

## Effect of Surfactants on Kinetics and Oxidation of Decoloration of Methyl Violet and Ethyl Violet by Potassium Peroxydisulphate

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The kinetics of oxidation of methyl violet (MV) and ethyl violet (EV) by potassium peroxy disulphate ( $K_2S_2O_8$ ) have been studied colorimetrically in the presence of cationic surfactant cetyl trimethyl ammonium bromide ( $C_{16}TABr$ ), anionic sodium dodecyl sulphate (SDS) and nonionic (Triton X-100) surfactants at 30°C. The reaction is slowed down in the presence of SDS and Triton X-100 while rate acceleration is observed in  $C_{16}TABr$  micellar media. On the basis of kinetic results, it can be inferred that only electrostatic interactions are dominant in the case of SDS whereas hydrophobic and electrostatic interactions play an important role for  $C_{16}TABr$ .

**Key Words:** Surfactants, Kinetics, Oxidation, Decoloration, Methyl violet, Ethyl violet, Potassium peroxy disulphate..

### INTRODUCTION

During the last decade there has been growing interest in the influence of surfactant on chemical reactions because of their wide applications in biological, medical and dyes industries<sup>1-3</sup>. Organic reactions<sup>4</sup> in aqueous surfactants undergo either rate enhancement or inhibition and this phenomenon has been attributed to electrostatic and hydrophobic interactions between the substrate and surfactant aggregates. The effect of surfactants sodium dodecyl sulphate (SDS), Triton X-100 and  $C_{16}TABr$  on the rate constants for oxidation of  $[Co(terpy)_2]^{2-}$  by a series of Co(III) complexes of phenanthroline ligand and its substituted derivatives has been measured; the kinetic data revealed that rate inhibits in SDS micelles<sup>5</sup>. Nonionic surfactants show a retardation effect on the kinetics of Fe(III) ion with ferrocene and its 1,1'-dimethyl and 1,1'-dibutyl derivatives<sup>6</sup>. The kinetics of oxidation of malachite green (MG) by potassium peroxydisulphate<sup>7</sup>, Mn(III)<sup>8</sup> have been reported. The present investigation reports the effect of  $C_{16}TABr$ , SDS and Triton X-100 micelles on the oxidation of methyl violet (MV) and ethyl violet (EV) by  $S_2O_8^{2-}$  ion.

### EXPERIMENTAL

Methyl violet and ethyl violet were purified by dissolving in dimethyl formamide and precipitating with the help of trichloro ethylene<sup>9</sup>. Potassium peroxydisulphate was obtained from Ranbaxy. All the surfactants were of Sigma Chemicals and used as such. All solutions were prepared in double distilled water and used within three days of their preparation. The experiments were carried out by EQ-650 colorimeter (Equip-Tronics). Methyl violet and ethyl violet in micellar media are found to obey Beer's law up to  $3.5 \times 10^{-5}M$ . The concentration of the substrate in the reaction system has been kept below this value.

## RESULTS AND DISCUSSION

Cationic surfactant  $C_{16}TABr$  micelles affect the pseudo first order rate constant for the oxidation of methyl violet and ethyl violet at different concentrations of  $C_{16}TABr$  at  $30^\circ C$ ; the values of rate constants are collected in Table-1. The rate constant ( $K_{obs}$ ) increases with increase in cationic surfactant concentration, passes through a maximum and decreases at high surfactant concentration in the premicellar concentration region. Considerable evidence<sup>10</sup> is available to show that concentration of reactants into a small bulk at the micellar surface is a major source of enhancement of bimolecular reactions. It is quite possible that the mixed micelle of dye ion and  $C_{16}TABr$  are formed and  $S_2O_8^{2-}$  are bound in the micelle. The mixed cationic dye and  $C_{16}TABr$  micelles formed can also affect the proximate approach of  $S_2O_8^{2-}$  by hydrophobic and electrostatic forces respectively. Thus with increase in the concentration of  $C_{16}TABr$  the rate increases and attains a maximum value. Further increase in the concentration of  $C_{16}TABr$  produces increases in the concentration of counter ion  $Br^-$  that displaces the  $S_2O_8^{2-}$  in the micelles in proximity of the bound dye molecules. This could account for descending branch of the experimental curve observed.

TABLE-1  
EFFECT OF VARYING  $[C_{16}TABr]$  ON THE OXIDATION OF METHYL VIOLET AND ETHYL VIOLET BY POTASSIUM PEROXYDISULPHATE AT  $30^\circ C$

$[Dyes] = 3.5 \times 10^{-5} M$ ;  $[K_2S_2O_8] = 7.5 \times 10^{-2} M$

$[C_{16}TABr]$ $\times 10^4 M$	$k_{obs} (min^{-1})$	
	Methyl violet	Ethyl violet
0.0	0.1502	0.1775
0.1	0.1746	0.2132
0.2	0.2149	0.2426
0.3	0.2378	0.2625
0.4	0.2533	0.2801
0.6	0.2149	0.2425
0.8	0.1842	0.2075
1.0	0.1842	0.2075

An anionic surfactant SDS inhibited the rate of oxidation of methyl violet and ethyl violet. The variation of the pseudo first order rate constant for methyl violet and ethyl violet at different concentrations of SDS at  $30^\circ C$  is shown in Fig. 1. It is seen from the figure, that the inhibition in reaction rate by SDS not only starts below CMC but also attains at saturation well below the reported value of CMC for SDS (CMC = 8.3 mM). The observation of micellar effects in this case is indicative of the fact that catalytically functional micellar aggregates are found in the reaction system. At very low SDS concentration, well below the CMC, the inhibition rate for the alkaline fading of the crystal violet is explained in terms of "monomeric-dye-SDS oligomer" interacted product<sup>11</sup>. Therefore, the retardation in the reaction rate by SDS in the premicellar concentration region in the

present reaction may be assumed with the formation of "monomeric-dye-surfactant oligomer" at the lower concentrations of SDS bearing a negative charge on it which would repel the attacking  $S_2O_8^{2-}$  ions. Hence SDS retards the reaction rate in the premicellar concentration region.

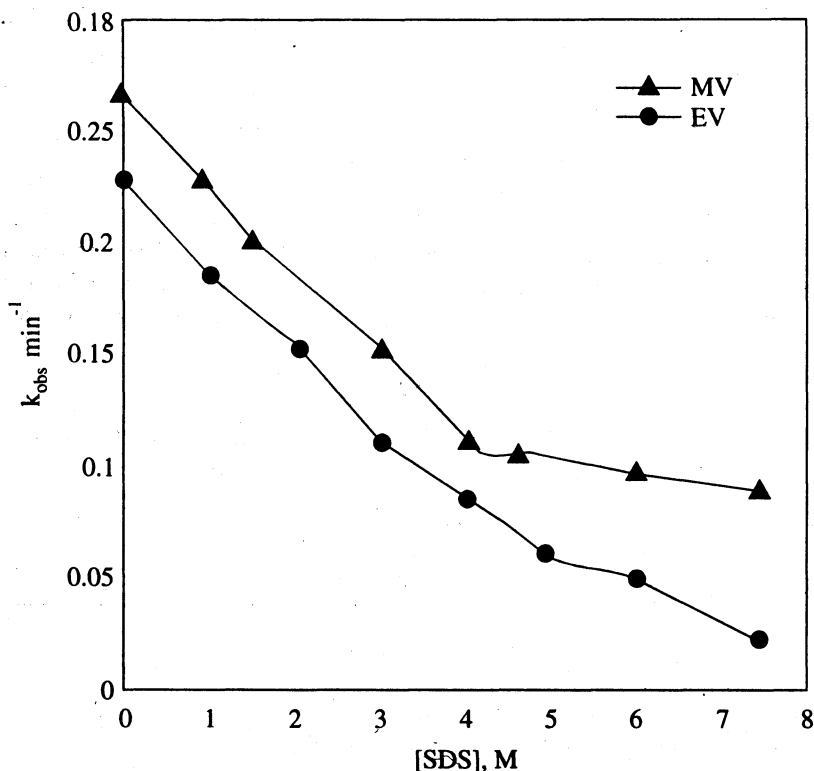


Fig. 1 Influence of SDS on the oxidation of Methyl Violet and Ethyl Violet by  $K_2S_2O_8$  at 30°C. [MV AND EV] =  $3.5 \times 10^{-5}$  M;  $[K_2S_2O_8] = 0.075$  M.

Nonionic surfactant Triton X-100 inhibited the rate of oxidation of methyl violet and ethyl violet. For variation of pseudo first order rate constant for methyl violet and ethyl violet at different surfactant concentrations at 30°C, the kinetic data for the oxidation reaction are given in Table-2. The rate decreases rapidly and then becomes almost constant with the increase in the nonionic surfactant concentration. It has been found that nonionic surfactants have good affinity for TPM dyes; to form complex, the nonionic surfactant does not carry any ionizable group so that the binding has to be accomplished by intermolecular forces, possibly consisting of mixed micelles, involving both dye and surfactant. The fast decrease in the rate may be due to the strong complex formation between the dye and surfactant. The decrease in the rate constant in case of Triton X-100 may be due to the neutral surface of nonionic micelles; the oxygen of polyoxyethylene

group creates a negative surface, which attracts a positively charged dye cation and repels the  $S_2O_8^{2-}$  ion.

TABLE-2  
PSEUDO FIRST ORDER RATE CONSTANT FOR THE OXIDATION OF METHYL VIOLET AND ETHYL VIOLET BY POTASSIUM PEROXYDISULPHATE AT 30°C IN PRESENCE OF VARYING CONCENTRATION OF TRITON X-100

[Dyes] =  $3.5 \times 10^{-5}$  M;  $[K_2S_2O_8] = 7.5 \times 10^{-2}$  M

[Triton X-100] % (v/v)	$k_{obs}$ ( $min^{-1}$ )	
	Methyl violet	Ethyl violet
0.00	0.2303	0.2631
0.03	0.1934	0.2301
0.06	0.1250	0.2142
0.09	0.0907	0.2001
0.12	0.0658	0.1899
0.15	0.0518	0.1844
0.18	0.0383	0.1798

The effect of temperature on the reaction of dye with  $S_2O_8^{2-}$  ion has been studied at fixed concentration of  $C_{16}TABr$ , substrate and potassium peroxydisulphate. The reaction is found to obey Arrhenius equation. The values of activation parameters, viz.,  $E_a^\ddagger$ , frequency factor  $Z$ ,  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ , in the aqueous and micellar media are summarized in Table-3. The values of activation energy obtained from the Arrhenius plots for  $C_{16}TABr$  catalyzed reaction in aqueous solutions suggest that a decrease in activation energy in presence of  $C_{16}TABr$  relative to aqueous medium is one of the factors responsible for the catalysis. Nearly same values of  $\Delta G^\ddagger$  in the absence and presence of surfactant shows that similar mechanism for oxidation is operative in aqueous and micellar media. Negative values of the entropy of activation suggest that the reaction of dye and  $S_2O_8^{2-}$  ion takes place between ionic species. The values of frequency factor in presence of  $C_{16}TABr$  and in the absence of surfactant show lesser number of collisions required in forward reaction in the presence of  $C_{16}TABr$ .

The quantitative analysis of the data has been used by the model proposed by Piszkiwicz<sup>12</sup>, according to this scheme:

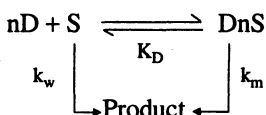


Fig. 1. Influence of SDS on the SDA on the oxidation of methyl violet and ethyl violet by  $K_2S_2O_8$  at 30°C.  $[MV \text{ AND } EV] = 3.5 \times 10^{-5}$  M;  $[K_2S_2O_8] = 0.075$  M

The observed rate constant ( $k_{obs}$ ) can be expressed as a function of the concentration of the surfactant D by equation (1).

$$\log (K_w - K_{\text{obs}})/(K_{\text{obs}} - K_m) = n \log [D] - \log K_D \quad (1)$$

where  $K_D$  is the dissociation constant of the micelle substrate complex,  $K_m$  is rate constant within the micelle and  $K_w$  is the rate constant in the absence of surfactant.

TABLE-3  
ACTIVATION PARAMETERS FOR THE OXIDATION OF METHYL VIOLET AND  
ETHYL VIOLET WITH POTASSIUM PEROXYDISULPHATE IN ABSENCE  
AND PRESENCE OF  $C_{16}\text{TABr}$

Parameters	$E_a^\ddagger$ (kJ mol <sup>-1</sup> )	Z (L mol <sup>-1</sup> sec <sup>-1</sup> )	$\Delta S^\ddagger$ (J K <sup>-1</sup> /mol <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )
<b>Methyl Violet</b>					
In aqueous solution	24.78	$2.81 \times 10^3$	-195.65	19.75	79.03
$C_{16}\text{TABr}$	13.52	$5.42 \times 10^1$	-228.49	84.85	77.71
<b>Ethyl Violet</b>					
In aqueous solution	27.59	$1.01 \times 10^4$	-185.00	22.55	78.61
$C_{16}\text{TABr}$	15.07	$1.11 \times 10^2$	-222.53	10.03	77.46

As required by eq. (1), plots of  $\log (k_w - k_{\text{obs}}/k_{\text{obs}} - k_m)$  vs.  $\log D$  are linear (Fig. 2) for catalyzed and inhibited reactions. The values of  $n$ ,  $\log[D]_{50}$ ,  $1/K_D$ ,  $K_D$ , in fading of methyl violet and ethyl violet by  $\text{S}_2\text{O}_8^{2-}$  ions in presence of  $C_{16}\text{TABr}$ , SDS and Triton X-100 are obtained from the plots and are given in Table-4. The values of  $\log [D]_{50}$  represent the concentration of detergent required for half maximal catalysis or inhibition of reaction. This demonstrates the existence of functional sub-micellar aggregates involving detergent and substrate molecules of varying stoichiometries. In cationic catalyzed and anionic inhibited reaction the value of  $n$  is greater than 1.0. The value of  $n > 1$  indicated positive co-operativity, which implies the stimulation of additional substrate molecule by interaction of the first molecule with the micelle<sup>12</sup>. It is seen from the Table-4 that the values of binding constant ( $K_b$  which is reciprocal of  $K_D$ ) for anionic surfactants are higher than  $C_{16}\text{TABr}$ . This shows that in the case of SDS both hydrophobic and electrostatic interactions between positively charged substrate and negatively charged aggregate favour each other, whereas in  $C_{16}\text{TABr}$  and Triton X-100, only hydrophobic interactions are responsible for the binding between substrate and  $C_{16}\text{TABr}$  and Triton X-100 aggregates.

However, the catalysis by  $C_{16}\text{TABr}$  occurs because the opposite charge on the micelle and reactant facilitated the approach of  $\text{S}_2\text{O}_8^{2-}$  to the catalytic aggregate and due to destabilization of the ground state of TPM dyes as compared to the transition states, whereas in presence of SDS inhibitory effect is observed due to

the non-approachability  $S_2O_8^{2-}$  to the strongly bound substrate in the catalytic aggregate of similar charge and due to the stabilization of ground state of TPM dyes. However, the inhibition in case of Triton X-100 may be due to strongly bound substrate in the catalytic aggregate of substrate and surfactant aggregate. Although the surface of nonionic micelle is neutral, the oxygen of polyoxyethylene group creates a negative surface, which attracts a positively charged dye cation and repels  $S_2O_8^{2-}$  ion.

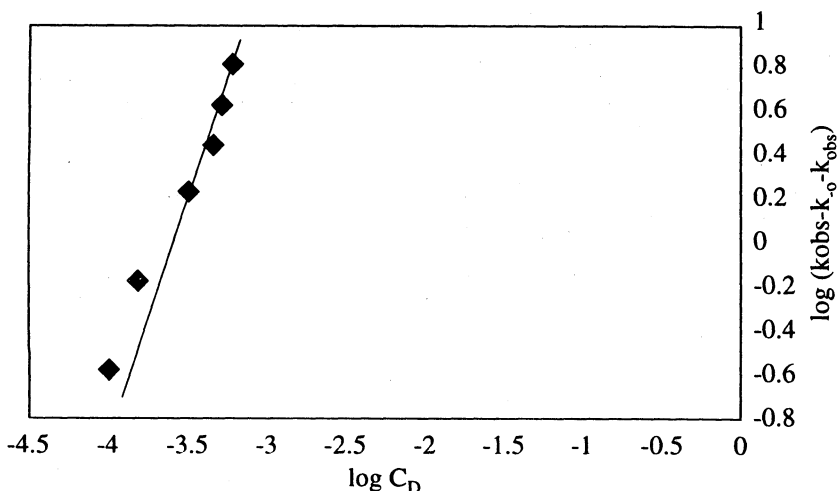


Fig. 2 Index of co-operativity ( $n$ ) for the oxidation of methyl violet by potassium peroxydisulphate in presence of SDS

TABLE-4  
VALUES OF  $n$ ,  $\log [D]_{50}$ ,  $1/K_D$  AND  $K_D$  IN OXIDATION OF METHYL VIOLET AND ETHYL VIOLET BY POTASSIUM PEROXYDISULPHATE IN PRESENCE OF CATIONIC, ANIONIC AND NONIONIC SURFACTANTS AT 30°C

Surfactant	$n$	$\log[D]_{50}$	$1/K_D$	$K_D$
<b>Methyl Violet</b>				
$C_{16}TABr$	1.26	-4.90	$1.69 \times 10^6$	$6.07 \times 10^7$
SDS	2.21	-3.58	$8.18 \times 10^7$	$1.22 \times 10^{-8}$
Triton X-100	3.14	-2.96	$2.08 \times 10^9$	$4.79 \times 10^{-10}$
<b>Ethyl Violet</b>				
$C_{16}TABr$	1.70	-4.83	$1.68 \times 10^8$	$5.93 \times 10^{-9}$
SDS	2.32	-3.71	$4.29 \times 10^8$	$2.32 \times 10^{-9}$
Triton X-100	3.34	-2.91	$7.25 \times 10^9$	$1.37 \times 10^{-10}$

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