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Micellar effects on the reduction of Orange-II by sulphite ions

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Abstract : The kinetic studies on the reduction of Orange-II by sulphite ion in a buffer medium of pH 7.0 revealed that the reaction is first order with respect to Orange-II and sulphite ion concentrations. A suitable mechanism is proposed based on the results. Cationic surfactant cetyltrimethyl ammonium bromide (CTAB) catalysed the reduction by 23 times whereas anionic surfactant sodium dodecyl sulphate (SDS) and nonionic surfactant polyoxy ethylene (23) dodecanol (Brij-35) inhibited the reduction by 4.7 and 31 times. These effects are discussed on the basis of interactions of the above compounds and micelles of different charge type. Binding parameters have been calculated by analysing the data using pseudo phase model.

Keywords : Micellar effect, Orange-II, sulphite ion.

Azo dyes are well known[1,2] for the analytical applications. These compounds have strong pharmacological activity[3,4]. The reduction of azo benzenes to hydrazo benzenes constitutes a convenient route to the latters synthesis[5]. The reduction is brought about by using hydrazine[6], titanous chloride[7], lithium aluminium hydride[8,9], etc. as reducing agents.

Ogawa *et al.*[10] have studied the kinetics of reduction of a series of azo dyes and have found that $SnCl_2$ reduces the compounds to amines directly while Na_2SO_3 reduces them to hydrazo derivatives initially which gradually get converted to the corresponding amines.

However, no attempts have been made to systematically study the kinetics of reduction of azo dyes in micellar media. We have, therefore, attempted to explore the micellar media for the reduction of azo dyes by sulphite ions. This paper deals with the kinetics of reduction of Orange-II by SO_3^{2-} in micelles of different charge type.

Results and discussion

Kinetic studies in the absence of surfactants :

The reduction of Orange-II by SO_3^{2-} was carried out in phosphate buffer of pH 7.0. Kinetic runs were carried out under pseudo-first order conditions keeping the concentration of sulphite ions much higher than that of the substrate Orange-II. A decrease in absorbance of the substrate with time was noted at 484 nm. The dependence of the reduction rate on the substrate concentration was examined by recording kinetic runs at varying [Orange-II] in the range $3 \times 10^{-5} - 5 \times 10^{-5}$ M (Table 1). Plots of log (absorbance) versus time were found to be linear indicating first order of the reaction with respect to the substrate.

The dependence of the reduction rate on $[SO_3^{2-}]$ was examined by recording the kinetic runs at varying $[SO_3^{2-}]$ in the range $5 \times 10^{-3} - 3 \times 10^{-2}$ M . Increase in $[SO_3^{2-}]$ increases the rate linearly indicating that the reaction is first order with respect to SO_3^{2-} (Table 1). Influence of added NaCI on the rate of reduction of Orange-II by SO_3^{2-} was studied by varying the concentration of NaCl. Increase in [NaCl] has negligible effect on the rate. Dependence of the rate of reduction of Orange-II on H^+ concentration was examined in the pH range of 2.4–11.9. Rate increased with the increase in pH upto 8.0 (Table 1).

Kinetic studies in the presence of surfactants :

Kinetics of reduction of Orange-II by SO_3^{2-} was studied in the presence of cationic surfactant CTAB, nonionic surfactant Brij-35 and anionic surfactant SDS.

The effect of [Orange-II], $[SO_3^{2-}]$ and pH on the rate of reduction of Orange-II by SO_3^{2-} was studied in the presence of 0.001 M CTAB and their effect on the rate

Table 1. Effect of Orange-II, SO_3^{2-}, Cl^- concentrations and pH on the rate of reduction of Orange-II by SO_3^{2-} at 25 °C (pH = 7.0)

$[SO_3^{2-}] = 1 \times 10^{-2}$ *M*;		[Orange-II] $= 4 \times 10^{-5}$ *M*;		[Orange-II] $= 4 \times 10^{-5}$ *M*, $[SO_3^{2-}] = 1 \times 10^{-2}$ *M*			
[Orange-II] $\times 10^5$, *M*	$k \times 10^3$, s^{-1}	$[SO_3^{2-}] \times 10^2$, *M*	$k \times 10^3$, s^{-1}	$[Cl^-]$, *M*	$k \times 10^3$, s^{-1}	pH	$k \times 10^4$, s^{-1}
3.0	1.23	0.5	0.89	0	1.46	2.4	0.13
4.0	1.17	1.0	1.69	0.01	1.51	4.34	0 14
4.5	1.25	1.5	2.51	0.02	1.54	5.0	0.12
5.0	1.39	2.0	3.46	0.03	1.55	5.5	1.34
		3.0	5.35	0.04	1.42	6.0	1.24
				0.05	1.44	6.5	6.57
				0.07	1.43	7.0	12.36
				0.09	1.49	7.5	11.97
				0.11	1.55	8.0	17 00
				0.15	1.51	9.22	5 16
				0.21	1.5	10.0	3.15
				0.31	1.51	11.9	0.02
					1.61		

Table 2. Effect of Orange-II, SO_3^{2-}, Cl^- concentrations and pH on the rate of reduction of Orange-II by SO_3^{2-} in presence CTAB at 25 °C (pH = 7.0)

$[SO_3^{2-}] = 5 \times 10^{-3}$ *M*;		[Orange-II] $= 4 \times 10^{-5}$ *M*;		[Orange-II] $= 4 \times 10^{-5}$ *M*, $[SO_3^{2-}] = 5 \times 10^{-3}$ *M*			
[Orange-II] $\times 10^5$, *M*	$k \times 10^3$, s^{-1}	$[SO_3^{2-}] \times 10^2$, *M*	$k \times 10^3$, s^{-1}	$[Cl^-]$, *M*	$k \times 10^3$, s^{-1}	pH	$k \times 10^4$, s^{-1}
2.0	1.25	2.5	0.56	0.00	13.66	2.4	0.007
3.0	1.30	5.0	1.23	0.005	11.47	4.34	0.16
4.0	1.20	7.5	1.72	0.01	8.15	5.0	4.73
5.0	1.28	10.0	2.14	0.02	5.90	5.5	5.25
				0.03	5.05	6.0	6.81
				0.04	3.53	6.5	9.43
				0.05	2.82	7.0	11.92
				0.06	2.14	7.5	12.90
				0.07	1.75	8.0	13.87
				0.09	1.18	9.22	5.28
				0.11	0.18	10.00	0.55
				0.13	0.058		
				0.21	0.045		
				0.31	0.023		
					0.002		

was similar to that in absence of surfactant (Table 2). Rate of the reaction decreased significantly with increase in $[Cl^-]$. Effect of cationic micelles on the rate of reduction of Orange-II by SO_3^{2-} was studied by varying the CTAB concentration in the range $1 \times 10^{-5} - 1 \times 10^{-2}$ *M*.

Effect of anionic surfactant SDS and nonionic surfactant Brij-35 on the rate of reduction of Orange-II by SO_3^{2-} was studied by varying the concentration in the range $1 \times 10^{-5} - 6 \times 10^{-2}$ *M*. The reaction exhibited first order dependence on substrate and SO_3^{2-} concentrations. Based on the observed results the following scheme of mechanism is proposed for the reduction of Orange-II by SO_3^{2-}.

The observed rate law under experimental conditions may be given as

$$-\frac{d}{dt}\,[\text{Orange-II}] = K'[S^-][SO_3^{2-}] \qquad (1)$$

According to Scheme 1, the rate of disappearence of Orange-II is given by

$$\text{Rate} = k_1[S^-][SO_3^{2-}] + k_2[SH][SO_3^{2-}] \qquad (2)$$

The total concentration of the substrate can be expressed as

$$[S^-]_T = [S^-]\ [SH] \qquad (3)$$

The concentrations of S^- and SH in terms of S_T and the protonation constant (K_p) can be given as

$$[S^-] = \frac{[S^-]_T}{1 + K_p[H^+]} \qquad (4)$$

$$[SH] = \frac{[S^-]_T\, K_p[H^+]}{1+K_p[H^+]} \qquad (5)$$

Substituting for [SH] and $[S^-]$ in eq. (2), the rate of the reaction can be expressed as

$$\text{Rate} = \frac{k_1 + k_2K_p[H^+]}{1 + K_p[H^+]}\,[S^-]_T[SO_3^{2-}] \qquad (6)$$

Rate equation is consistent with the observed rate law. Comparison of eqs. (1) and (6) yields

$$K' = \frac{k_1 + k_2K_p[H^+]}{1+K_p[H^+]} \qquad (7)$$

Eq. (7) explains the rate dependence on H^+ concentration. Rate decrease with increase in the H^+ concentration till pH 8.0 indicating that the reaction proceeds predominantly through the path involving S^- in this pH range (Scheme 1).

$$S^- + H^+ \overset{K_p}{\longleftrightarrow} SH$$

$$S^- + SO_3^{2-} \xrightarrow{k_1} \text{Products}$$

$$SH + SO_3^{2-} \xrightarrow{k_2} \text{Products}$$

Scheme 1

Effect of cationic surfactant :

Catalysis of the reaction in the presence of 1×10^{-3} *M* CTAB is found to be 23 times. At very low [CTAB] the rate constant decreased but in the concentration range $1 \times 10^{-4} - 1 \times 10^{-3}$ *M* rate increased steeply leading to a maximum. Above 1×10^{-3} *M* CTAB rate decreased from the maximum value. Catalysis may be qualitatively rationalised on the basis of charges on the reactive species and their hydrophobic character. Hydrophobic nature of the substrate anion (S^-) and favourable electrostatic forces between S^- and CTA^+ micelle result in the incorporation of S^- into the micellar phase. Concentration of SO_3^{2-} at the CTA^+ micellar surface should be more than that in the bulk phase due to electrostatic attractive forces. The observed catalysis may be the manifestation of the increased concentration of both the substrate and SO_3^{2-} at the micellar surface.

Quantitative treatment of the effect of CTAB :

Rate-surfactant concentration profile for the reduction of Orange-II by SO_3^{2-} in the presence of CTAB showed a maximum at 0.001 *M* CTAB. Similar effect has been observed in micellar catalysis of carbocation reactions[11,12]. Romsted[13] analysed the data at high detergent concentrations of the reactions which exhibited the rate maxima, by an ion-exchange model. He incorporated the concept of counterion exchange between micellar and bulk phases, into the Menger and Portnoy[14].

In this treatment the decrease in the rate at high detergent concentrations has been attributed to (i) dilution of reactants in the micellar phase and (ii) a decrease in the micellar bound reactive counterion concentration as a result of competition between it and the non reactive counterion for binding to Stern layer of the micelle[15]. This competition in the case of reduction of Orange-II by SO_3^{2-} in the presence of CTAB can be represented by the following exchange equilibrium.

$$SO_3^{2-}{}_w + Br_m^- \longrightarrow SO_3^{2-}{}_m + Br_w^- \qquad (1)$$

where the subscripts w and m denote the reactants in water and micellar phase respectively.

The observed first order rate constant (K_ψ) according to Menger and Portnoy[14], is given by

$$K_\psi = \frac{k_w + k_mK_s\,(C_D - \text{cmc})}{1 + K_s\,(C_D - \text{cmc})} \qquad (2)$$

In this equation k_w and k_m are the first order rate constants in aqueous and micellar phases, respectively. These first order rate constants are related to their respective second order rate constants k_w and k_m by the following equations

$$k_w = K'_w\,[SO_3^{2-}{}_w] \text{ and } k_m = K'_m\, m_m\,[SO_3^{2-}] \qquad (3)$$

where $m_m SO_3^{2-}$ is the mole ratio of SO_3^{2-} bound to micellized surfactant and is given by

$$m_m[SO_3^{2-}] = [SO_3^{2-}{}_m]/(C_D - \text{cmc}) \tag{4}$$

Here, $SO_3^{2-}{}_m$ is the molarity of micellar bound SO_3^{2-} in terms of the total solution volume. Now, using eqs. (3) and (4) the expression for k_ψ can be written as

$$k_\psi = \frac{k'_w[SO_3^{2-}{}_w] + k'_m K_s[SO_3^{2-}{}_m]}{1 + K_s(C_D - \text{cmc})} \tag{5}$$

The concentration of $SO_3^{2-}{}_w$ and $SO_3^{2-}{}_m$ can be written in terms of the degree of ionization of micelles (α) and the ion-exchange constant (p). The overall second order rate constant (k_2) at high concentrations of detergent is then given by

$$k_2 = \frac{\alpha k'_w + p\beta k^1_m K_s}{(\alpha + p\beta)(1 + K_s C_D)} \tag{6}$$

where $\alpha = 1 - \beta$ and $p = \dfrac{[SO_3^{2-}{}_m][Br^-{}_w]}{[SO_3^{2-}{}_w][Br^-{}_m]}$

Eq. (6) can be transformed into

$$\frac{1}{k_2} = \frac{\alpha + p\beta}{\alpha k'_w + p\beta k'_m K_s} + \frac{(\alpha + p\beta)K_s C_D}{\alpha k'_w + p\beta k'_m K_s} \tag{7}$$

Data at high detergent concentration of the CTAB catalysed reaction of Orange-II by SO_3^{2-} has been analysed according to eq. (7). As required by the equation, a plot of $1/k_2$ against C_D at high CTAB concentrations is found to be linear (Fig. 1) with a correlation coefficient of 0.999. Linearity of the plot justifies the application of the model to this reaction. Binding constant (K_s) calculated from the slope and intercept of the plot is found to be 237 M^{-1}. This value is a measure of binding of the substrate to the CTAB micelles. The observed catalysis must be a consequence of this binding.

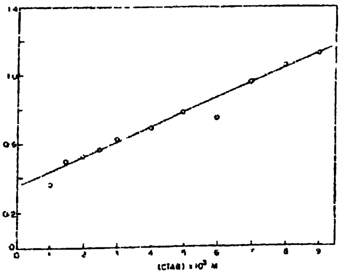
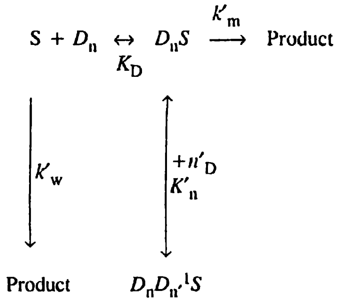


Fig. 1. Quantitative treatment of the effect of CTAB on the reduction of Orange-II

Applicability of the model proposed by Piszkiewicz[16] for the micellar catalysed bimolecular reactions, in which the rate maxima were observed, is tested for the catalytic effect of CTAB on the reduction of Orange-II. Piszkiewicz considered the phenomenon of decrease in the catalysed rate at high detergent concentrations as being analogous to substrate inhibition of an enzymatic reaction with the exception that the substrate and catalyst reverse their roles so that inhibition by catalyst is seen. This scheme is outlined below.



Scheme 2

Here n is the number of detergent molecules D and n' is the additional number of detergent molecules which associates with the catalytic micelle, D_nS, to completely inactivate it. K_n is the association constant of this interaction. The second reactant would be at a steady-state concentration and reacts with catalytic micelle, D_nS, in the step defined by the rate constant k'_m. According to this model, the second order rate constant, k_2, for a micellar catalysed bimolecular reaction is given by the expression.

$$k_2 = \frac{k'_m[C_D]^n + k'_w K_D}{K_D + [C_D]^n + K'_n[C_D]^n [C_D]^{n'}} \tag{8}$$

At high detergent concentrations eq. (8) reduces to

$$k_2 = \frac{k'_m}{1 + K'_n[C_D]^{n'}} \tag{9}$$

Eq. (9) may be rearranged to

$$\log[(k'_m/k_2) - 1] = \log K'_n + n'\log[C_D] \tag{10}$$

So, this model envisages that a plot of $\log[(k'_m / k_2) - 1]$ against $\log[C_D]$ should be linear for the bimolecular micellar catalysed reactions in which rate passes through a maximum as the concentration of detergent increases. Such plot in the case of CTAB catalysed reaction of Orange-II with SO_3^{2-} is found to be linear (Fig. 2). A value of 1.06 for n' is obtained from the slope.

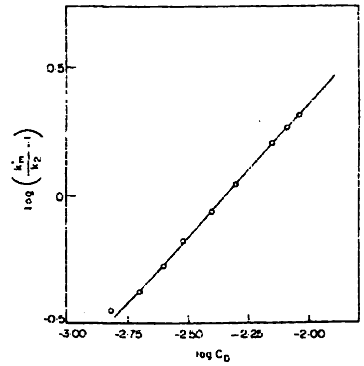


Fig. 2. Applicability of Piszkiewicz treatment to the catalytic effect of CTAB on the reduction of Orange-II.

At log $[(k'_m/k_2) - 1] = 0$, log $[C_D] = -(\log K'_n)/n'$. The term $-\log K'_n/n'$ is that concentration of detergent at which inhibition by detergent reduces k_2 to one-half of its maximum value, k_m. Formally n and n' are stoichiometries of the aggregation reactions. Functionally, n' is considered as index of cooperativity in formation of catalytic micelle and n' as index of cooperativity in formation of the inactive detergent-substrate complex D_nD_nS. At very high detergent concentrations, probably there is non-cooperativity in micelle formation. Only a simple association equilibrium exists whereby single molecules of detergent (as indicated by $n' = 1$) are absorbed by fully formed micelles.

Effect of SDS and Brij-35 :

0.01 M nonionic micelles of Brij-35 and 0.06 M anionic micelles of SDS inhibited the reduction of Orange-II by SO_3^{2-} by factors 31 and 4.7, respectively. Rate-surfactant concentration profile is found to be similar to that expected for micellar inhibited reactions. The rate is constant till 2.0×10^{-3} M, but around cmc rate decreased and appeared to approach a saturation value at high detergent concentration. Incorporation of SH into the SDS micellar phase in preference to S^- should be favourable due to the repulsive electrostatic forces in the case of S^-. As the concentration of SDS increases, more SH binds to the anionic micelles. This results in the reaction path (Scheme 1) involving less contribution of SH to the overall rate. Consequently, inhibition of the reaction takes place.

The binding of SH to Brij-35 micelles is expected to be stronger than to SDS micelles due to the hydrophobic interactions and absence of electrostatic forces. This interactions depletes more reactive S^- concentration in the bulk phase and causes strong inhibition.

The inhibitory effect of SDS and Brij-35 on the reduction of Orange-II by SO_3^{2-} has been analysed by model out lined in Scheme 2. Plots of $1/(k_w - k_\psi)$ against $1/(C_D$ - cmc) for the effects of SDS and Brij-35 are found to be linear (Fig. 3). Values of k_m and K_s calculated from the intercepts and slopes of the plots are given in Table 3.

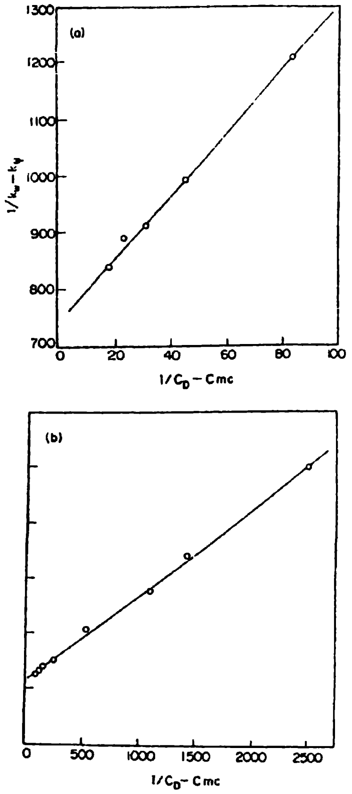


Fig. 3. Quantitative analysis of the inhibitory effect of SDS (a) and Brij-35 (b) on the reduction of Orange-II.

As predicted, k_m values are lower than the minimum observed rate constants. Higher values of K_s in the case of Brij-35 than that in the case of SDS indicates that the extent of binding of substrate to Brij-35 micelles is more than that to the SDS micelles. Greater inhibition in the presence of Brij-35 micelles is thus understandable.

The inhibitory effects are also analysed by Piszkiewicz[17] model. Parameters obtained from this analysis are given in Table 3. The k_m values obtained from the analysis of the data following Menger and Portnoy model were utilised to analyse the data by Piszkiewicz model values of $n > 1$ obtained for Brij-35 and SDS inhibited

Table 3. Parameters obtained from the analysis of the inhibitory effect of SDS and Brij-35 by Menger and Portnoy and Piszkiewicz models

Surfactant	Menger and Portnoy		Piszkiewicz		
	k_m	K_s	N	$\log [D]_{50}$	$1/K_D$
Brij-35	2.11×10^{-5}	5274	1.08	-3.6	7475
SDS	1.61×10^{-4}	135	1.58	-1.82	748

reactions indicates the existance of positive cooperativity. $1/K_D$ values which are a measure of detergent-substrate association are of the same order as K_s. Considering the difference in the two approaches, the agreement seems to be reasonable.

The catalytic effect of CTAB on the rate of reduction of Orange-II can be used as a facile route to the reduction of azo groups to their respective hydrazo derivatives.

Experimental

Orange-II was prepared and recrystallised by known method[18]. Sodium sulphite, potassium dihydrogen phosphate, disodium hydrogen phosphate used were of analytical grade. SDS and CTAB were recrystallised[19,20]. Sodium sulphite solution was standardised against iodine just before use[21]. The rate of reduction of Orange-II by SO_3^{2-} was followed spectrophotometrically by observing the decrease in absorbance at the visible absorption maxima (λ_{max} = 484 nm). The temperature of the reaction mixture was maintained constant using cryostatic water bath. Unless specified otherwise, all the kinetic runs were recorded at 298 K. The product was identified as amine by chemical analysis and by IR spectra.

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