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Importance of hydrophobic interaction in the micellar catalysed diphenyl sulfide oxidation with Iron(III)bipyridyl complex

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ABSTRACT

The effect of various surfactants on the oxidation of diphenyl sulfide (DPS) by iron(III)bipyridyl complex have been studied by observing the increase in absorbance corresponding to iron(II)bipyridyl complex. In this study, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 are used as the anionic, cationic and non-ionic surfactants respectively. In all the cases rate acceleration has been observed above their critical micellar concentrations and it is more pronounced in the presence of CTAB. The catalysis has been explained by the application of pseudophase model.

Key words : Micellar catalysis, Diphenyl sulfide, Iron(III)bipyridyl complex, Oxidation reaction, Pseudo phase model
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INTRODUCTION

Micelles are known to significantly affect the kinetics of chemical reaction [1, 2]. Only few reports have appeared so far, on the effect of micelles in the oxidation of organic sulfides [3-6]. The importance of micelles, which are used as membrane biomimetic agents in biological systems, lies in their capacity to provide a matrix for arranging the reactants sequentially for efficient interaction i.e., they help in compartmentalization of the reactants dynamically [7-13]. Surfactant entrapped water molecule provides unique micro environments for interactions and reactions, as a result of which attention has been drawn to the effect of micelles on the nature and rates of reactions. Water molecules, which are tightly bound to the surfactant head groups of micelles, resemble the hydrophilic pockets of enzymes and have high viscosities, low mobilities and polarities [14]. The solubilisation of reactants and their distribution among micelles play the most important role in micelle catalysed reactions. The kinetics of micellar solutions is governed by electrostatic and hydrophobic interactions between micelles and reactants, transition states and products. If any one of the reaction species interacts with micelles, then the presence of micelles will affect the reaction rate. The present study to investigate the effect of anionic, cationic and non-ionic surfactants on the oxidation of diphenyl sulfide with iron(III)bipyridyl complex, $[Fe(bpy)_3]^{3+}$ by spectrophotometric technique is more helpful in understanding the role of electrostatic and hydrophobic interactions. The observed results are explained in terms of pseudophase ion exchange model of micelles.

MATERIALS AND METHODS

Stoichiometry and product analysis
The stoichiometry of the reaction was determined by taking different ratios of oxidant and DPS concentrations. A known excess of $[Fe(bpy)_3]^{3+}$ was mixed with a known concentration of DPS under the experimental conditions and allowed to complete the reaction. After the reaction was complete, the concentration of the product, $[Fe(bpy)_3]^{2+}$

was calculated from its absorbance maximum and molar extinction coefficient. This gave the amount of $[Fe(bpy)_3]^{3+}$ consumed in the reaction. These results indicate that one mole of DPS was consumed per two moles of $[Fe(bpy)_3]^{3+}$. The oxidation of DPS by $[Fe(bpy)_3]^{3+}$ resulted in the formation of corresponding sulfoxide and the overall reaction may be represented as

$$2[Fe(bpy)_3]^{3+} + C_6H_5 \, S \, C_6H_5 + H_2O \quad \rightarrow \quad 2[Fe(bpy)_3]^{2+} + C_6H_5 \, S(O) \, C_6H_5 + 2H^+$$
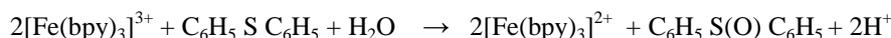
Kinetic measurements

All kinetic measurements were performed under pseudo-first order conditions with diphenyl sulfide in excess over the iron(III)-bipyridyl complex in the presence of ionic and non-ionic micelles at 303K. As the diphenyl sulfide is not completely soluble in water, the reactions were carried out in 5% of methanol medium. In the study with CTAB, sulphuric acid was used for maintaining $[H^+]$ and potassium sulphate was used for maintaining ionic strength. For SDS and TX-100 kinetics, perchloric acid was used for maintaining $[H^+]$ and ionic strength was maintained by using sodium perchlorate. The reported critical micellar concentration of SDS, CTAB and TX-100 are 8×10^{-3} M, 9.2×10^{-4} M and 3×10^{-4} M respectively. Therefore all the reactions were carried out above the CMC value of micelles, i.e., in the range of 0.001 M to 0.15 M. The reactions were followed spectrophotometrically by measuring the increase in absorbance of the product, $[Fe(bpy)_3]^{2+}$ at 522 nm. The pseudo first order rate constants were calculated from the slopes of the linear plots of log $(A_\infty - A_t)$ versus time by the method of least squares. The linearity of each fit is confirmed in terms of the values of correlation coefficient and standard deviation. The second-order rate constant is evaluated from the relation, $k_2 = k_1 / [DPS]$. The precision of k value in all the kinetic runs is given in terms of 95% confidence limits of the Student 't' test.

Determination of binding constant

The values of the binding constant, k_s of diphenyl sulfide with anionic, cationic and non-ionic surfactants were determined spectrophotometrically from the variation of absorbance, A, with [micelle] using the equation

$$\frac{A_s - A_w}{[D_n]} = A_m k_s - A_s k_s$$

where A_w and A_m are the absorbance in the absence of surfactant and the limiting absorbance upon complete incorporation into the micellar phase respectively, A_s is the absorbance in the presence of micelle and D_n is the surfactant concentration exceeding the CMC. From the spectral data a plot of $A_s - A_w / [D_n]$ vs A_s has been made. The plot gives a straight line with negative slope $(- k_s)$ and from which k_s can be evaluated. The calculated binding constants for DPS are 160, 220 and 150 M^{-1} respectively with SDS, CTAB and TX-100. These values are in good agreement with the values reported by Bunton and co-workers [15]. They have established that organic sulfides bind efficiently with anionic as well as cationic surfactants and the binding constants are in the range of 80–340 M^{-1}.

RESULTS AND DISCUSSION

The kinetic study has been carried out for the oxidation of DPS with $[Fe(bpy)_3]^{3+}$ in the presence of anionic, cationic and non-ionic micelles. In all cases the pseudo first order rate constant increases and are greater than that observed in the absence of micelles. In the oxidation of DPS with $[Fe(bpy)_3]^{3+}$, when the concentration of SDS is changed from 0.01 M to 0.15 M the rate constant increases from 0.189 M^{-1} s^{-1} to 0.623 M^{-1} s^{-1}, while in the absence of micelle the rate constant is only 0.179 M^{-1} s^{-1} (Table-1). When the concentration of CTAB and TX-100 are increased, the rate constants increase from 1.37 M^{-1} s^{-1} to 7.10 M^{-1} s^{-1} and 0.308 M^{-1} s^{-1} to 0.860 M^{-1} s^{-1} respectively.

Table-1 Effect of changing [micelle] on the rate of $[Fe(bpy)_3]^{3+}$ oxidation of DPS

[DPS] = 9.0 x 10⁻³ M [Fe(bpy)₃]³⁺ = 6.0 x 10⁻⁴ M   Temp. = 30° C
MeOH = 5% (v/v)   μ = 0.7 M   [H⁺] = 0.5 M

[SDS] (M)	k_2 ($M^{-1}s^{-1}$)	[CTAB]* (M)	k_2 ($M^{-1}s^{-1}$)	[TX-100] (M)	k_2 ($M^{-1}s^{-1}$)
0	0.179± 0.19	0	1.21± 0.13	0	0.179± 0.19
-	-	0.001	1.37± 0.13	0.005	0.308± 0.24
0.01	0.189± 0.14	0.01	1.527±0.26	0.01	0.483± 0.14
0.03	0.286± 0.03	0.03	3.09±0.35	0.03	0.583± 0.06
0.05	0.307± 0.03	0.05	4.03±0.06	0.05	0.627± 0.05
0.07	0.380± 0.03	0.07	4.77±0.05	0.07	0.640± 0.04
0.09	0.390± 0.04	0.09	5.27±0.06	0.09	0.673± 0.08
0.10	0.467± 0.04	0.10	5.96±0.07	0.10	0.730± 0.09
0.12	0.540± 0.05	0.12	6.93±0.40	0.12	0.747± 0.09
0.15	0.623± 0.04	0.15	7.10±0.07	0.15	0.860± 0.10

* [H⁺] was maintained using H₂SO₄

It was proposed that this reaction proceeds through an electron transfer mechanism with the development of positive charge on the sulfur center in the transition state [16] as shown in Scheme 1. The observed 2:1 stoichiometry between $[Fe(bpy)_3]^{3+}$ and DPS and the product, sulfoxide formed are in favour of this ET mechanism.

$$[Fe(bpy)_3]^{3+} \quad + \quad C_6H_5\,S\,C_6H_5 \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad [\,Fe(bpy)_3{}^{3+} \text{-----} C_6H_5\,S\,C_6H_5\,]$$

$$[Fe(bpy)_3]^{2+} \quad + \quad C_6H_5\,\overset{+\bullet}{S}\,C_6H_5$$

$$[Fe(bpy)_3]^{3+} \quad + \quad C_6H_5\,\overset{+\bullet}{S}\,C_6H_5 \quad + \quad H_2O \quad \xrightarrow{\text{fast}} \quad [Fe(bpy)_3]^{2+} \quad + \quad C_6H_5\,S(O)\,C_6H_5 \; + \; 2H^+$$

Scheme 1

In the presence of SDS the sulfate head group attracts the positive charge on sulfur in the transition state. The oxidant carrying a triple positive charge binds strongly with the surface of the anionic micelle by columbic interaction. Though coloumbic interaction is involved for the binding of $[Fe(bpy)_3]^{3+}$ with SDS, the reaction rate in SDS medium is least as compared to CTAB and TX-100. This can be explained by the partial neutralization of negative charges on SDS micelles by H^+ ion which is present in large excess than $[Fe(bpy)_3]^{3+}$ in the reaction medium. This factor reduces the binding of $[Fe(bpy)_3]^{3+}$ with the micelle.

As TX-100 has no charge on the surface, the possibility of binding positively charged oxidant, $[Fe(bpy)_3]^{3+}$ by electrostatic attraction can be ruled out. The observed rate enhancement demonstrates the importance of hydrophobic interaction in the binding of charged metal complex to micelles. As one of the reactants is a cation and the other is a neutral molecule, the reactants are expected to bind to the non-ionic surfactant only by hydrophobic interaction.

As $[Fe(bpy)_3]^{3+}$ carries a triple positive charge it is expected that it is expelled from the surface of the cationic micelle, as a result there will be retardation in rate. However, the rate enhancement in [CTAB] clearly demonstrates the importance of hydrophobic interaction in the binding of positively charged metal complexes to micelles. The hydrophobic interaction of the ligands of the $[Fe(bpy)_3]^{3+}$ complex with the hydrophobic part of micelles is apparently sufficient to overcome the columbic repulsion between $[Fe(bpy)_3]^{3+}$ and the cationic micellar surface. Similar explanation has been given for the aryl methyl sulfide oxidation by $[Fe(bpy)_3]^{3+}$ complexes in the presence of cationic micelle by Balakumar et al [17].

With the reasonable assumption that both the substrate and oxidant distributes between the aqueous and micellar phases and the reaction occurs in the aqueous as well as in the micellar pseudophases, the oxidation reaction in the presence of micelles can be explained by the following Scheme 2 [18,19].

$$[C_6H_5SC_6H_5]_m \quad + \quad [Fe(bpy)_3]^{3+}_m \xrightarrow{} \text{Products}$$

$$\Big\Updownarrow K_s \qquad\qquad\qquad \Big\Updownarrow K_{Fe}$$

$$[C_6H_5SC_6H_5]_w \quad + \quad [Fe(bpy)_3]^{3+}_w \xrightarrow{} \text{Products}$$

Scheme 2

The subscripts m and w stand for micellar and aqueous phases, respectively. According to Scheme 2, the Berezin [20] expression for a second order rate constant for the micellar effect on the reaction between $[Fe(bpy)_3]^{3+}$ and DPS can be given in the form of equation 1.

$$k_{obs} = \frac{k_m\,P_s\,P_{Fe}\,C_m\,V \; + k_w\,(1 - C_m V)}{[\,1 + (P_s - 1)\,C_m V\,][\,1 + (P_{Fe} - 1)\,C_m V} \tag{1}$$

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In eq.1, P_s and P_{Fe} represent the partition coefficients between micelles and water of DPS and $[Fe(bpy)_3]^{3+}$ respectively, k_m and k_w are the rate constants in the micellar and aqueous phases respectively, V is the partial molar volume of the micelles and C_m is the concentration of the micellized surfactant (C_m = [surfactant] − CMC). The volume fraction of the micelle, C_m V is small at all [surfactant] under the present experimental conditions. The partition coefficients of both reactants, P_s and P_{Fe} are also much larger than unity because of large binding constants of DPS and $[Fe(bpy)_3]^{3+}$. Hence equation 1 can be simplified into equation 2.

$$k_{obs} = \frac{k_m \ K_S \ K_{Fe} \ C_m + k_w}{(1 + K_s \ C_m) \ (1 + K_{Fe} \ C_m)} \tag{2}$$

where K_s and K_{Fe} are binding constants of sulfides and $[Fe(bpy)_3]^{3+}$ respectively.

The rearrangement of equation 2 leads to equation 3.

$$1 / k_{obs} \ (1 + K_s C_m) - k_w = 1 / k^I_m \ K_s - \ k_w \ (1 + K_{Fe} \ C_m) \tag{3}$$

The value of k_w is the rate constant obtained for the reaction without the surfactant. The rate constant in the micellar pseudophase, k^I_m and the binding constant of $[Fe(bpy)_3]^{3+}$ with the micelle, K_{Fe}, can be evaluated from equation 3 by plotting the terms in the left hand side against $1/C_m$. The values of k^I_m evaluated from the plots are collected in Table-2.

Table-2 Second order rate constants (k^I_m) for the micellar pseudo phase and $k_2{}^m/ k_w$ for the $[Fe(bpy)_3]^{3+}$ oxidation of DPS

Micelle	k^I_m x 10	k_w	$k_2{}^m/ k_w$
SDS	0.031	0.179	0.170
CTAB	0.04	1.213	0.120
TX-100	0.094	0.179	0.194

To compare the second order rate constants in water, k_w with the second order rate constants in the micellar phase, the volume of micellar phase must be known. Second order rate constants in the micellar phase with same units as that in aqueous phase, $k_2{}^m$ $M^{-1}s^{-1}$ is calculated by multiplying k^I_m with molar volume of the reactive region at the micellar surface, $V = 0.37$ M^{-1}, on the basis of earlier reports [17]. To compare the rate constants in the micellar phase ($k_2{}^m$) with the corresponding values in aqueous phase (k_w), the values of the ratio ($k_2{}^m / k_w$) for different micelles are calculated and given in Table-2.

Figure. 1. Plot of k_m / k_{aq} vs. C_m for various micelles
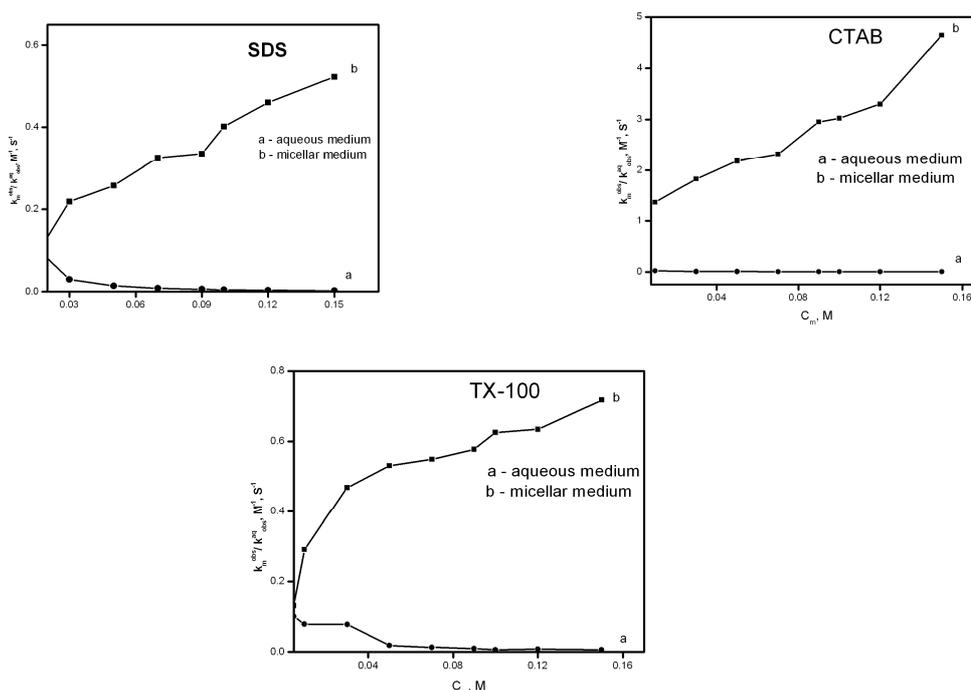
The contribution of rate constants in micellar medium (k^m_{obs}) and aqueous medium (k^{aq}_{obs}) towards the observed rate constant can be separated using equations 4 and 5 at various concentrations of micelles and are given in Table-3 and Figure 1. These results show that the observed rate constant in aqueous phase (k^{aq}_{obs}) is always less than that of the reaction in micellar phase (k^m_{obs}).

$$k^m_{obs} = \frac{k_m \ K_S \ K_{Fe} \ C_m}{(1+K_s \ C_m) \ (1+ K_{Fe} \ C_m)} \qquad (4)$$

$$k^{aq}_{obs} = \frac{k_w}{(1+K_s \ C_m) \ (1+ K_{Fe} \ C_m)} \qquad (5)$$

Table -3: Second order rate constants in micellar (k^m_{obs}) and aqueous media (k^{aq}_{obs}) for[Fe(bpy)$_3$]$^{3+}$oxidation of DPS at 303K

SDS				CTAB				TX-100			
[C_m], M	k_{obs}	k^m_{obs}	k^{aq}_{obs} x 10	[C_m], M x 10^2	k_{obs}	k^m_{obs}	k^{aq}_{obs} x 10	[C_m],M x 10^2	k_{obs}	k^m_{obs}	k^{aq}_{obs} x 10
-	-	-	-	0.408	1.21	0.570	0.387	0.0474	0.308	0.132	1.01
0.002	0.189	0.046	1.317	0.908	1.37	0.905	0.243	0.0974	0.483	0.291	0.794
0.022	0.286	0.218	0.298	2.908	1.83	1.54	0.095	0.2974	0.583	0.468	0.789
0.042	0.307	0.257	0.142	1.908	2.18	1.90	0.057	0.4974	0.627	0.531	0.190
0.062	0.38	0.325	0.085	6.908	2.32	2.04	0.041	0.6974	0.64	0.549	0.132
0.082	0.39	0.335	0.057	8.908	2.95	2.58	0.031	0.8974	0.673	0.577	0.101
0.092.	0.467	0.401	0.048	9.908	3.02	2.62	0.027	0.9974	0.73	0.625	0.066
0.112	0.54	0.460	0.035	11.908	3.30	2.84	0.023	1.1974	0.747	0.634	0.079
0.142	0.923	0.823	0.024	14.908	4.64	3.92	0.017	1.4974	0.86	0.718	0.062

CONCLUSION

The oxidation reaction is found to be catalysed by SDS, CTAB and TX-100 micelles. The increase in rate with increase in [micelle] can be explained with hydrophobic interaction. The micellar effect in this oxidation can be explained by pseudophase ion exchange model.

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