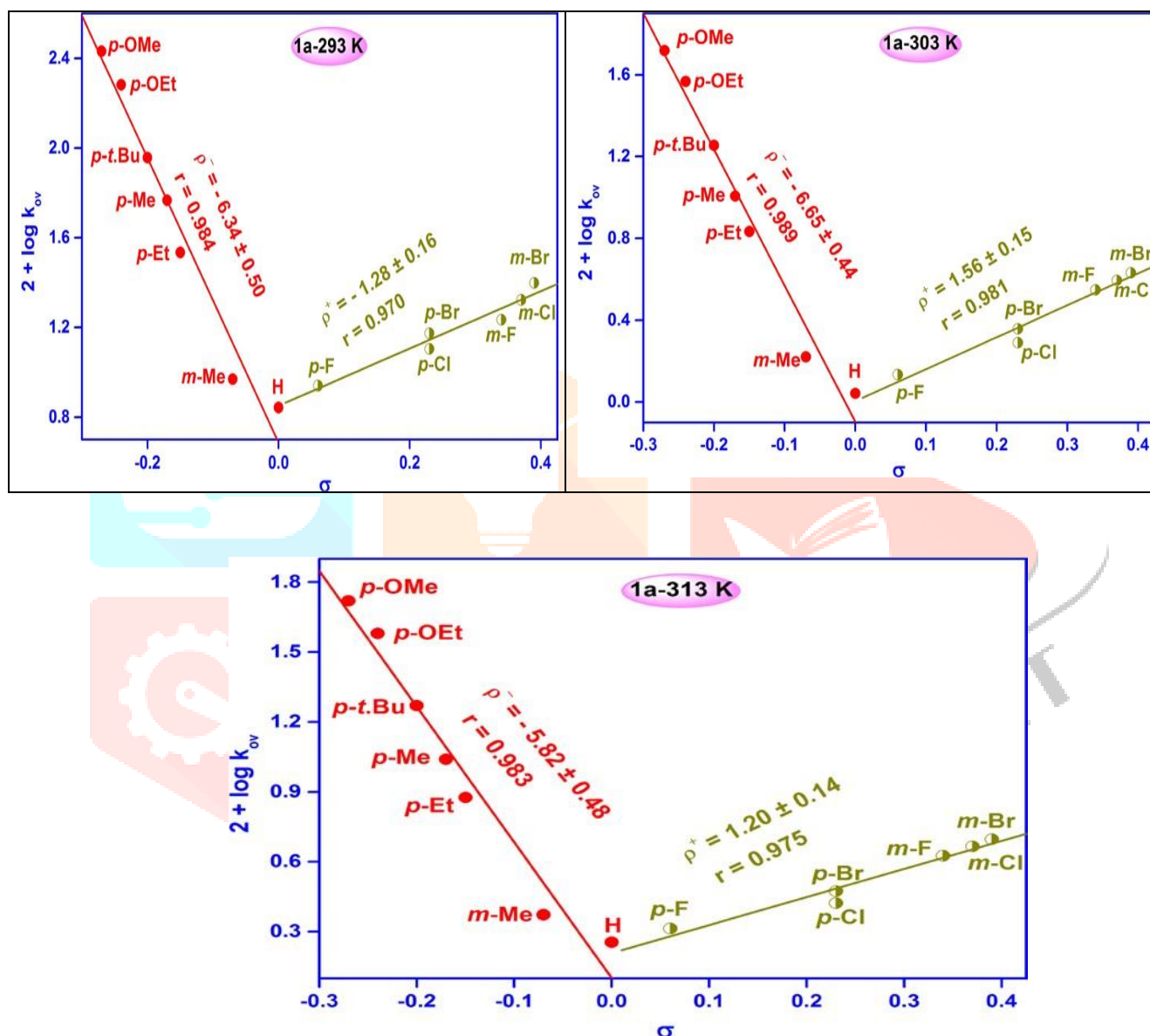


Figure 9. Non-linear Hammett plots for 1a at different temperatures.

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

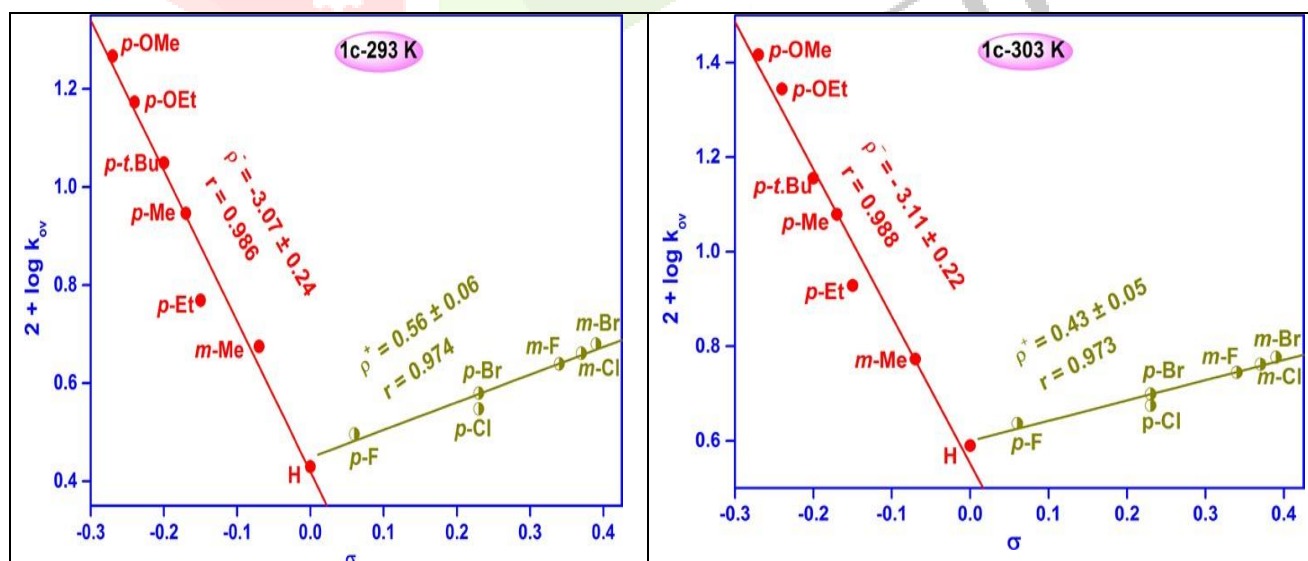
No.X	$10^2 k_{ov}$ (M <sup>-1</sup> ) <sup>n</sup> (s <sup>-1</sup> )			$-\Delta^\ddagger S$	
	293 K	303 K	313 K	$\Delta^\ddagger H$ kJ mol <sup>-1</sup>	J K <sup>-1</sup> mol <sup>-1</sup>
1.p-F	$3.13 \pm 0.14$	$4.33 \pm 0.03$	$6.93 \pm 0.02$	$27.7 \pm 1.39$	$83.6 \pm 4.88$
2.p-Cl	$3.53 \pm 0.08$	$4.73 \pm 0.11$	$7.16 \pm 0.06$	$24.4 \pm 1.38$	$93.8 \pm 4.86$
3.p-Br	$3.79 \pm 0.12$	$4.99 \pm 0.12$	$7.59 \pm 0.02$	$23.8 \pm 1.48$	$95.3 \pm 5.22$



4. <i>m</i> -F	4.36 ± 0.22	5.56 ± 0.05	8.15 ± 0.03	21.3 ± 1.60	103 ± 5.65
5. <i>m</i> -Cl	4.58 ± 0.06	5.78 ± 0.07	8.38 ± 0.08	20.5 ± 0.88	105 ± 3.11
6. <i>m</i> -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. <i>m</i> -Me	4.73 ± 0.04	5.93 ± 0.06	8.53 ± 0.04	19.9 ± 0.59	107 ± 2.08
9. <i>p</i> -Et	5.87 ± 0.06	8.48 ± 0.12	14.1 ± 0.04	30.8 ± 0.69	67.8 ± 2.44
10. <i>p</i> -Me	8.84 ± 0.02	12.0 ± 0.08	17.9 ± 0.02	24.4 ± 0.26	86.4 ± 0.90
11. <i>p</i> - <i>t</i> -Bu	11.2 ± 0.16	14.3 ± 0.06	21.2 ± 0.14	21.8 ± 0.64	93.4 ± 2.25
12. <i>p</i> -OEt	14.9 ± 0.18	22.1 ± 0.02	27.3 ± 0.12	20.7 ± 0.44	94.3 ± 1.56
13. <i>p</i> -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		
$r$	0.974	0.973	0.941		
$\rho^-$	-3.07 ± 0.24	-3.11 ± 0.22	-2.80 ± 0.09		
$r$	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 et al 2001, Ruff et al 1975 & 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).



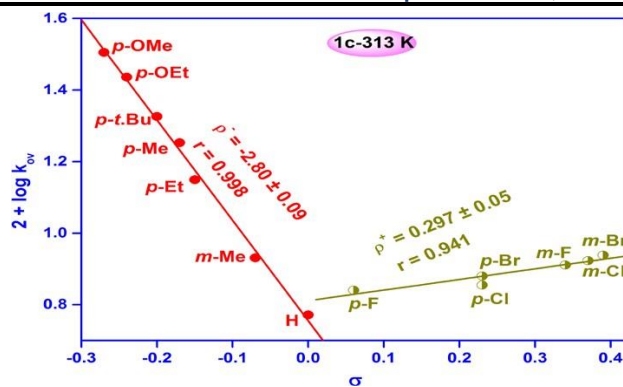


Figure 10. Non-linear Hammett plots for **1c** at different temperatures.

### 3.4. Thermodynamic parameters

The reactions of all substituted PSAAs with **1a** and **1c** were carried out at three different temperatures in order to calculate the thermodynamic parameters and isokinetic temperature in SDS medium. 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.  $1/T$  (Figure 11). The calculated thermodynamic parameters are given in Tables 3 and 4.

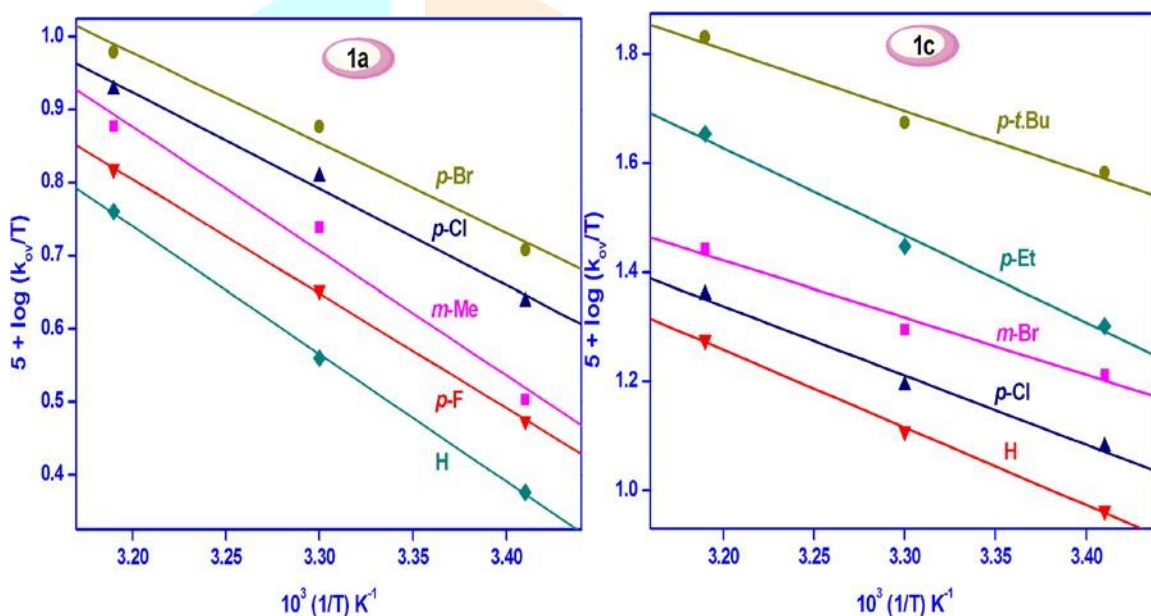


Figure 11. Eyring's plots for the reaction between PSAAs and **1a** and **1c** in SDS.

The almost constant  $\Delta^\ddagger H$  values for both complexes and for all substituted PSAAs prove 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 for **1a** and **1c** suggest the extensive solvation of the products over the reactants. 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 (Subramaniam et al 2016). 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.

### 3.6 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 the  $[\text{Fe}(\text{NN})_3]^{3+}$  complexes (**1a** and **1c**) 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. The observed pseudo-first order rate constants without and with SDS at different concentrations are reported in Table 5. The rate data clearly shows that the rate acceleration with an increase in [SDS] is up to a certain concentration of SDS for the 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, Bunton 1968 & 1973 & Buist et al 1970) or saturation (Pandey & Upadhyay, 2005) of rate at higher concentration of micelle.

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

[SDS]M	$10^4 k_1$ (s <sup>-1</sup> )	
	<b>1a</b>	<b>1c</b>
0	7.14 ± 0.04	8.33 ± 0.02
0.8	7.94 ± 0.01	9.80 ± 0.12
0.9	8.15 ± 0.02	10.1 ± 0.01
1.0	8.43 ± 0.04	11.3 ± 0.02
2.0	11.1 ± 0.06	12.3 ± 0.11
3.0	14.0 ± 0.05	13.7 ± 0.05
4.0	16.4 ± 0.01	14.8 ± 0.07
5.0	19.6 ± 0.02	15.6 ± 0.02
7.0	21.2 ± 0.01	18.9 ± 0.06
9.0	23.0 ± 0.12	21.7 ± 0.03
10	23.4 ± 0.08	20.2 ± 0.02
12	22.3 ± 0.04	18.0 ± 0.01
15	21.5 ± 0.05	17.8 ± 0.07

$$[\text{PSAA}] = 3 \times 10^{-3} \text{ M}; [\mathbf{1a}, \mathbf{1c}] = 4 \times 10^{-4} \text{ M}; [\text{H}^+] = 5 \times 10^{-1} \text{ M}; \\ \mu = 0.6 \text{ M}; \text{solvent} = 97 \% \text{ H}_2\text{O} - 3 \% \text{ CH}_3\text{CN}.$$

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, since one of the reactants is a cation  $[\text{Fe}(\text{NN})_3]^{3+}$  and the other is 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.

### 3. CONCLUSION

The electron transfer reactions between Phenylsulfinylacetic acids and iron (III) polypyridyl complexes in sodium dodecylsulfate micellar medium has been studied spectrophotometrically. The kinetic studies demonstrate fractional order dependence on PSAA and the operation of Michaelis-Menten kinetics is inferred under pseudo-first order conditions. The electron transfer reaction is clear first order with respect to  $[\text{Fe}(\text{NN})_3]^{3+}$  and the rate constant is found to increase with increase in  $[\text{H}^+]$ . 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  $[\text{Fe}(\text{NN})_3]^{3+}$ . 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. 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 micellar catalysis is observed here as expected, since 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.

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