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Micellar effects on the reduction of *p*-nitroso-N,N-dimethylaniline by sulphite ions

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Micellar effects on the rate of reduction of *p*-nitroso-N,N-dimethylaniline by sulphite ions in a buffer medium of *p*H 6.5 have been investigated. A nonionic surfactant, polyoxyethylene (23) dodecanol (Brij-35, 1×10^{-2} *M*), catalyses the reaction and increases the rate by 34 times whereas the same concentration of a cationic surfactant cetyltrimethylammonium bromide (CTAB) catalyses the reduction by 11 times. Anionic surfactant sodium dodecyl sulphate (SDS) has little effect on the reduction rate. Catalytic effects have been attributed to the hydrophobic and electrostatic interactions between the substrate, reductant and micelles. Micelle-substrate binding constants have been found to be 470 and 759 M^{-1} for CTAB and Brij-35 catalysed reactions respectively. Influence of micelles on the activation parameters of the reaction has been discussed.

Kinetics of reduction of inorganic compounds by sulphite ions has been extensively studied but comparatively less attention has been focussed on the reduction of organic compounds by sulphite ions[1]. Though kinetics of reduction of nitroso compounds by a number of reductants has been reported[2-8], studies on their reduction by sulphite ions are few[9].

As nitroso compounds are carcinogenic in nature[10], studies concerning facile methods of their reduction to less harmful hydroxylamines assume importance. We have, therefore, attempted to explore the use of micellar media for the reduction of nitroso compounds by sulphite ions. This paper deals with the kinetics of reduction of *p*-nitroso-N,N-dimethylaniline (PNDMA) by SO_3^{2-} in micelles of polyoxyethylene (23) dodecanol (Brij-35), sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB).

Materials and Methods

p-Nitroso-N,N-dimethylaniline (PNDMA) was prepared and recrystallised by reported method[11]. Sodium sulphite, acetic acid and sodium acetate were of AR grade. Sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) were purified by recrystallisation[12,13]. Brij-35 obtained from Koch-light laboratories was used as such. All the solutions were prepared in doubly distilled water. Sodium sulphite solution was standardised against iodine just before use[14].

The reaction was initiated by adding the requisite quantity of pre-equilibrated sodium sulphite solution to a solution containing nitroso compound and other reagents. Reaction was followed spectrophotometrically using Shimadzu 160A UV-visible spectrophotometer by observing decrease in absorbance of *p*-nitroso-N,N-dimethylaniline at 439 nm as a function of time. At this wavelength there is no interference on the absorption by other reagents or by the reduction product. Ionic strength was maintained constant with sodium chloride. The cell containing reaction mixture was maintained at the desired temperature within ± 0.1°C by water circulation around the cell holder from a INSREF cryostatic bath. Calculations and analysis of the kinetic data were carried out using a DCM personal computer.

Results and Discussion

Effect of cationic micelles of CTAB, anionic micelles of SDS and non-ionic micelles of Brij-35 on the reduction of PNDMA by SO_3^{2-} was studied in acetate buffer. Kinetic studies were made under pseudo-first order conditions by keeping of $[SO_3^{2-}]$ very high (~ 100 times) than [PNDMA]. Girgis[9] studied the kinetics and mechanism of this reaction in the absence of micelles. The product of the reaction is *p*-hydroxylamino-N,N-dimethyl aniline. Stoichiometry of the overall reaction is

$$C_8H_{10}N_2O + SO_3^{2-} + H_2O \rightarrow C_8H_{12}N_2O + SO_4^{2-} \quad \ldots (1)$$

Rate dependence on PNDMA, SO_3^{2-} and H^+ in the absence and presence of micelles

The linear plots of log absorbance versus time revealed that the reaction is first order in PNDMA in micellar medium[9]. Increase in $[SO_3^{2-}]$ increased the rate linearly in the presence of CTAB and Brij-35 indicating first order dependence on SO_3^{2-} also. The values of rate constants at different [PNDMA] and $[SO_3^{2-}]$ are given in Table 1. Effect of ionic strength has been found to be very little in the absence of micelles, whereas it has a decreasing effect in the presence of micelles (Fig. 1). Rate increased with increase in $[H^+]$ in nonmicellar and SDS micellar media but remained constant in the presence of CTAB and Brij-35 (Table 2).

The following mechanism (Scheme 1) is proposed in support of the experimental results.

$$PNDMA + H^+ \overset{K_p}{\rightleftarrows} PNDMAH^+ \text{ (fast)} \quad \ldots (2)$$

$$PNDMAH^+ + SO_3^{2-} \overset{k_1}{\rightarrow} \text{Products (slow)} \quad \ldots (3)$$

$$PNDMA + SO_3^{2-} \overset{k_2}{\rightarrow} \text{Products (slow)} \quad \ldots (4)$$

Scheme 1

Scheme 1 leads to rate law (5) for the disappearance of PNDMA

$$-\frac{d[PNDMA]}{dt} = [k_1 K_p[H^+] + k_2] \times [PNDMA]\,[SO_3^{2-}] \quad \ldots (5)$$

Effect of cationic micelles

The rate of the catalytic reduction by CTAB micelles (at 0.01 *M*) is found to be 11 times higher than without CTAB. The catalysis takes place well below the reported CMC of CTAB (9.2×10^{-4} *M*) indicating either substrate induced micellisation or formation of premicellar aggregates. The concentration effect of CTAB on the rate of reduction at *p*H 6.5 is shown in Fig. 2.

This catalytic effect can be qualitatively understood on the basis of electrostatic and hydrophobic interactions between micelles of CTAB, PNDMA and SO_3^{2-}. Hydrophobicity of PNDMA may be responsible for its incorporation into the micellar pseudophase. Concentration of SO_3^{2-} at the micellar surface will be more than that in the

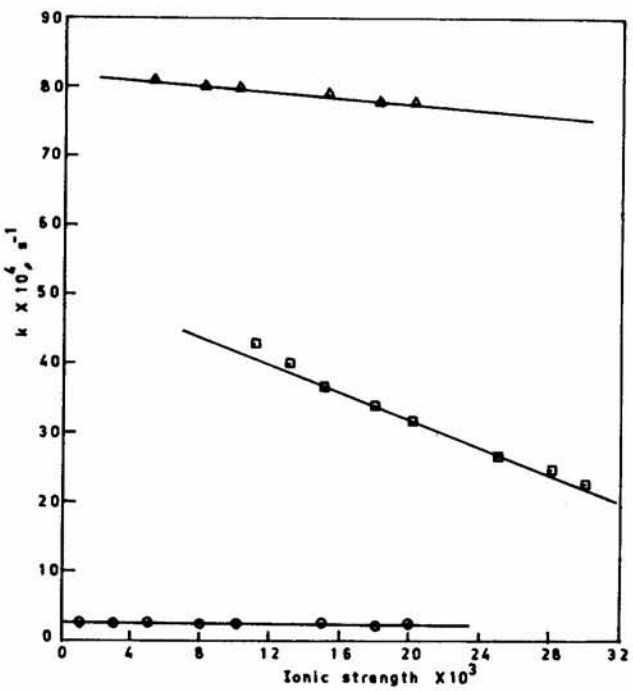


Fig. 1—Plots showing variation of rate constant with ionic strength. Absence of surfactant (⊙), CATB (□), Brij-35 (Δ) in acetate buffer of *p*H 6.5 at 298 K. [PNDMA] = 3.5×10^{-5} *M*; $[SO_3^{2-}] = 3 \times 10^{-3}$ *M*; [surfactant] = 1×10^{-2} *M*; temp. = 298 K)

Table 1—Effect of varying [PNDMA] and $[SO_3^{2-}]$ on the rate of reduction of PNDMA in the absence and presence of surfactants at 298 K and *p*H 6.5, $\mu = 0.02$ *M*

Effect of [PNDMA] $[SO_3^{2-}] = 3 \times 10^{-3}$ *M*				Effet of $[SO_3^{2-}]$ [PNDMA] $= 3.5 \times 10^{-5}$ *M*			
[PNDMA] $\times 10^5$, *M*	$k \times 10^4$, s^{-1}			$[SO_3^{2-}] \times 10^3$, *M*	$k \times 10^4$, s^{-1}		
	In the absence of micelles	In CTAB	In Brij-35		In the absence of micelles	In CTAB	In Brij-35
1.5	2.89	28.5	87.8	1.0	1.10	15.0	19.1
2.0	2.85	28.9	85.0	1.5	1.54	18.7	32.8
2.5	2.64	28.2	84.9	2.0	1.88	22.3	50.1
3.0	2.71	26.8	83.0	2.5	2.39	25.1	66.3
3.5	2.75	26.0	80.1	3.0	2.84	27.9	82.2

Table 2—Effect of *p*H on the reduction of PNDMA by SO_3^{2-} in the absence and presence of surfactants at 298 K. [PNDMA] = 3.5×10^{-5} *M*; [SO_3^{2-}] = 3×10^{-3} *M*; [Surfactant] = 1×10^{-2} *M* $\mu = 0.02$ *M*

*p*H	$k \times 10^3$, s^{-1}			
	No surfactant	With surfactant		
		CTAB	SDS	Brij-35
4.0	11.04	3.92	3.52	6.88
5.0	3.04	3.38	2.65	7.83
5.5	0.63	3.08	0.45	6.63
6.0	0.27	2.94	0.19	6.96
6.5	0.24	3.16	0.19	8.60

bulk phase due to favourable electrostatic interactions between SO_3^{2-} and CTAB micelles. Enhanced concentration of both PNDMA and SO_3^{2-} at the micellar interface leads to catalysis of the reaction.

This argument is supported by the fact that increase in added [Cl^-] has greater inhibitory effect on the CTAB catalysed reaction than in pure aqueous medium or in nonionic micellar medium (Fig. 1). As [Cl^-] is increased, exchange of added counter ions with those already present at the micellar surface takes place[15]. This results in the decrease of [SO_3^{2-}] at the micellar surface. Consequently, the rate of CTAB catalysed reaction decreases.

Rate decreased as the *p*H is increased from 4.0 to 6.5 in the absence of micelles but is found to be independent of *p*H in the presence of CTAB (Table 2). The proposed mechanism (Scheme 1) with two paths, one involving the protonated substrate (Eq. 3) and the other involving the unprotonated substrate (Eq. 4), is consistent with this interesting observation. Due to the electrostatic repulsion between $PNDMAH^+$ and CTAB micelles, binding between them should be less favourable than between PNDMA and CTAB micelles. Catalysis must be due to the reaction proceeding predominantly in micellar phase, and the step involving PNDMA mainly contributing to the observed rate. This explanation is also consistent with the *p*H independent nature of the reaction in the presence of CTAB.

The data on variation of the observed rate constant (k_ψ) with [CTAB] is analysed on the basis of Scheme 2 (ref. 16).

Here S^+, the unprotonated substrate in aqueous phase is in equilibrium with D_nS, the substrate in micellar phase. D_n is the concentration of micellised surfactant. Under experimental condition of

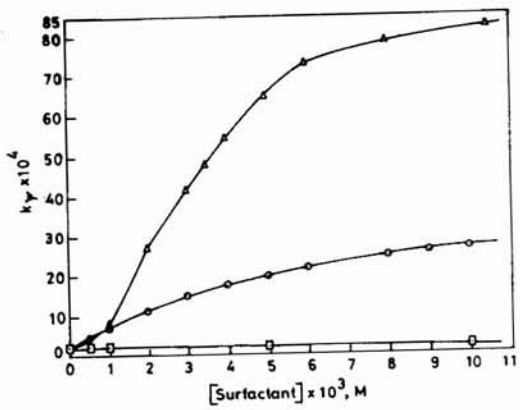
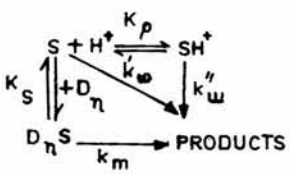


Fig. 2—Dependence of rate constant on [surfactant]. CTAB (⊙), Brij-35 (Δ), SDS (□) in acetate buffer of *p*H 6.5 [PNDMA] = 3.5×10^{-5} *M*; [SO_3^{2-}] = 3×10^{-3} *M*; $\mu = 0.02$ *M*; temp. = 298 K.



Scheme 2

*p*H, ionic strength and [SO_3^{2-}], Scheme 2 gives rise to expression (6)

$$\frac{k_\psi - k_w}{k_m - k_\psi} = K_s (C_D - CMC) \qquad \ldots (6)$$

Here k_w is the rate constant in aqueous phase and is given by $k'_w + k''_w K_p [H^+]$, K_s is micelle-substrate binding constant expressed in terms of micellised surfactant and C_D is the detergent concentration. A plot of $k_\psi - k_w / k_m - k_\psi$ versus C_D is found to be linear. K_s value obtained from the plot is found to be 470 M^{-1}. This indicates significant binding between PNDMA and CTAB micelles.

Application of the model given in Scheme 2 to the bimolecular reaction under investigation is justified considering the arguments put forward by Raghavan and Sreenivasan[17]. They proposed a kinetic model for bimolecular reactions considering distribution of both reactant and nucleophile in aqueous and micellar phases. The product formation is assumed to result from the decomposition of ternary complex involving substrate, nucleophile and micelle. After analysing the data on the basis of this model, they concluded that almost all the nucleophile is present in the bulk phase, an idea which parallels the assumption of Romsted[18] as well as Reeve[19]. They emphasised that, in cases where nucleophile resides predominantly in the stern layer of the micelle, Menger

and Portnoy[16] treatment for unimolecular reactions should also hold good for bimolecular reactions.

Effect of anionic micelles

Anionic micelles of SDS have very small inhibitory effect on the rate of reduction (Fig. 2). This may be due to the binding of SH^+ to SDS micelles. In this case, both electrostatic and hydrophobic forces favour binding. But approach of SO_3^{2-} to the micelle bound SH^+ is expected to be prevented by electrostatic repulsions. Very little inhibitory effect may be due to the shielding of micelle bound SH^+ from the attack of SO_3^{2-}. The observed rate in the presence of SDS may be due to the fraction of the reaction taking place in aqueous phase. The effects are too small for any quantitative analysis.

Effect of non-ionic micelles

Non-ionic micelles of Brij-35 catalysed the reaction of PNDMA more efficiently than cationic micelles. The catalysis by 0.01 *M* Brij-35 is 34-fold. The variation of rate constant with [Brij-35] is shown in Fig. 2. Added NaCl decreased the rate of Brij-35 catalysed reaction but to a lesser extent than CTAB catalysed reaction. This is because counterions have little effect on the surface properties of nonionic micelles. *p*H has little effect on the rate of the reaction in this micellar system. This reveals that the reaction proceeds mostly through H^+ independent path (Table 2). Catalysis can be attributed to the concentration of PNDMA at the micellar surface due to hydrophobic interactions between non-ionic aggregates of Brij-35 and PNDMA.

Application of the model in Scheme 2 to the catalytic effect of Brij-35 gives a value of 759 M^{-1} for K_s. This value of K_s indicates that PNDMA binds more strongly to Brij-35 micelles than to CTAB micelles. Absence of electrostatic forces in these micelles might be responsible for this stronger binding. Higher catalytic efficiency of Brij-35 micelles is probably due to this stronger binding.

Applicability of Hill-type model

The data of CTAB and Brij-35 catalysed reaction of PNDMA with SO_3^{2-} is also analysed by Hill-type model suggested by Piszkiewicz[20]. The rearranged form of the equation for the observed rate constant (k_ψ) according to this model is given by

$$\log \frac{(k_\psi - k_w)}{(k_m - k_\psi)} = n \log [D] - \log K_D \quad \ldots (7)$$

Here n is referred to as index of cooperativity and K_D is the decomposition constant of detergent-substrate complex back to its components. Other parameters have the same meaning as in (Scheme 2).

Plots of $\log \frac{(k_\psi - k_w)}{(k_m - k_\psi)}$ versus log[D] are found to be linear with high correlation coefficients (0.997). Values of n obtained from slopes of these plots are found to be 1.78 and 1.92 for CTAB and Brij-35 catalysed reactions respectively. These values are in keeping with the earlier observations of Piszkiewicz[20] and are viewed as indices of positive cooperativity. These values are far less than the number of detergent molecules found in micelle and have previously been interpreted as indicative of the existence of catalytically productive submicellar aggregates[20]. Observed catalysis at detergent concentration as low as 1×10^{-5} *M* is probably due to those aggregates. $[D]_{50}$ values, which are detergent concentrations at which half maximal catalytic effect is observed are obtained from the plots. These are found to be 2.0×10^{-3} and 2.82×10^{-3} *M* for CTAB and Brij-35 respectively. These low values also support the view that premicellar aggregates are involved in the catalytic process.

Temperature effect in the presence of micelles

The plots of log *k* versus 1/T for the reaction in the presence of 0.01 *M* of CTAB, SDS and Brij-35 have been found to be linear. The activation parameters calculated from the plots are given in Table 3. Catalysis and inhibition may be understood in terms of the combined conbtributions of E_a and $\Delta S^{\neq}$. Large negative values of activation entropy indicate that more ordered activated complex is formed. Nearly same values of $\Delta G^{\neq}$ in pure aqueous medium and in the presence of surfactants show that the reaction mechanism is same in both the media.

Table 3—Activation parameters for the reduction of PNDMA by SO_3^{2-} in the absence and presence of surfactants

Activation parameter	With acetate buffer (*p*H 6.5)			
	No Surfactant	With CTAB	With SDS	With Brij-35
E_a (kJ mol^{-1})	36.4	26.9	25.0	9.5
$\Delta G^{\neq}$ (kJ mol^{-1})	93.1	87.0	93.8	84.9
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	−190	−202	−231	−253

Results of this study also demonstrate that micelle-substrate interactions are specific and depend on both electrostatic and hydrophobic forces. The findings of this investigation suggest that the reduction of nitroso compounds by SO_3^{2-} can be carried out very fast at neutral *p*H by using cationic micelles or nonionic micelles. This method may be used to reduce the pollution caused by nitroso compounds without appreciable amounts of additives.

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