



SDS MEDIATED ELECTRON TRANSFER REACTIONS AND THE KINETIC MODELS IN THE OXIDATION OF PHENYLSULFINYLACETIC ACIDS BY IRON(III) POLYPYRIDYL COMPLEXES

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ABSTRACT

Oxidative decarboxylation of phenylsulfinylacetic acids (PSAAs) by iron(III) polypyridyl complexes in anionic surfactant 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. Non-linear concave upward Hammett plots are obtained on applying the Hammett substituent constants to the overall rate constants obtained in SDS medium. 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. Kinetic models are proposed to explain the SDS micellar effects.

Keywords: Menger-Portnoy model, Piszkiwicz model, Raghvan and Srinivasan model, Berezin model; Iron(III) polypyridyl complexes.

1. INTRODUCTION

Various theoretical models have been proposed to interpret the formulation of mixed micelles composition and interaction parameter and monolayer formation. The first model, given by Lange (1953) and used by Clint (1992) is a phase separation model which relates the mole fraction and the critical micellar concentration of the i^{th} components ($i = 1, 2$) in an ideal mixture, which is successfully applicable to systems of mixed surfactants of similar structure, but hardly applicable to combinations with dissimilar structures.

Rubingh's model is the first model developed for non-ideal mixed system (Mittal 1979). Due to its simplicity, it has been mostly used even after the development of more complex models. Although Rubingh's treatment found to be reasonably satisfactory in many cases, the theory was criticized on thermodynamic grounds. Rosen and co-workers (1989, 2003) extended the nonideal solution treatment of Rubingh for mixed micelle formation by binary surfactant systems, to estimate the surfactant molecular interactions and also the composition in the adsorbed mixed monolayer at air/water interface from surface tension data.

Motomura et al. (1984) developed a model in order to overcome the limitations of the Rubingh's model and improve the predictions of the phase separation model. Basically, it is a thermodynamic method which considers the micelles as a macroscopic bulk phase, the thermodynamic quantities associated with the mixed micelle formation process being expressed as a function of the excess thermodynamic quantities. Rodenas et al. (1999) used a simple theoretical treatment, based on Lange's model that utilizes the Gibbs-Duhem equation to relate the activity coefficients of the surfactants in the mixed micelles. Maeda (1995) introduced a term, G_{mic} , as a measure of stability of mixed systems. Attempts by other workers (Nagarajan & Ruckenstein 1991, Shiloach, A. & Blankshtein, D. 1998, Bergstrom, M. and Eriksson, 2000 and Matsubara et al 2000) have also been made to predict the properties of mixed micelles and interactions in binary surfactant systems. In this paper, the SDS micellar effects in the oxidation of PSAAs by the iron(III) polypyridyl complexes, **1a–1e** has been explained with the various kinetic models.

2. EXPERIMENTAL

2.1 Synthesis of Fe(III) polypyridyl $[Fe(NN)_3]^{3+}$ 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 $[Fe(NN)_3]^{3+}$ 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 $[Fe(NN)_3]^{3+}$ 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.

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 structure of substituted phenylsulfinyl acetic acids used in this work is shown in Figure 2.

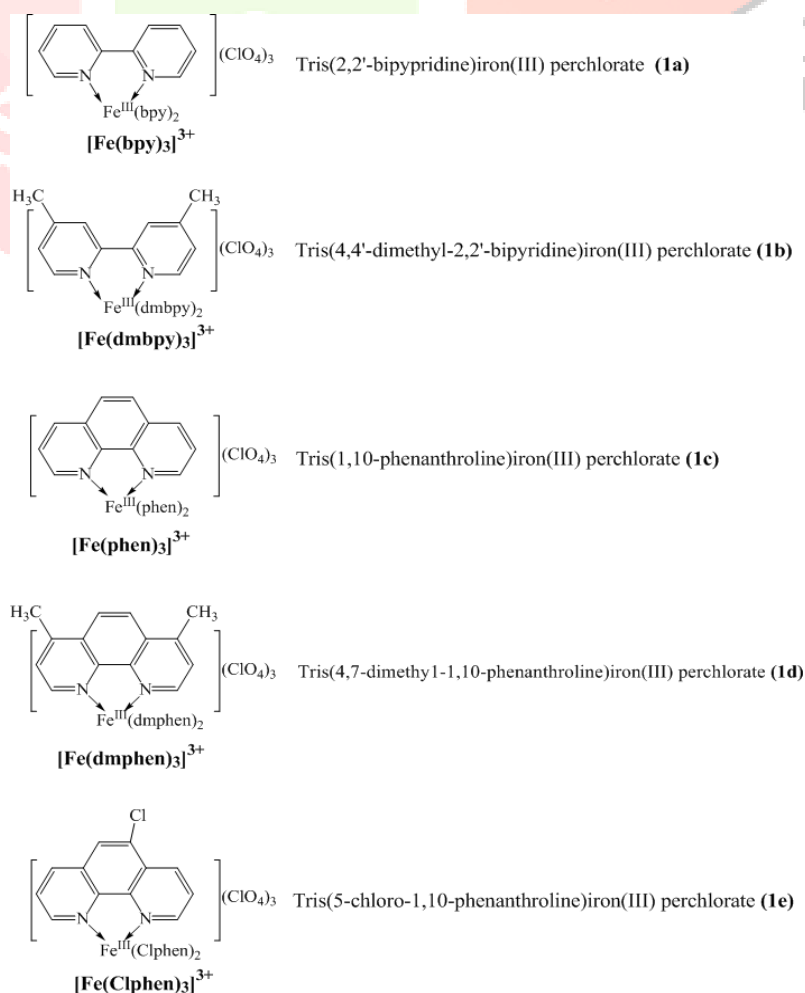
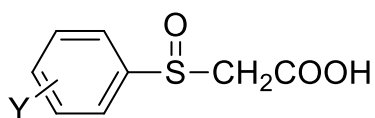


Figure 1. Structure of iron(III) polypyridyl complexes.

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 PSAA atleast 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 8×10^{-3} M (Frescura et al 1995 & Van Os et al 1993), the reactions were carried out in the concentration range of 0.8×10^{-2} M to 15×10^{-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_2O -3% CH_3CN (v/v) medium. The ionic strength was maintained in all the reactions using NaClO_4 .

In SDS micellar medium a blue shift to the tune of 6 - 10 nm in the λ_{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 λ_{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 $[\text{Fe}(\text{Clphen})_3]^{2+}$. 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.

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.

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, complexes at fixed concentration of $[\text{H}^+]$, ionic strength and at constant temperature. The results clearly demonstrate the fractional order dependence on PSAA. Michaelis-Menten kinetics observed confirms the binding among the reactants to form an intermediate before the rate determining step in the reaction mechanism. The observed low Michaelis-Menten constants (K_M) ensure strong binding of PSAA with iron(III) polypyridyl complexes in SDS medium.

Kinetic results show 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 $[\text{Fe}(\text{NN})_3]^{3+}$. Also the overall rate constants recorded reveal that the rate constant increases with increase in $[\text{H}^+]$.

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. From the study of substituent effect it is clear that both electron releasing groups (ERG) and electron withdrawing groups (EWG) accelerate the reaction rate (Jeevi Esther Rathnakumari et al 2024). 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 ρ value and the EWG on the other side, with positive ρ values. The observed non-linear Hammett behaviour with upward curvature in the present series of reactions can be interpreted on the basis of a change in the rate determining step on changing the substituents in PSAA from ERG to EWG. From the ρ values it is observed that the accelerating effect due to ERG is significantly greater than EWG. Such high ρ values are also obtained in many electron transfer reactions reported in the literature (Hemmati & Saboori, 2016 and Burchett & Meloan, 1972). Further, from the observed ρ 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 thermodynamic parameters, $\Delta^\ddagger H$ and $\Delta^\ddagger S$ are evaluated respectively from the intercept and slope of the Eyring's plot of $\log(k_{\text{ov}}/T)$ vs. $1/T$. (Jeevi Esther Rathnakumari et al 2024). The almost constant $\Delta^\ddagger H$ values for the 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 ($\Delta^\ddagger S$) observed suggest the extensive solvation of the products over the reactants in the rate determining step. The $\Delta^\ddagger S$ value is almost constant in all the reactions and 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.

3.3 Effect of SDS on the reaction rate

In order to investigate 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. The observed pseudo-first-order rate constants without and with SDS at different concentrations are reported in Table 1. The rate data 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 (Schmid, R. & Han, 1983) or saturation (Van Os et al 1993 and Hey 1982) 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 (Ishikawa et al 1990). The variation in rate constants with increase in [SDS] is shown in Figure 3.

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

[SDS][M]	$10^4 k_1$ (s ⁻¹)				
	1a	1b	1c	1d	1e
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
15	21.5 ± 0.05	7.12 ± 0.02	17.8 ± 0.07	5.02 ± 0.01	56.7 ± 0.09

[PSAA] = 3×10^{-3} M; [1a-1e] = 4×10^{-4} M; [H⁺] = 5×10^{-1} M; μ = 0.6 M;
solvent = 97 % H₂O-3% CH₃CN.

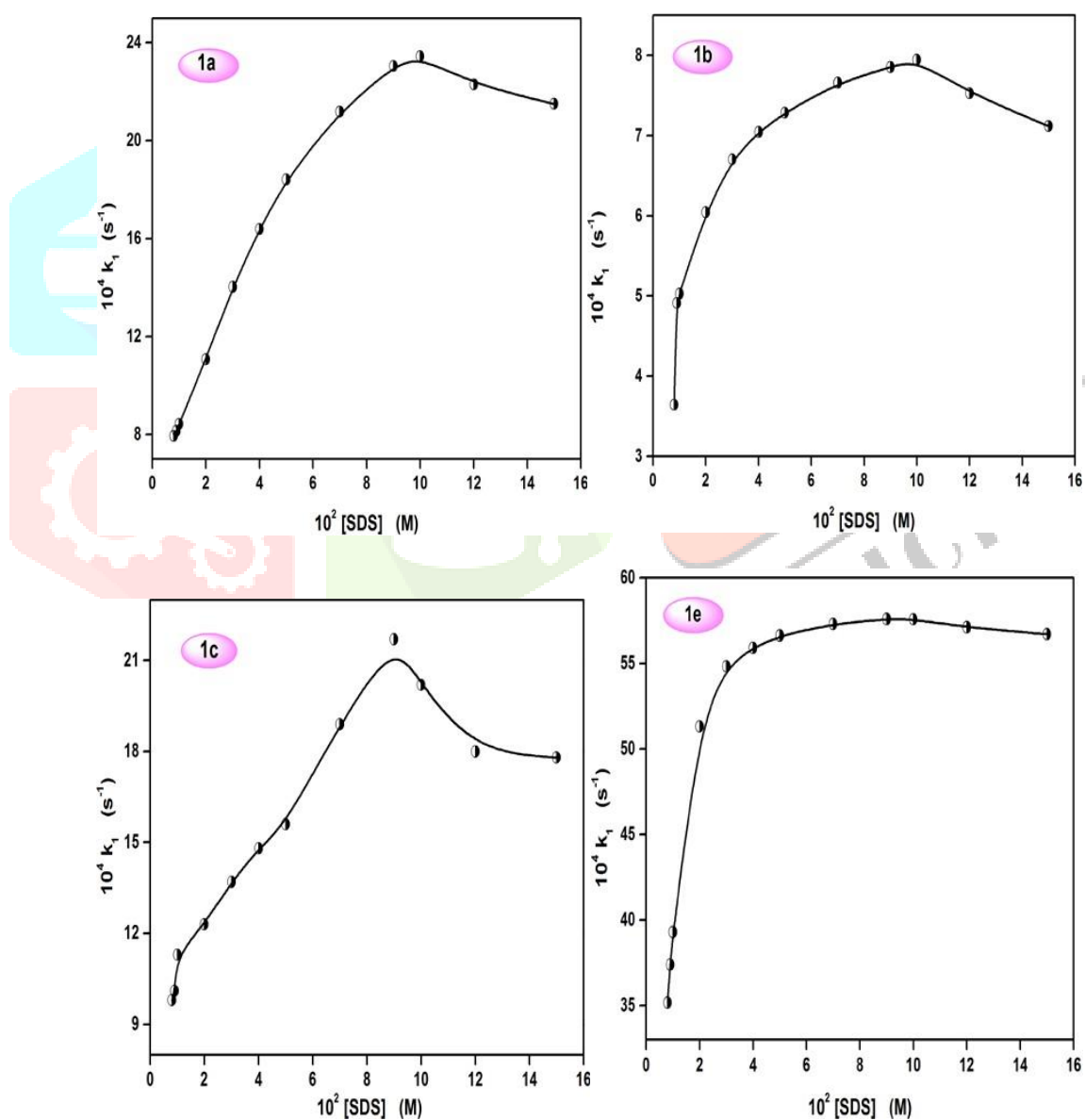


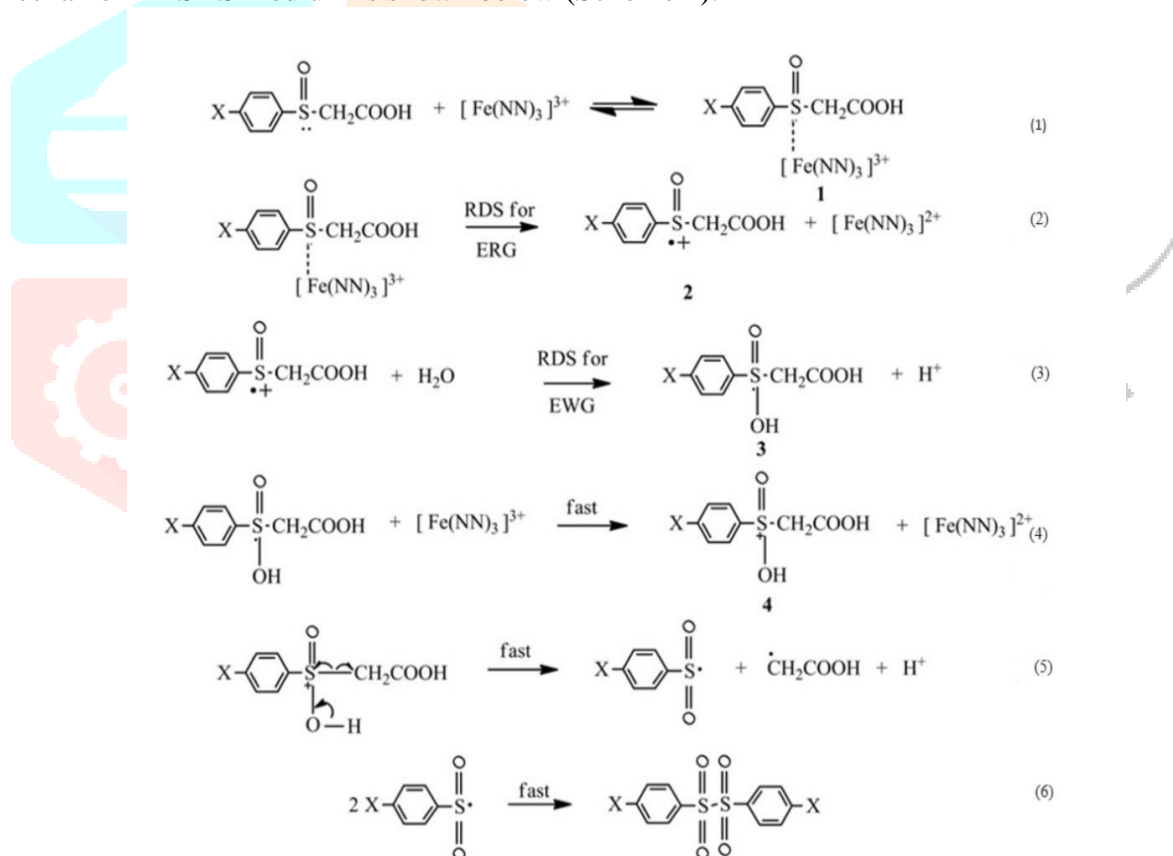
Figure 3. Effect of SDS on rate constants.

3.4 Mechanism

The reaction between $[\text{Fe}(\text{NN})_3]^{3+}$ 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 $[\text{Fe}(\text{NN})_3]^{3+}$ (1). Since $[\text{Fe}(\text{NN})_3]^{3+}$ is a strong one electron oxidant, it accepts an electron from PSAA and gets converted into $[\text{Fe}(\text{NN})_3]^{2+}$. The formation of $[\text{Fe}(\text{NN})_3]^{2+}$ is evident from the increase in the characteristic λ_{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 (Adam & Nunez, 1991 and 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 $[\text{Fe}(\text{NN})_3]^{3+}$. The rate of the electron transfer reaction is accelerated more by the electron releasing groups substituted in the phenyl ring of PSAA. The sulfoxide cation radical formation by the transfer of electron from PSAA to $[\text{Fe}(\text{NN})_3]^{3+}$ in the adduct (2) is strongly favoured by the electron releasing groups. It has been shown in the literature that higher concentration of H^+ stabilizes the sulfur cation radical (Gawandi et al 2000).

The nucleophilic attack of water on the sulfoxide cation radical leads to the formation of sulfoxide radical (3). The sulfoxide radical then transfers its electron to $[\text{Fe}(\text{NN})_3]^{3+}$ 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. The Schematic representation of the mechanism in SDS medium is shown below (Scheme 1).



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

3.5 Interpretation of micellar effect

In micellar reactions, if any reactant is interacting with the micelle then the reaction rate in micellar medium is different from that in aqueous medium. 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 the reactants in SDS micelles is shown in figure 4.

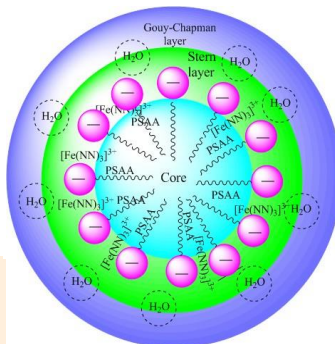


Figure 4. Schematic representation of location of reactants in SDS micelle.

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 (Hey 1982), 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). The rate acceleration observed in SDS medium is explained by preferential partitioning of the positively charged oxidizing species by electrostatic attraction and the neutral substrate by hydrophobic attraction by SDS.

3.6 Kinetic models

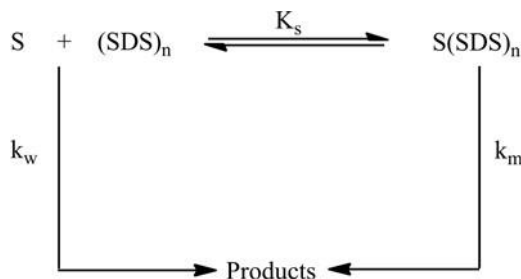
Several models have been proposed (Olatunji et al 1988) to describe the phenomenon of catalysis of rate in the presence of micelle. Micelle catalysis critically depends on the interactions of the micelle with the reactants and the activated complex. This is an extremely complicated problem because a number of different interactions are involved including those associated with the head group of the surfactant, different segments of the alkyl chain and the counterions. These models cannot be used to study the interaction between the substrate and surfactant molecules below the CMC.

Analysis of various micelle-catalysed reactions on the basis of the pseudo-phase kinetic model led to the conclusion that two principal factors are responsible for the efficiency of micellar catalysis. The first one is the concentration effects in the micellar pseudo-phase due to the hydrophobic, electrostatic and specific interactions of reactants with the micelles and another one is the change in the reactivity of reactants on transfer from aqueous phase to the micellar pseudo-phase. Study of various micelle-catalysed reactions has shown that the major source of rate enhancement is the increase in the concentration of reactants in the micellar pseudo-phase. Micellar catalysis can occur when the reactants concentrate on the micellar surface where the reaction takes place. The following sections explain some of the important pseudo-phase models.

3.6.1 Menger-Portnoy model:

To evaluate the binding constant between PSAA and SDS and to explain the micellar catalysis, kinetic data have been analysed in terms of pseudo-phase kinetic model reported by Germani et al (1989). According to Menger and Portnoy model, the variation of rate constant with $[\text{surfactant}]$ is treated on the assumption that substrate (s) is distributed between the aqueous and micellar pseudo-phase

as given in Scheme 2.



Scheme 2. Menger and Portnoy pseudo-phase model

The Scheme 2 leads the rate law (7)

$$k_1 = \frac{k_w + k_m K_s \{[D] - \text{CMC}\}}{1 + K_s \{[D] - \text{CMC}\}} \tag{7}$$

The above equation can be rearranged to Eq. 8

$$\frac{1}{k_1 - k_w} = \frac{1}{(k_m - k_w)} + \frac{1}{K_s (k_m - k_w) \{[D] - \text{CMC}\}} \tag{8}$$

where k_w and k_m are the rate constants in aqueous phase and SDS micellar medium respectively, k_1 is the observed pseudo-first-order rate constant, K_s is the binding constant of PSAA with SDS and $\{[D] - \text{CMC}\}$ represents the stoichiometric concentration of the micellar surfactant.

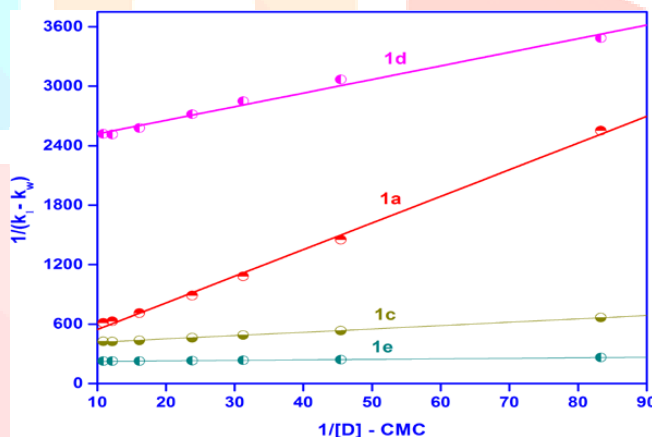


Figure 5. Linear Menger-Portnoy plots for different complexes.

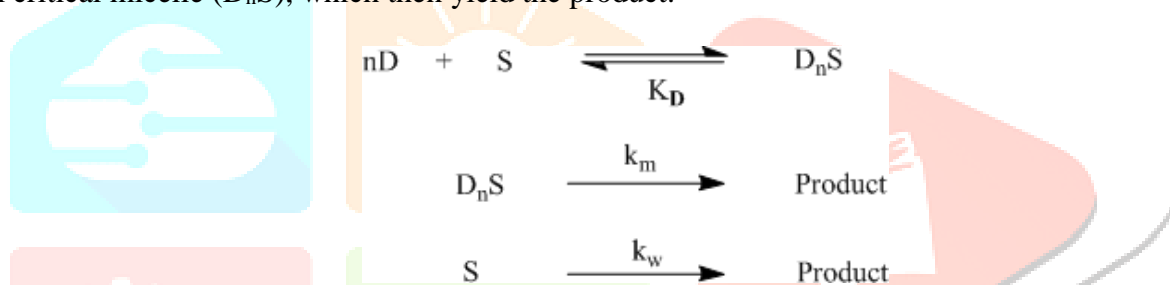
According to Eq. 8, a plot of $\frac{1}{(k_1 - k_w)}$ against $\frac{1}{([D] - \text{CMC})}$ should be linear with an intercept. The value of k_m and K_s may be evaluated from the intercept and slope of the linear plot. Linear Menger and Portnoy plots are shown in Figure 5. The values of k_m and K_s calculated from the intercept and slope of the linear plots for different complexes are tabulated in Table 2.

Table 2. Parameters evaluated employing Menger-Portnoy model.

complex	K_S (M)	$10^4 k_m$ (s ⁻¹)
1a	45.7	8.05
1b	273	0.259
1c	238	14.5
1d	567	2.07
1e	698	31.1

3.6.2 Piszkiwicz model

A kinetic model which explains an accurate dependence of the observed rate constants on surfactant concentration was developed by Piszkiwicz (1977). This model is applicable especially at low concentration of surfactant and the data may be treated without reference to CMC. According to Piszkiwicz model, (scheme 3) the substrate (S) and n number of surfactant molecules (D) aggregate to form critical micelle (D_nS), which then yield the product.

**Scheme 3.** Piszkiwicz model

where, K_D is the dissociation constant of critical micelle back to its free component, k_m is the rate constant of the reaction within the micelle and k_w is the rate constant in aqueous phase.

According to this model, the observed pseudo-first-order rate constant k_1 is expressed as a function of concentration of surfactant [D] by,

$$k_1 = \frac{k_m [D]^n k_w K_D}{K_D + [D]^n} \quad (9)$$

Eq. 9 can be rearranged to .

$$\log \left\{ \frac{k_1 - k_w}{k_m - k_1} \right\} = n \log [D] - \log K_D \quad (10)$$

A plot of $\log [(k_1 - k_w)/(k_m - k_1)]$ vs. $\log [D]$ should be linear with a slope of 'n' i.e. cooperativity index. At $\log [(k_1 - k_w)/(k_m - k_1)] = 0$, $n \log [D] = \log K_D$. Also at $[\log [(k_1 - k_w)/(k_m - k_1)] = 0]$, the surfactant shows one half of its maximum effect on catalytic rate constant. The value of $\log (D)$ at this point is designated as $\log [D]_{50}$.

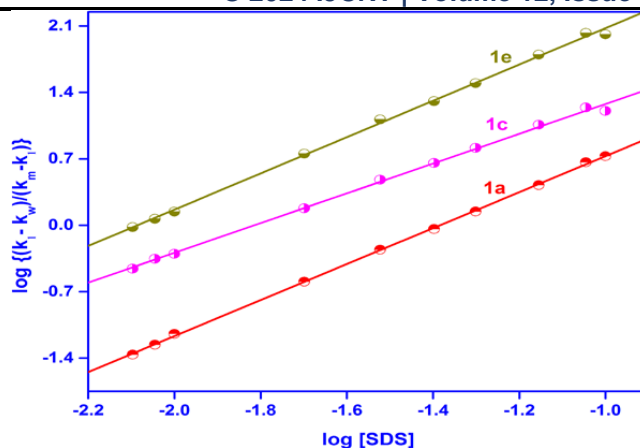


Figure 6. Piszkievich plots for different complexes.

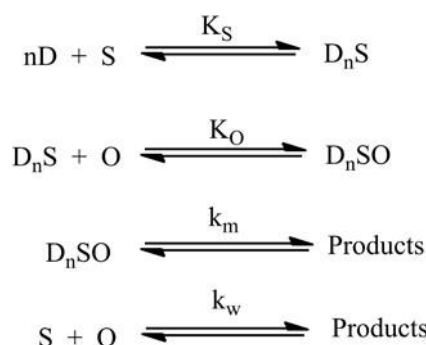
The kinetic data were analysed using Piszkievich model by plotting $\log [(k_1 - k_w)/(k_m - k_1)]$ vs. $\log [D]$ (Figure 6) and are found linear. k_m was taken as the maximum rate constant in the presence of SDS. From these double log plots, n values were calculated by least square analysis. The values of n , $\log [D]_{50}$ and decomposition constant K_D obtained with the help of these plots are given in Table 3. The observed values of n ($n > 1$) show that cooperativity of interaction is positive.

Table 3. Piszkievich cooperativity index values.

complex	cooperativity Index (n)	$-\log[D]_{50}$	$10^2 [D]_{50}$	$10^3 K_D$	$10^{-2} (1/K_D)$
1a	1.89	1.39	4.08	2.37	4.21
1b	1.24	1.69	2.06	8.09	1.24
1c	1.57	1.82	1.52	1.41	7.08
1d	1.10	1.95	1.13	7.14	1.40
1e	1.91	2.09	0.819	0.103	97.49

3.6.3 Raghvan and Srinivasan model

Raghvan and Srinivasan (1987) developed a model, for bimolecular surfactant catalysed reactions. This model is used for evaluating the binding constant of reactants with the surfactant for the reactions which predicts constancy in the values of k_1 at higher surfactant concentrations.



Scheme 4. Raghvan and Srinivasan model.

where, D and D_nSO refer to surfactant monomer and ternary complex.

The distribution of both PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ ion in aqueous and micellar pseudo-phases is considered in this model. The products are expected to form, from the reactions in aqueous medium as well as in micellar medium. This model assumes that the substrate (S) associates with surfactant aggregates to form an aggregated complex (D_nS) to which the oxidizing species (O) binds to give a

ternary complex which is represented by Scheme 4. The product formation is expected as a result of decomposition of ternary complex involving substrate, oxidant and micelle.

According to Raghvan and Srinivasan model, the observed rate constant in the presence of surfactant is given as

$$k_1 = \frac{k_w + k_m K_S [D]^n}{1 + K_S [D]^n \{1 + K_o [S]_T\}} \quad (11)$$

The Eq. 11 on rearrangement gives the following equation (Eq. 12)

$$\left[\frac{k_1 - k_w}{k_1} \right] \frac{1}{[D]^n} = K_S K_o \left[\frac{k_m}{k_1} \right] - K_S \{1 + K_o [S]_T\} \quad (12)$$

The Eq. 12 predicts a linear relationship between $\left(\frac{k_1 - k_w}{k_1} \right) \frac{1}{[D]^n}$ and (k_m / k_1) , where K_S and K_o are the binding constants of PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ respectively. Using the experimentally obtained k_w and k_m values and n from the Piszkiwicz model (Table 3), plots of $\left(\frac{k_1 - k_w}{k_1} \right) \frac{1}{[D]^n}$ vs. (k_m / k_1) were made. The plots of $\left(\frac{k_1 - k_w}{k_1} \right) \frac{1}{[D]^n}$ vs. (k_m / k_1) were found to be linear (Figure 7). The values of binding constants, K_S and K_o were calculated using intercepts and slopes of these plots. The evaluated values of K_S and K_o are reported in Table 4.

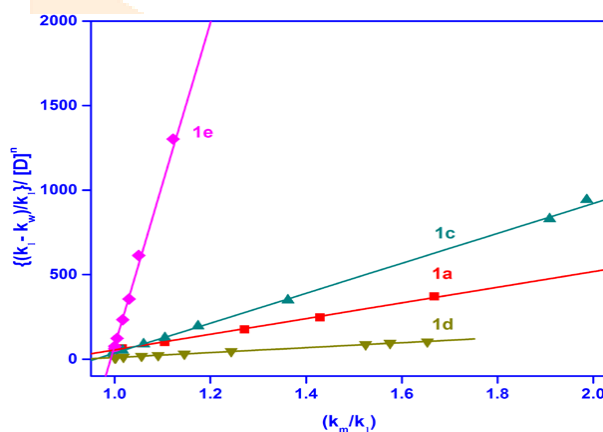


Figure 7. Raghvan and Srinivasan plot for different complexes (1a-1e).

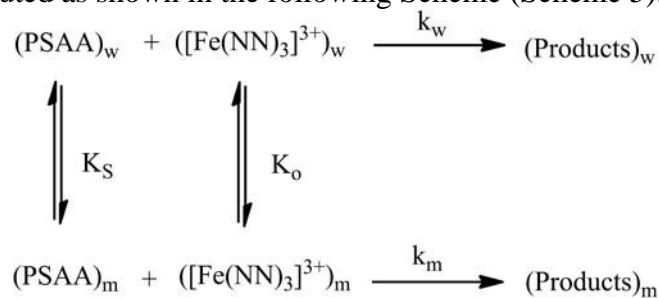
Table 4. Evaluated binding constants using Raghvan and Srinivasan model.

complex	cooperativity Index (n)	10^{-2} intercept	$10^{-2} K_S$	K_o	$10^{-2} (1/K_D)$
1a	1.89	-4.08	4.08	1.14	4.21
1b	1.24	-1.19	1.19	1.08	1.24
1c	1.57	-8.49	8.49	1.04	7.08
1d	1.10	-1.36	1.36	1.07	1.40
1e	1.91	-94.73	94.73	1.01	97.49

The values of intercept and K_S in all cases are almost same in magnitude as $K_o[S] \ll 1$. The calculated value of K_S from Raghvan and Srinivasan model is also in good agreement with the value of $1/K_D$ obtained from Piszkiwicz model (Table 3). K_D is the dissociation constant of the micelle reverts back to its free component and $1/K_D$ is the binding constant of the substrate with the micelle. The above results reveal that in SDS medium the reaction takes place through the formation of an aggregate between the SDS and PSAA. The lower values of K_o compared to K_S show that only PSAA is distributed between the micellar and aqueous phases and not $[\text{Fe}(\text{NN})_3]^{3+}$.

3.6.4 Berezin model

In Berezin model (1973), the concentration of the solution above CMC value may be assumed as a two-phase system consisting of an aqueous phase and a micellar pseudo phase. The reactants PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ may be distributed as shown in the following Scheme (Scheme 5).



Scheme 5. Berezin model

A quantitative rate expression for a bimolecular reaction occurring in aqueous phase (k_w) and micellar phase (k_m) for the pseudo-first-order rate constant is given as

$$k_1 = \frac{k_w + k'_m K_s K_o ([D] - \text{CMC})}{[1 + K_s ([D] - \text{CMC})][1 + K_o ([D] - \text{CMC})]} \quad (13)$$

where K_s and K_o are the association constants of PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ respectively with SDS, $[D]$ is the concentration of surfactant, $k'_m = (k_m/V)$, V being the molar volume of the micelle and k_w and k_m are the pseudo-first-order rate constant for electron transfer reaction between PSAA and $[\text{Fe}(\text{NN})_3]^{3+}$ in the absence and in the presence of SDS respectively. Since PSAA will be a uncharged neutral species and the oxidant, $[\text{Fe}(\text{NN})_3]^{3+}$ is a positively charged ion, the hydrophobic and electrostatic interactions will be large. Since $[D]$ is small it may be possible that $k_w \gg k'_m K_s K_o ([D] - \text{CMC})$, so that the Eq. (13) takes the following form.

$$k_1 = \frac{k_w}{[1 + (K_s + K_o)[D] - \text{CMC}] + K_s K_o ([D] - \text{CMC})^2} \quad (14)$$

The value of $([D] - \text{CMC})$ is very small and therefore $([D] - \text{CMC})^2$ can be neglected.

So the Eq. (14) can be rearranged in the following form

$$\frac{1}{k_1} = \frac{1}{k_w} + \frac{K_s + K_o}{k_w} ([D] - \text{CMC}) \quad (15)$$

The plot of $1/k_1$ vs. $([D] - \text{CMC})$ for the oxidation of PSAA by oxidants **1a** to **1d** (Figure 8) are linear only for the lower concentration of SDS. Hence Berezin model is applicable to the present reaction under study to a certain extent.

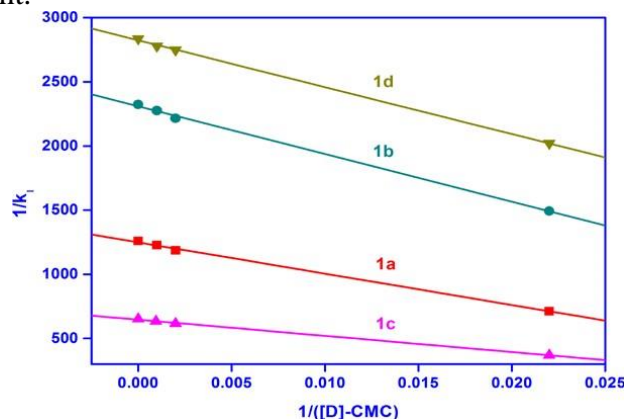


Figure 8. Berezin plots for different complexes.

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. On applying the Hammett substituent constants to the overall rate constants obtained in SDS medium, non-linear concave upward Hammett plots were obtained. The observed non-linear Hammett behaviour with upward curvature in the present study can be interpreted on the basis of 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. A suitable mechanism has been proposed. Application of different kinetic models confirms the behavior of micellar catalyzed reactions.

Acknowledgement

RJER thanks the UGC, SERO, Hyderabad, the Management of Nazareth Margoschis College and Manonmaniam Sundaranar University for the award of a fellowship under FDP. The authors gratefully thank the Management, Aditanar College of Arts and Science, Tiruchendur for providing Laboratory facilities to do the research.

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