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Applicability of Positive Cooperativity Model in Surfactant Mediated Chemical Reaction

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Reaction of crystal violet carbonium ion with hydroxide has been investigated in micellar media under pseudo-first order condition. The reaction is strongly catalyzed in the presence of cetyl trimethyl ammonium bromide (CTAB) micelle, but is inhibited in presence of sodium dodecyl sulphate (SDS) micelle. This can be explained by considering both the electrostatic and hydrophobic interactions which are simultaneously operating in the reaction system. Quantitative analysis of the micellar data obtained is done by applying positive cooperativity model of enzyme catalysis. Presences of counter ions on the reaction system further inhibit the reaction rates. Thermodynamic activation parameters and binding constants have also been evaluated.

Key Words: Positive cooperativity, Surfactants.

INTRODUCTION

Studies of chemical reactions catalyzed by micelles have been viewed as models of enzyme catalyzed reactions. Investigations of chemical reactions in micellar media have been reported in several texts, comprehensive reviews and research papers[1-10]. The surfactant molecules are characterized by the presence of both hydrophobic (nonpolar) and hydrophilic (polar) regions in the same molecule. Due to ability in providing the catalytic interfaces, many physico-chemical properties are affected in the micellar systems, leading to numerous analytical, biological, chemical and industrial applications. Crystal violet, which is one of the triphenyl methane dye is known to be an important analytical reagent for bacteriology. Micellar kinetics of alkaline fading of such dyes as well as the kinetic studies in relation to their pharmaceutical uses have been reported[11,12]. Carbonium ions are frequently encountered as intermediates in many organic and enzymatic reactions[13,14]. Micellar systems also serve as simple models for many biological processes which occur at or involve amphipathic surfaces[5,6]. The present paper reports the effect of anionic surfactant sodium dodecyl sulphate (SDS) and cationic surfactant cetyl trimethyl ammonium bromide (CTAB) on the reaction of crystal violet carbonium ion (CV^+) with hydroxide. Analysis and quantitative treatment of the experimental data successfully applying

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the positive cooperativity model of enzyme catalysis have been reported. The effects of counter ions on the reaction system have also been investigated. The observed catalysis and inhibition have been explained on the basis of both hydrophobic and hydrophilic interactions in catalytic micellar aggregates of various species. The values of binding constants of the substrate with micellar aggregates have been calculated. The effect of temperature on reaction rate and calculation of thermodynamic parameters have been reported. The structure of crystal violet carbonium ion and its reaction with OH^- is given in Fig. 1.

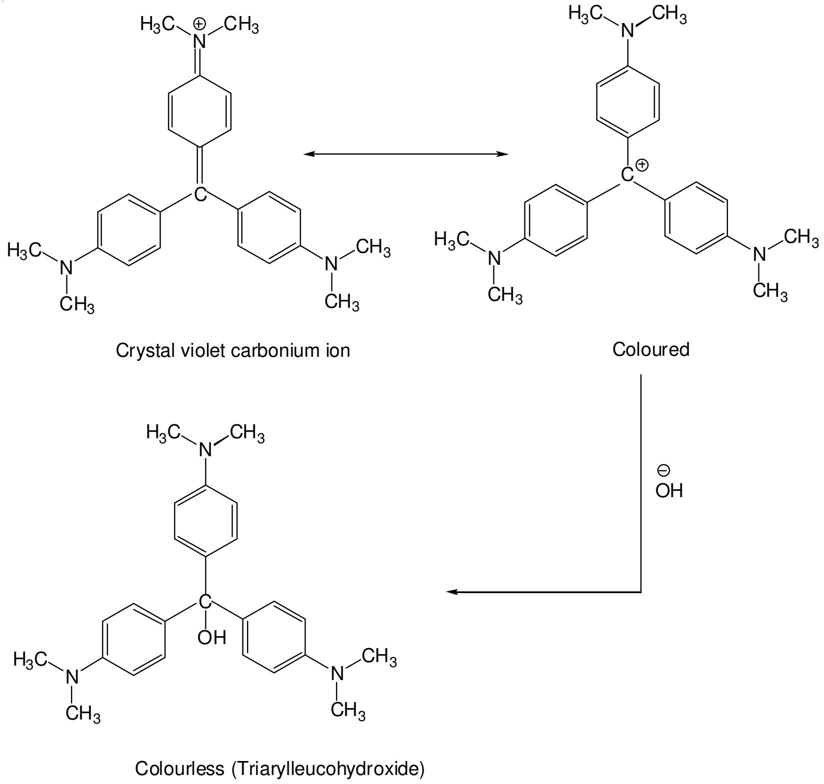


Fig. 1. Reaction of crystal violet carbonium ion with OH^-

EXPERIMENTAL

The cationic surfactant cetyl trimethyl ammonium (CTAB), anionic surfactant sodium dodecyl sulphate (SDS), sodium hydroxide, crystal violet (CV), sodium fluoride, sodium chloride and sodium bromide were analytical grade reagents and obtained from Himedia. Double distilled water was used throughout the work for the preparation of solutions. All the kinetic investigations were carried out by following the decolourisation reactions on a Shimadzu-UV visible spectrophotometer-2450 (with Quartz cell of path length 10 mm) in visible range at 25 ± 0.1 ºC.

The temperature of the cell compartment was maintained using a high precision refrigerated thermostatic bath (HAAKE DC-10). The reactions which follow pseudo-first order kinetics were monitored by observing the change in the absorbance as a function of time at the absorption maxima 593 nm (in presence of CTAB) and 596 nm (in presence of SDS) in the time drive mode. Slopes and rate constants were calculated from the straight line plots by linear regression method. All the graphs and graphics were drawn with the help of KyPlot (Version 2.0 beta 1) and ChemDraw Ultra8.0 software, respectively.

RESULTS AND DISCUSSION

The bathochromic shifts of absorption maxima of dye from 590 nm (in absence of surfactant) to 593 nm (in presence of 1.003×10^{-2} M CTAB) and to 596 nm (in presence of 1.007×10^{-2} M SDS) give evidence of binding of substrate crystal violet carbonium ion (CV^+) with micelles. It was observed that CTAB strongly catalyzed the reaction of CV^+ with OH^- with overall catalysis factor k^+_{rel} (= k_m/k_w, where k_m is the rate constant in the micellar phase and k_w is the rate constant in absence of surfactant) being 16.60. However, SDS micelle inhibited the reaction and the overall inhibition factor k^-_{rel} (= k_w/k_m) was found to be 11.05. The variation of pseudo-first order rate constant as a function of CTAB concentration (at $[CV^+] = 5.269 \times 10^{-5}$ M and $[OH^-] = 4.613 \times 10^{-3}$ M) and rate constant *versus* SDS concentration (at $[CV^+] = 5.269 \times 10^{-5}$ M and $[OH^-] = 1.692 \times 10^{-1}$ M) are shown in Fig. 2. The catalytic effect of micelles can be explained by considering both the electrostatics and hydrophobic interactions which operate simultaneously in the reaction system. The reagent $[OH^-]$ being negatively charged has favourable interaction with positively charged CTAB micellar aggregates containing the hydrophobic substrate. Thus, the approach of $[OH^-]$ is facilitated towards substrate and local concentration of $[OH^-]$ increases around the micellar

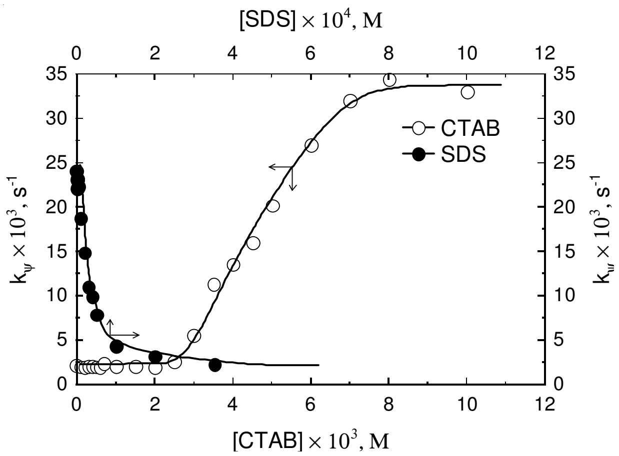
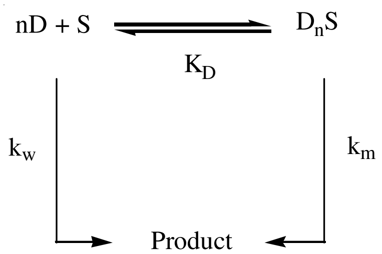


Fig. 2. Dependence of the rate constant (k_ψ) on surfactant concentrations on the reaction of CV^+ with OH^-

aggregates, leading to the catalytic effect by CTAB. Whereas in presence of SDS, hydroxyl ions are unable to approach the strongly bound substrate with negatively charged SDS micelles thus exhibiting inhibitory effect.

A kinetic model developed by Piszkiewicz[15,16] has been used for quantitative analysis of micellar data. This model is analogous to Hill model which describes the positive cooperativity in enzyme catalysis. Thus, by analogy, with reference to micellar catalysis, cooperativity is defined as stimulation of association of additional surfactant molecules to an aggregate as a result of interaction of the first surfactant molecule. Piszkiewicz's model assumes that a substrate, S (dye carbonium ion in this case) and n number of surfactant (detergent) molecules D, aggregate to form catalytically functional micellar aggregate (D_nS), which may undergo reaction to yield product by following **Scheme-I**:



Scheme-I

where, K_D represents the dissociation constant of the micelle (its reciprocal is binding constant). k_m and k_w are the rate constants of the reaction in micellar and bulk (aqueous) phases, respectively.

For this reaction scheme, pseudo-first order rate constant k_ψ is expressed as a function of concentration of the detergent D, by equation

$$k_\psi = \frac{k_m[D]^n + k_w K_D}{K_D + [D]^n} \quad (1)$$

which can be written in the form,

$$\log \frac{k_\psi - k_w}{k_m - k_\psi} = n \log[D] - \log K_D \quad (2)$$

The point of half maximal catalysis or inhibition designated as $[D]_{50}$ or log $[D]_{50}$ can be obtained when the left hand side of eqn. 2 equal zero.

Thus, we have

$$\log[D]_{50} = \frac{\log K_D}{n} \quad (3)$$

In this model slope (n) of the double log plot described the stoichiometry of the reaction (**Scheme-I**). n is considered as an index of cooperativity in enzymatic reactions. Thus, index of cooperativity (already defined with reference to enzymatic or micellar reactions) is a sensitive measure of interaction between substrate and surfactant. The value of $n > 1$ reflects positive cooperativity.

The applicability of eqn. 2 was tested by using the micellar data for CTAB and SDS shown in Fig. 2. The Hill type double log plots and the quantitative analysis according to eqns. 2 and 3, for the reactions under study are shown in Fig. 3 and Table-1, respectively. It is to note that the value of n found was greater than 1 providing evidence for positive cooperativity in the reaction system. The applicability of Piszkiewicz's cooperativity model has also been tested for many micellar reactions. For the reaction of CV^+ with OH^- in presence of SDS, inhibition was found to begin in the pre-micellar region[5,6].

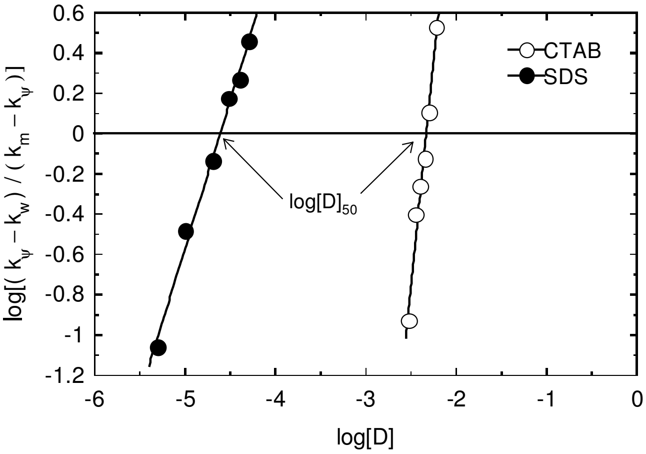


Fig. 3. Quantitative treatment of the effect of surfactants (CTAB and SDS) on the reaction of CV^+ with OH^-, applying positive cooperativity model of enzyme catalysis (Hill type plots)

TABLE-1
PISZKIEWICZ'S MODEL DERIVED PARAMETERS FOR CTAB AND SDS INFLUENCED REACTIONS OF CRYSTAL VIOLET CARBONIUM ION (CV^+) WITH OH^-

Micelles	No. of k_ψ and D values used	Slope (n)	$[D]_{50}$ M	Intercept (-log K_D)	K_D	Binding constant ($1/K_D$)
CTAB	6	4.45	4.52×10^{-3}	10.39	4.07×10^{-11}	2.45×10^{10}
SDS	6	1.46	2.45×10^{-5}	6.75	1.77×10^{-7}	5.63×10^{6}

The effect of the added counterions on the CTAB catalyzed reaction of CV^+ with OH^- was investigated by varying the concentration of electrolytes. Effect of counter ions on rate constant is shown in Fig. 4. All the added counterions (F^-, Cl^- and Br^-) exhibited inhibitory effects on the rate in presence of CTAB. The added counter ions reduced the extent of overall catalysis caused by CTAB micelles, in the order: $Br^- > Cl^- > F^-$. The result closely parallels the lyotropic series[17] which represent

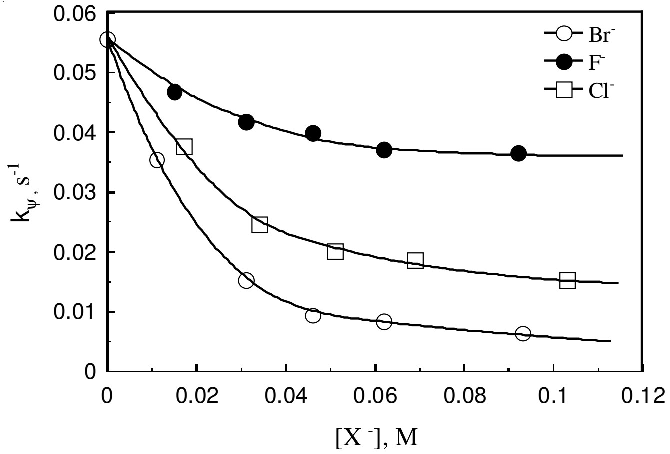


Fig. 4. Effects of added counterions on the rate constant for CTAB catalyzed reaction of CV^+ with OH^-

salt effects on precipitation and denaturation of proteins. The reaction is found to obey Arrhenius equation in the micellar media. Variation of rate constant with temperature in presence of CTAB, SDS and no surfactant is shown in Fig. 5. The activation parameters (Table-2) suggest that the decrease in $\Delta E^{\#}$ (activation energy) in presence of CTAB relative to the value in aqueous medium is one of the factors responsible for micellar catalysis. Similarly, a higher $\Delta E^{\#}$ in presence of SDS contributes towards inhibition. The entropies of activations in the presence and the absence of micelles of CTAB and SDS for the reaction are negative and are in the order of $\Delta S^{\#}_{CTAB} < \Delta S^{\#}_{aqueous} < \Delta S^{\#}_{SDS}$. This indicates that the reaction of dye carbonium ion with OH^- takes place between ionic species. Thus, micelles do not alter the mechanism of the reaction but

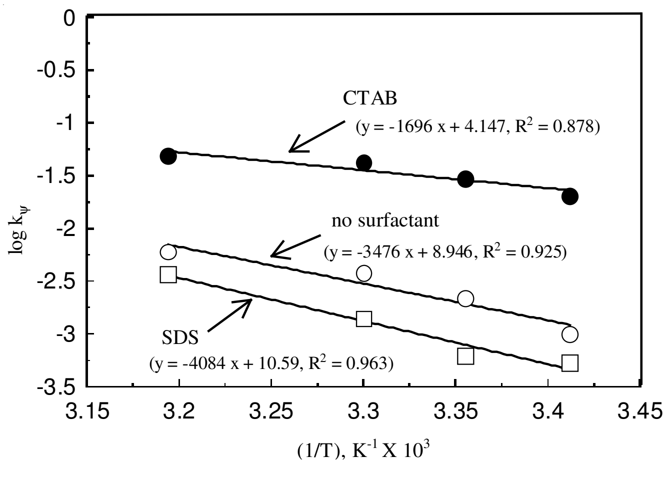


Fig. 5. Variation of rate constant with temperature for the reaction of CV^+ with OH^- in presence of CTAB, SDS and no surfactant

TABLE-2
VALUES OF THERMODYNAMIC PARAMETERS OF ACTIVATION FOR THE REACTION OF CV^+ WITH OH^- IN PRESENCE OF CTAB, NO SURFACTANTS AND SDS

Activation parameters	In presence of		
	No surfactant	(1.003×10^{-2}, M CTAB)	(1.007×10^{-2}, M SDS)
$\Delta E^{\#}$ (k J mol^{-1})	66.555	32.479	78.196
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-64.000	-156.000	-35.000
$\Delta H^{\#}$ (k J mol^{-1})	69.032	34.950	80.673
$\Delta G^{\#}$ (k J mol^{-1})	88.160	81.709	91.304
Z (s^{-1})	1.019×10^9	1.461×10^4	3.106×10^{10}

only affect the reaction rate. The observation shows that in the reaction system there is association of CV^+ ions with surfactant resulting in the perturbation of effective charge carried by the substrate molecules. The frequency factor (Z) is in the order: $Z_{CTAB} < Z_{aqueous} < Z_{SDS}$. This indicates that larger numbers of collisions are needed to produce forward reaction in presence of SDS micelles than in absence of micelles, whereas lesser collisions are needed in presence of CTAB micelles.

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