MICELLAR CATALYSIS ON THE RATES OF NUCLEOPHILIC ADDITION REACTIONS

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***Abstract* :** The kinetics of the addition reactions of cyanide ions to crystal violet carbocations in micellar media were catalyzed by cetyltrimethylammonium bromide micelles and inhibited by sodium dodecyl sulphate micelles. The observed rate constant depends on the surfactant concentration and follows pseudo-first-order kinetics. Micellar catalysis is attributed to the alteration of the microenvironment and interactions between various microenvironments. The positive cooperativity model of enzyme catalysis was analysed using micellar data, and a cooperativity index value greater than one indicates the validity of the enzyme catalysis model. The addition of solvents with long alkyl chains showed greater inhibitory effects on the overall catalysis and micelle formation.

***Index Terms* - Kinetics, Micelles, Cyanide, Catalytic, Positive cooperativity.**

Introduction

In recent years, many chemical reactions have been extensively studied in micellar media. In an aqueous medium, when surfactants reach a critical micellar concentration, they form larger aggregates of colloidal dimensions called micelles, which consist of two separate microphases: a nonpolar micellar core formed by the hydrophobic parts of amphiphiles and a polar surface layer formed by their head groups that are directed towards and in contact with the aqueous solution [1]. In nonpolar solvents, they form reverse micelles [1]. The properties of the surface are altered in micellar media. Micellar catalysis can be considered enzyme catalysis. Several comprehensive reviews have reported micellar reaction rates, ranging from inhibition to activation [2-15, 24]. The effect of micelles on these reactions can be attributed to the concentration of the reagents in the micelles, alteration of the microenvironment, and the presence of species in the micelles. These properties make them indispensable tools for numerous chemical reactions. Chao and Morawetz [25] has been demonstrated that the reaction of mercuric ions with Co $(NH_3)_2Cl_2$ ion catalysed 140000 fold by sodium hexadecyl sulphate micelles. This may help unravel the catalytic role of metal ions in metalloenzymes. The decolorization of dye carbocations in the presence of various nucleophiles has been reported in several papers [16-18, 24]. Shinkai et al. [19] have been demonstrated the oxidation of aldehydes with cyanide ion and flavin to the corresponding carboxylic acids facilitates in presence of cationic micelles.

In this study, we report the effect of micelles on the reaction of triphenylmethane carbonium ions (CV^+) with the nucleophile CN^- and the effect of solvents (alcohols) on the cetyltrimethylammoniumbromide (CTAB) and sodiumdodecylsulphate (SDS) micelle-inhibited reactions. The micellar catalysis has been attributed to the formation of catalyically functional micellar aggregates of various species in the reaction system. Furthermore, the enzyme catalysis model of positive cooperativity can be successfully applied to micelles. Stabilized carbonium ions (CV^+) were generated using crystal violet dye (CV). The structure of crystal violet (CV) is shown in Fig.1.

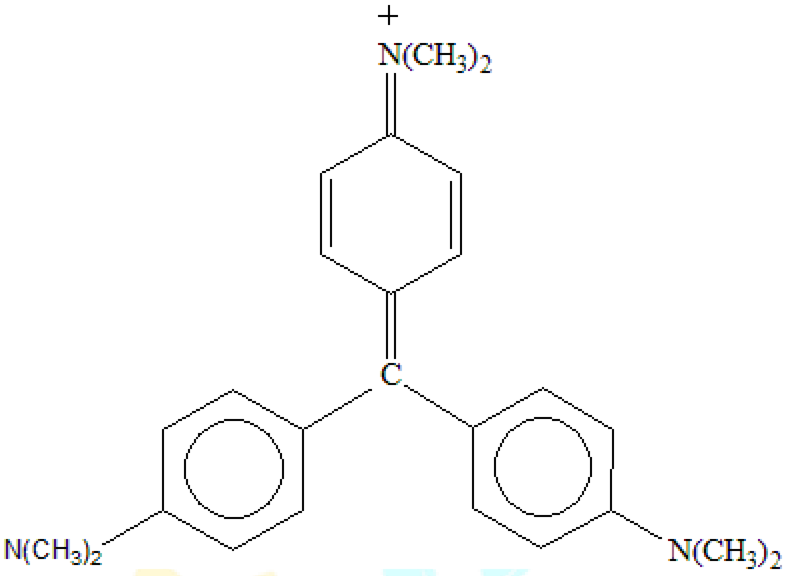


Figure 1: Structure of the substrate Crystal Violet (CV)

Experimental:

Materials

The surfactants sodiumdodecylsulphate (SDS) and cetyltrimethylammoniumbromide (CTAB) were obtained from Sisco Chemical Industries and used as received. Crystal violet (CV) was obtained from a Central Drug House. Sodium hydroxide and disodium hydrogen phosphate were obtained from the Glaxo Laboratories. Potassium cyanide was obtained from Loba Chemie Pvt. Ltd.. Methanol, ethanol, n- propanol, and n-butanol (all BDH analytical grade) were used as solvents. The solutions were prepared using double-distilled water.

Procedure

The reaction rates were determined by monitoring the fading of crystal violet (CV^+) at its maximum absorption wavelength (588 nm) as a function of time using a Beckmann DU-6 Spectrophotometer by maintaining the pH of the solution at 9.5 and temperature at $25^0C \pm 0.1^0C$.

Results and Discussion

The triphenylmethane carbocation (CV^+) exhibits an absorption maximum of 583 nm in an aqueous medium. In the presence of both 2×10^{-2} M CTAB and 5×10^{-4} M SDS micellar solutions, the absorption maximum was shifted to 588 nm. This red shift is evidence that the micelles bind to the substrate by incorporating carbocation into the micelles.

Reaction mechanism of the substrate dyes (CV^+) with the nucleophile CN^-

Figure.2 shows the interaction between the substrate dye carbocation and cyanide ion. In an aqueous solution, the substrate dye is ionized, yielding a positively charged carbonium ion. Owing to resonance stabilization, the positive charge of the carbonium ion was delocalized throughout the entire molecule. In the second step, the nucleophile CN^- reacts with the dye carbonium ion to produce a colorless triarylleuconitrile compound.

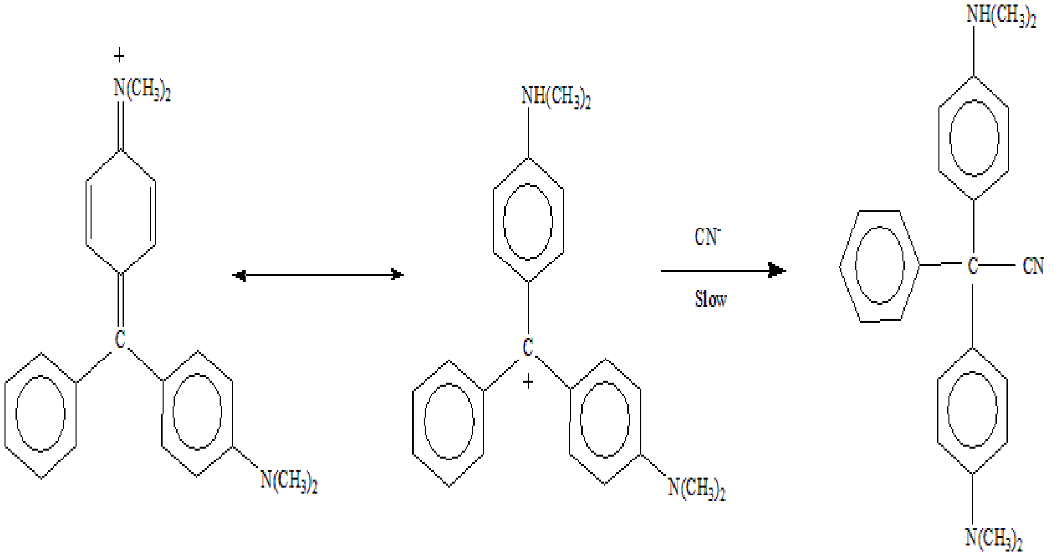


Figure 2: Reaction mechanism of the dye carbocation (CV^+) with nucleophile CN^-.

Influence of dye carbocation concentration (CV^+) on the rate constant of its reaction with CN^- at a fixed concentration of nucleophile CN^-

The dependence of the observed rate constant on the dye carbocation concentration at a fixed concentration of CN^- (2.60×10^{-2} M) is shown in Fig. 3(a). With an increase in the dye carbocation concentration from 5×10^{-6} M to 3×10^{-5} M, the observed rate constant did not change. These results show that the observed rate constant is independent of the dye carbocation and follows a zero-order reaction with respect to the dye carbocation. The observed rate constant for CV^+ was 1.02×10^{-3} s^{-1}.

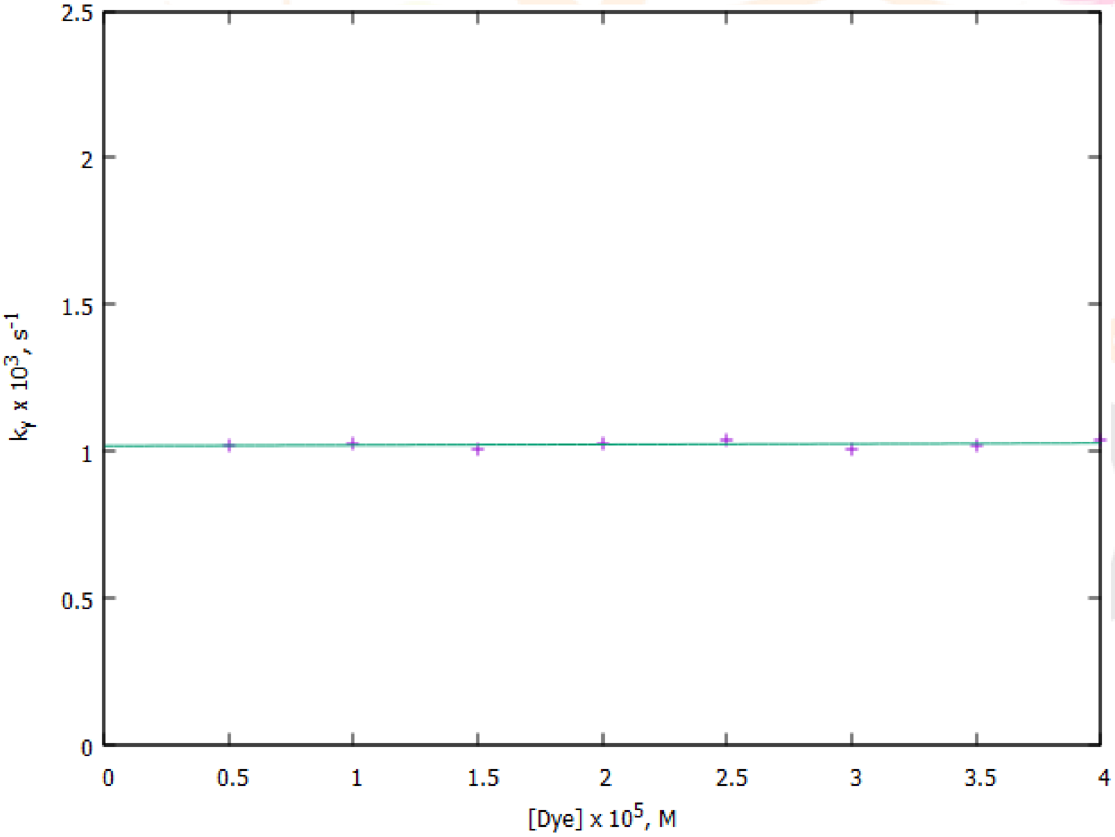


Figure 3(a): Impact of dye carbocation concentration on the rate constant of its reaction with CN^- at a fixed nucleophile (CN^-) concentration.

Effect of nucleophile (CN^-) concentration on the rate constant of its reaction with CV^+ at a fixed concentration of CV^+ dye carbocation (CV^+)

The relationship between the observed rate constant and the nucleophile CN^- concentration is shown in figure 3(b). At a fixed concentration of the dye carbocation (3×10^{-5} M), the observed rate constant increased linearly with an increase in the nucleophile concentration from 5×10^{-3} M to 4×10^{-2} M.

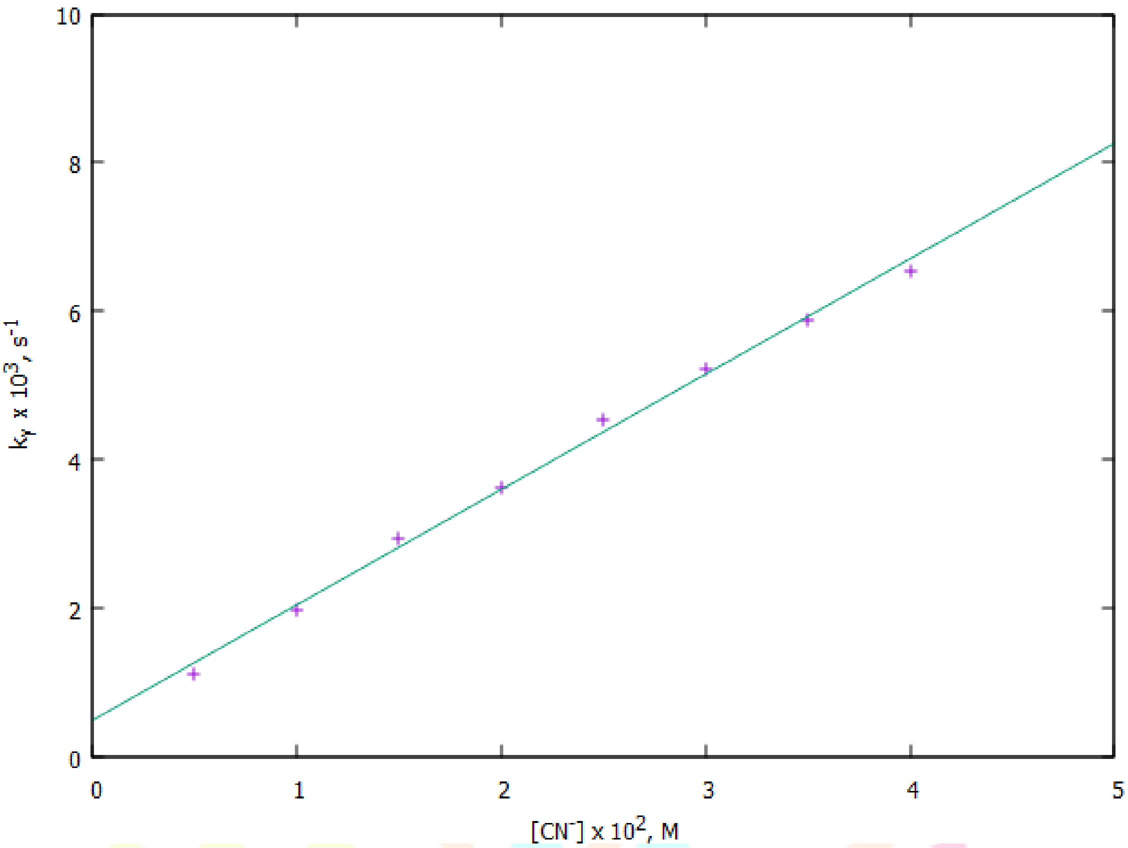


Figure 3(b): Dependence of the observed rate constant of the reaction of dye carbocation with nucleophile CN^-.

These results show that the observed rate constant depends on the nucleophile concentration and follows pseudo-first-order kinetics with respect to CN^-. The reaction system between the carbocation and nucleophile CN^- was maintained at pH 9.5 using a buffer solution of (Na_2HPO_4 and NaOH). At this pH, the effect of hydroxyl ions is negligible compared to that of the nucleophile CN^-.

Effect of CTAB micelles on the rate of the reaction between CV^+ and CN^-

The variation in the observed rate constant of the CTAB micelle concentration on the reaction of nucleophile CN^- with the dye carbocation is shown in figure 3(a). When the concentration of CTAB micelles in the reaction was increased, the observed rate constant first increased and became nearly saturated at higher concentrations of CTAB. The observed catalytic effect of the CTAB micelles can be explained by considering the formation of catalytically functional micellar aggregates with a net positive charge. This results in the destabilization of the substrate ground state with respect to the transition state. The favorable electrostatic interactions between the positively charged CTAB micellar aggregates and the negatively charged nucleophile CN^- facilitate the approach of nucleophile CN^- towards the substrate dye carbocation, and the local concentration of nucleophile CN^- increases around the micellar aggregate, leading to the catalytic effect of CTAB, which contains a hydrophobic substrate. The overall catalysis factor k^+_{rel}, the ratio of the reaction rate constant in the presence and absence of surfactant micelles for CV^+, was found to be 37.

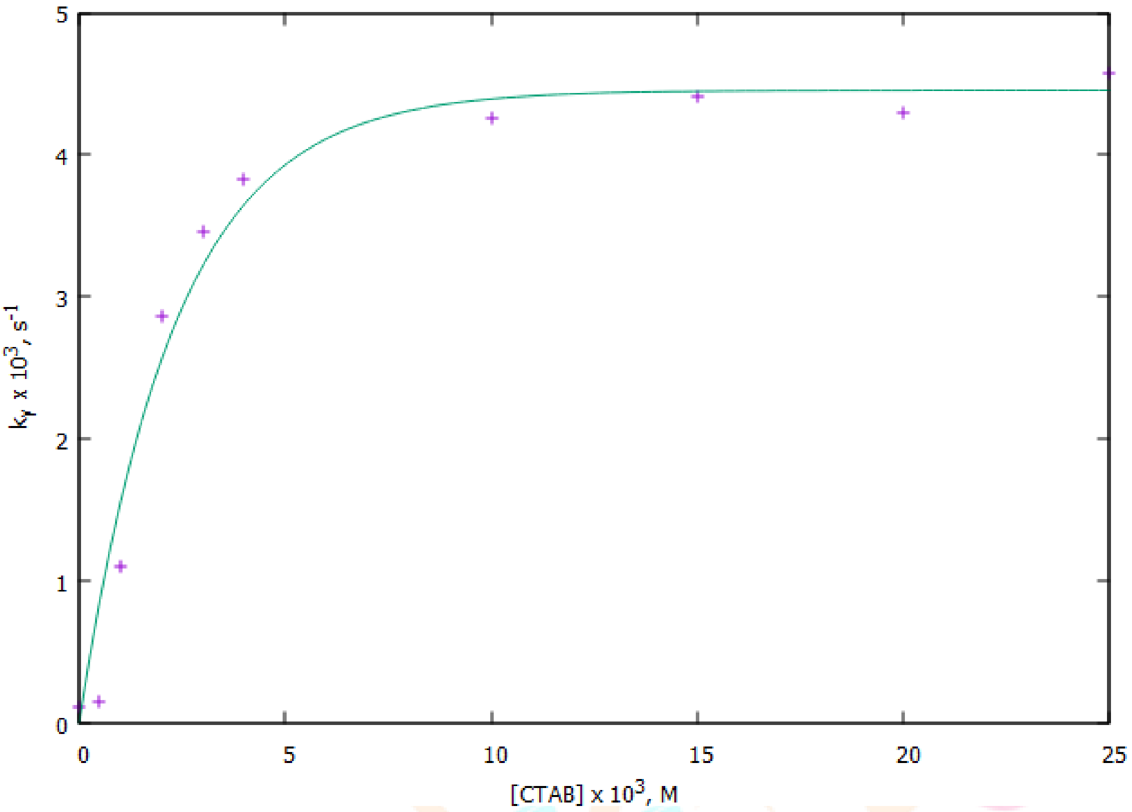


Figure 4: Dependence of CTAB micelle concentration on the observed rate constant of the reaction of CV^+ with CN^-.

Influence of SDS micelles on the reaction rate of CV^+ with CN^-

The influence of the observed rate constant on the SDS concentration for the reaction of substrate CV^+ with CN^- is shown in Figure 5. Initially, the observed rate decreased with an increase in SDS concentration, and became nearly saturated at higher concentrations. The observed inhibitory effect of SDS micelles can be explained by considering the formation of catalytically functional micellar aggregates with a net negative charge. The negatively charged nucleophile CN^- is excluded from the catalytically functional micellar aggregate because of its similar charge to that of the micellar aggregate and its lack of hydrophobicity. This makes the approach of CN^- to the strongly bound substrate in the catalytic aggregate of the micellar surface containing a similar charge non-approachable. The overall inhibition factor k^{-}_{rel} ,the ratio of the reaction rate constant in the presence and absence of surfactant micelles for CV^+, was found to be 6.

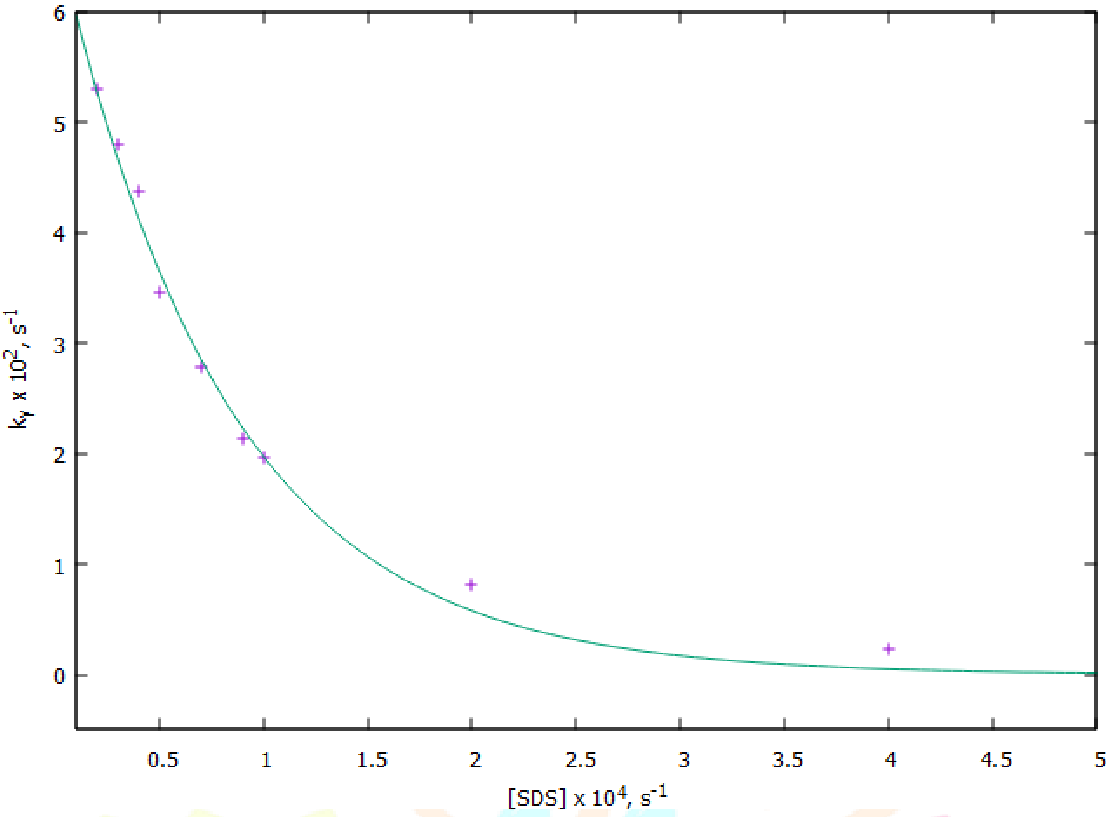
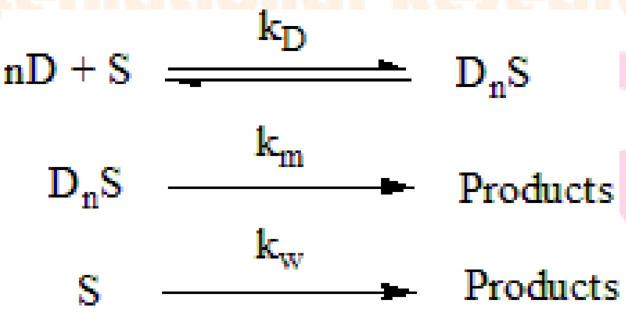


Figure 5: Dependence of SDS micelle concentration on the observed rate constant of the reaction of CV^+ with CN^-.

Quantitative analysis of micelle data

Surfactants and enzymes have polar and non-polar head groups on the same molecule. They have hydrophilic regions on their surfaces and hydrophobic cores. Owing to their unique structural features, many models have been developed to understand the mechanism of enzyme- catalyzed reactions by studying the mechanisms of simpler model chemical reactions [20-24].

The quantitative analysis of the micellar data was developed using Piszkiewicz's model (20, 21), as shown in Scheme 1.



Scheme: 1

Here, S is the substrate (dye carbocation), n is the number of surfactant molecules D, and D_nS is the functional micelle. K_D is the dissociation constant of D_nS, and k_w and km are the rate constants of the reaction in the bulk (aqueous) and micellar phases, respectively.

The reaction follows pseudo-first order kinetics and rate constant can be expressed as a function of surfactant D concentration and is given by

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

Equation (1) may also be modified as

$$\log \frac{k_{\psi} - k_{w}}{k_{m} - k_{\psi}} = n\log\,[D] - \log k_{D} \qquad (2)$$

A plot of log [D] against log [(k_{ψ} – k_w) / k_m - k_w)] should yield a linear relationship with an intercept (-log K_D) and slope "n". The slope of this plot is referred to as the index of cooperativity in enzymatic reactions [20, 21].

When log [(k_{ψ}- k_w) / (k_m - k_{ψ})] is equal to zero, the value of n log [D] becomes equivalent to log K_D.

The quantitative analysis of the micellar data for the systems shown in Fig. 2 (CTAB) and 3 (SDS) is presented in Table 1 and Fig. 6. The correlation coefficient (R^2) of the Hill-type plots for CTAB is 0.996 and SDS were 0.996. The linearity of these plots with high correlation coefficients indicates the applicability of Piszkiewicz's model. The binding constants for the CTAB and SDS systems were 1.02 × 10^8 and 1.02
× 10^{14}, respectively. The $[D]_{50}$ values for SDS were significantly lower than those for the CTAB-catalyzed reactions. This indicates that when electrostatic interactions are favorable, catalytically functional micellar aggregates can be formed at lower surfactant concentrations. An n value greater than 1 indicates positive cooperativity in the micelles. Furthermore, the interaction was found to initiate in the pre-micellar region of the surfactant.

TABLE 1: Parameter values obtained from the Hill-type plots (Fig. 6), based on equation (2), using Piszkiewicz's model for the CTAB-catalyzed and SDS-inhibited reaction between the dye carbocation and cyanide ion (CN^-).

Micelles	No. of $k\psi$ and D values used	Slope, n (index of cooperarivity)	$[D]_{50}$ or log $[D]_{50}$	Intercept (-log k_D)	K_D	Binding constant ($1/K_D$)
SDS	4	4.40	5.1×10^{-5}	12.03	9.33×10^{-13}	1.07×10^{14}
CTAB	4	2.17	1.7×10^{-3}	6.02	9.77×10^{-7}	1.03×10^{8}

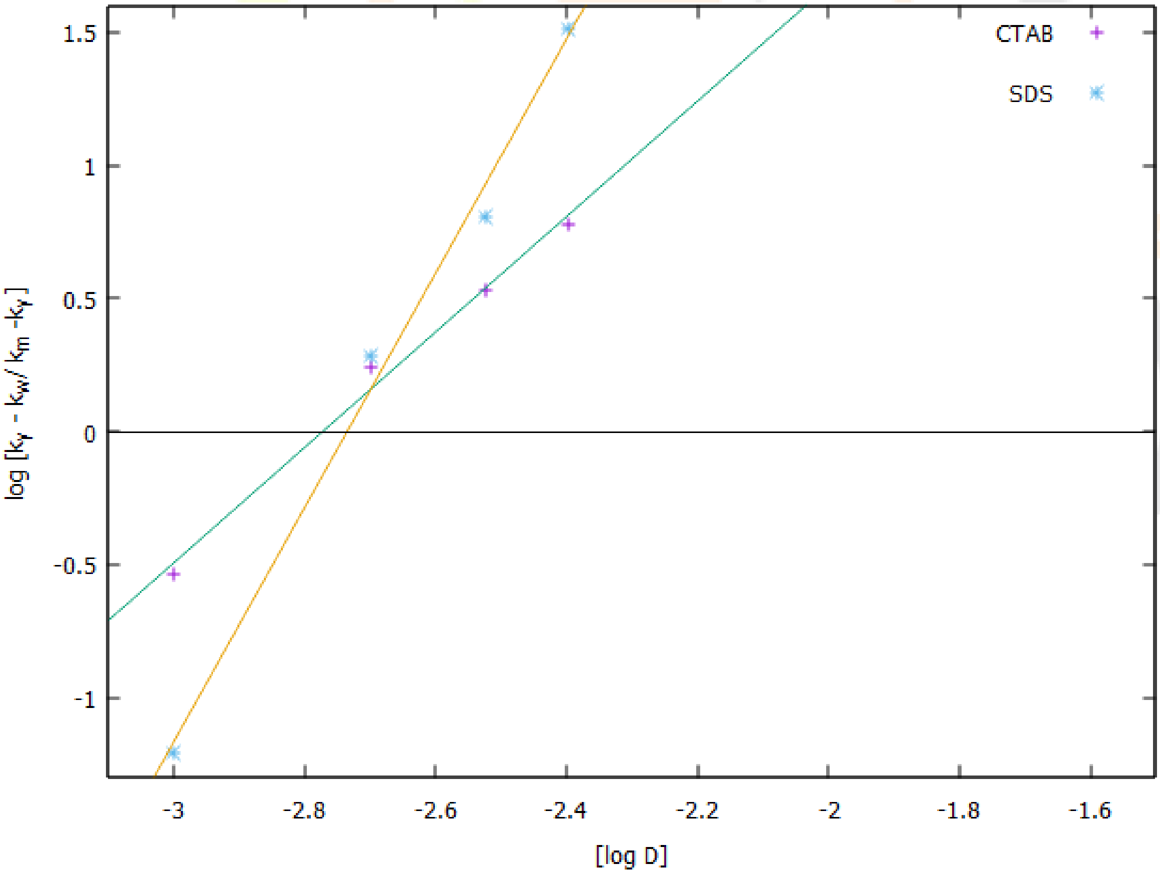


Figure 6. Quantitative analysis of CTAB and SDS micelles showing applicability of Piszkiewicz's model on the reaction of CV^+ with CN^-.

Effect of Organic Solvents

Fig. 7 (a) and (b) show the effect of organic solvents on the micellar reaction of CV^+ with CN^-The. The effect of organic solvents in micellar media was investigated by varying the concentration of n-alcohols, namely methanol, ethanol, n-propanol (1.6M), and n-butanol (0.5M), which were not too high to completely break the micellar aggregate in the reaction system at fixed concentrations of CTAB, SDS, CN^-, and substrate. Primary alcohols that do not have very long methyl chains are expected to remain close to the polar head groups of the micelles rather than their interior, as established by a fluorescence probe study (16). The plots of the observed rate constant vs. molar concentration of alcohol for the CTAB micelle-catalyzed and SDS micelle-inhibited reactions are shown in figure. The added alcohols reduced the overall catalytic or inhibitory effect of the CTAB and SDS micelles, resulting in the reorganization of the nucleophile (CN^-) at the reaction sites. Thus, alcohols with longer alkyl chains and lower dielectric constants were more effective in reducing the CTAB catalysed or SDS-inhibitory rate than those with shorter alkyl chains.

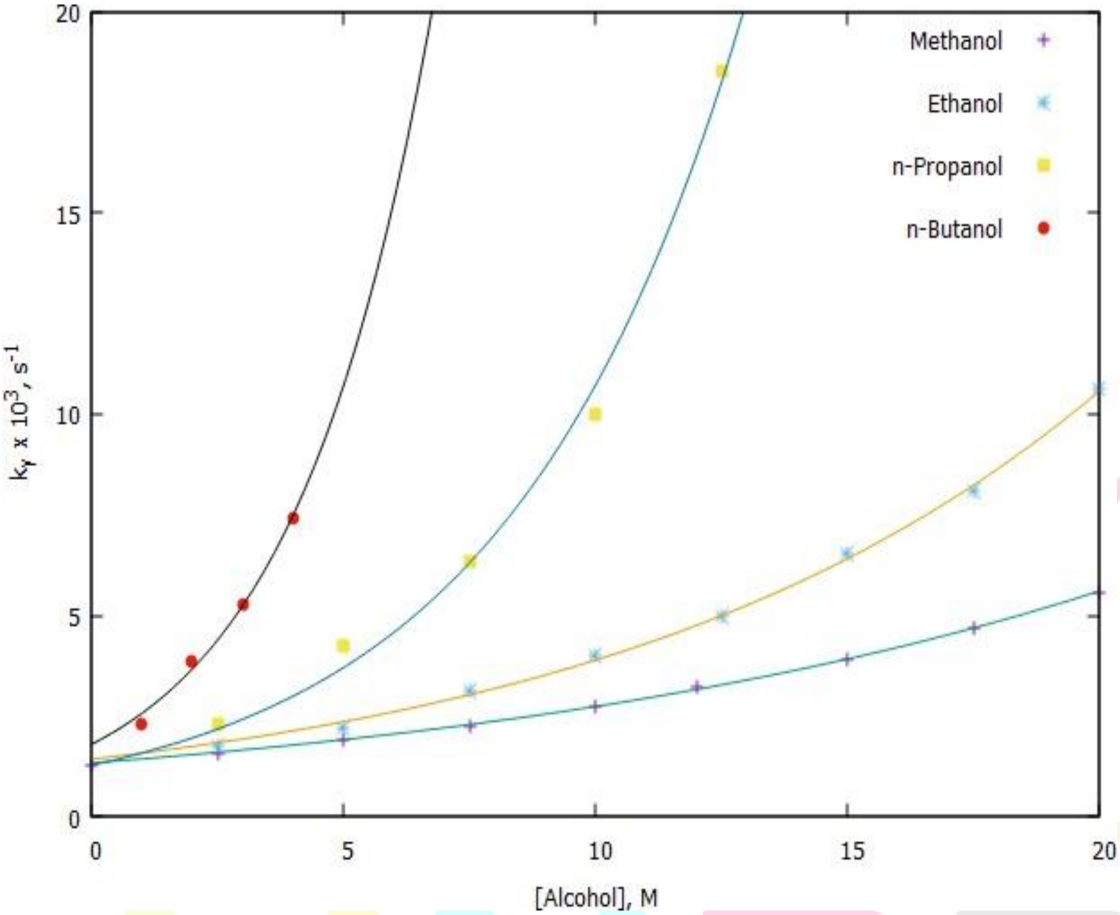


Figure 7(a): Effect of organic solvents on the reaction of nucleophile CN^- with dye carbocation in CTAB micelles.

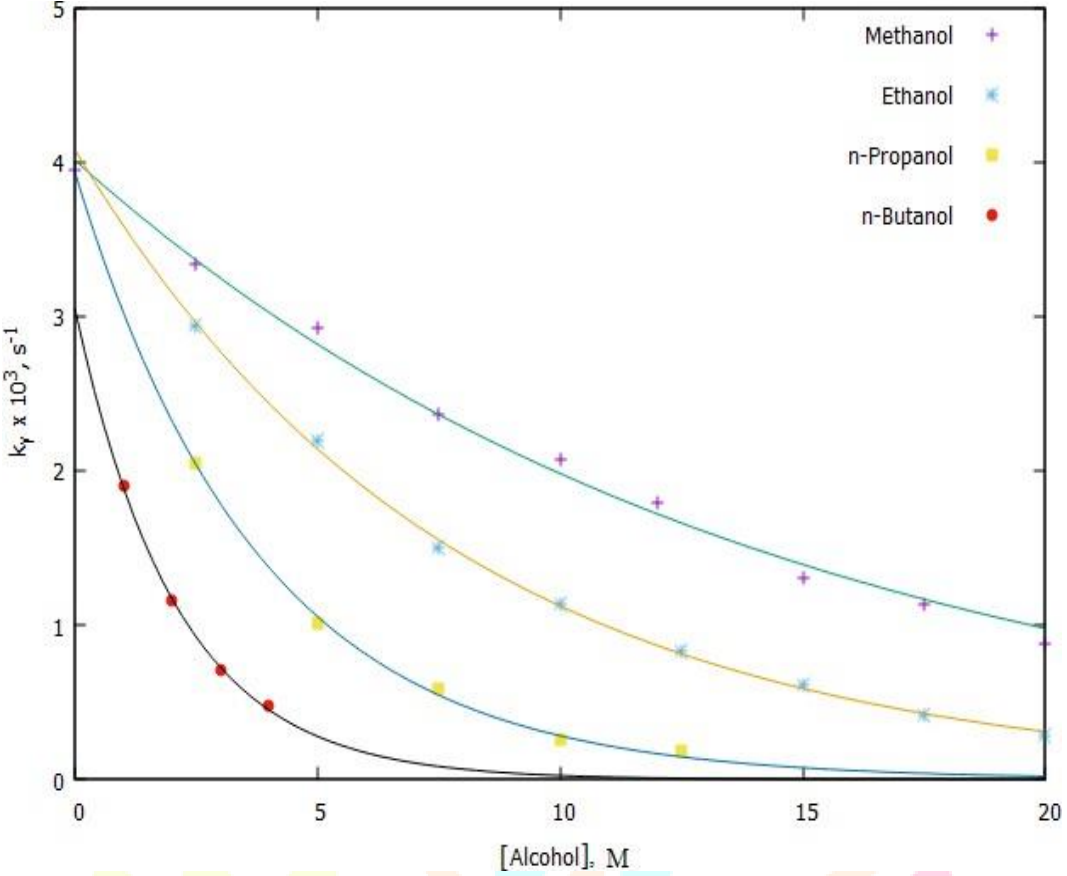


Figure 7(b): Effect of organic solvents on the reaction of dye carbocation with CN^- ion in SDS micelles at [SDS] = $5x10^{-3}$ M, [CN^-] = $3.5x10^{-1}$ M and [CV^+] = $2.5x10^{-5}$ M.

Conclusion

The present study successfully demonstrated the addition reaction of a nucleophile with a carbonium ion in the presence of a micelle. There is evidence of an interaction between carbonium ions and surfactants. The rate constant of the reaction showed a direct dependence on the nucleophile concentration and was independent of the carbonium ion concentration. CTAB micelles enhanced the overall reaction rate, whereas SDS micelles inhibited it. The positive cooperativity model of enzyme catalysis was effectively used to quantitatively analyze the kinetic data in micellar systems. The added organic solvents with long alkyl chains showed greater inhibitory effects on both overall catalysis and micelle formation.

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