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Kinetic Investigations On Nucleophilic Addition Reaction Of Cyanide Ion With Stabilized Carbonium Ions In Micellar Media.

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Abstract: The kinetics of the nucleophilic addition of cyanide ion (CN^-) to the stabilize malachite green carbonium ions (MG^+) in aqueous media is catalyzed by the cationic micelles of cetyltrimethylammonium bromide (CTAB) and is inhibited by anionic micelles of sodium dodecyl sulphate (SDS). The reactions follow pseudo-first order kinetics. The rate constant depends on surfactant concentration. The micellar data have been quantitatively analysed by Positive Cooperativity model of enzyme catalysis. The value of index of cooperativity (n) has been found to be greater than one. The catalytic and inhibitory effects have been explained in terms of hydrophobic and electrostatic interactions of various species present in the reaction systems. The added counterions show inhibitory effects on the overall catalysis.

Index Terms **- Micellar media, CTAB, SDS, Positive Cooperativity Model, Counterions**

Introduction

There has been growing interest in recent years in the studies of chemical reactions in presence of micelle forming surfactants. Micellar effects on the rate of chemical and biochemical processes vary, ranging from inhibition to activation. Various reactions in the area of micellar catalysis and inhibition have been reported in several comprehensive reviews [1-8]. The surfactants possess both hydrophobic (non-polar) and hydrophilic (polar) regions in the same molecule. Micelles are formed by the surfactants in aqueous medium which consist of two microphases :nonpolar micellar core formed by hydrophobic parts of amphiphiles and the polar surface layer formed by their headgroups. Such dual structure of micelles underlies the mechanism of their catalytic action and to a large extent causes their applicability as microreactors or nanoreactors [8,13]. Also, an analogy has been drawn between enzyme catalysis and micellar catalysis. Various physico-chemical properties are altered in micellar media leading to its numerous chemical, biological, medicinal and technological applications. Surfactants have also been successfully utilized to improve existing analytical methods and. to develop new analytical techniques[9-13]. Micellar systems have also been employed to affect the rates of several organic and inorganic reactions [6,14-22].

The reactions of cyanide ion in micellar systems, which have potential synthetic and analytical applicability, have not received wider attention. It has been demonstrated by Shinkai et al. [23] that the combination of cyanide ion with the cationic micelles of CTAB facilitates the isoalloxazine (a flavin analogues) oxidation of several aldehydes (PhCHO) to the corresponding carboxylic acids (PhCOOH). The acceleration of the reaction rate has been attributed to the enhanced local concentration of cyanide ion in the micellar phase. Further micellar systems involving CTAB and cyanide ion have been utilized to develope new analytical procedures for improving the spectrophotometric determination of cyanide ion in trace amounts [24, 25]. Such applicability is based upon the observation that CTAB micelles catalyze the nucleophilic addition reactions of cyanide ion with aromatic disulfides [24, 25] and quinine [25].

This paper reports a systematic study of the effect of cationic micelles of cetyltrimethylammonium bromide (CTAB) and anionic micelles of sodium dodecyl sulphate (SDS) on the reaction of triphenylmethane carbonium ion (MG^+) with cyanide ion (CN^-) and effect of added counterions on the CTAB catalysed reaction.The micellar catalysis has been attributed to the formation of catalytically functional micellar aggregates of various species present in the system. Further, it has also been established that the positive cooperativity model of enzyme catalysis could successfully be applied for the reaction under study. The stablized carbonium ions have been generated by malachite green (MG) dye (its structure is given in Fig.1).

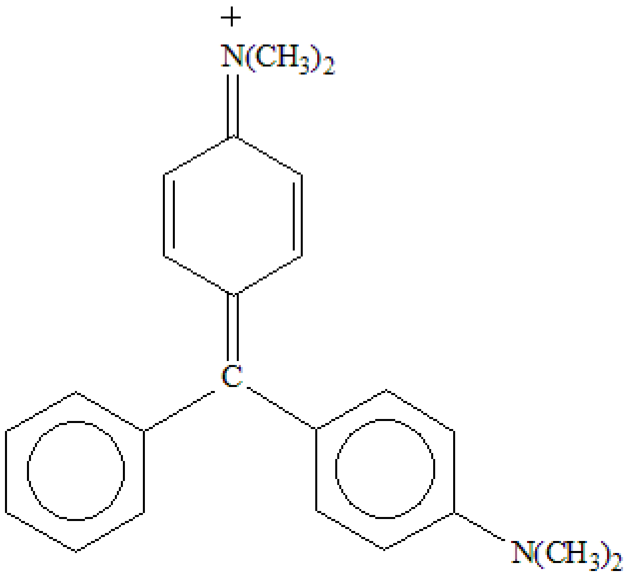


Fig.1: Structure of the substrate Malachite green carbonium ion

Experimental

Materials

Sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were procured from Sisco Chemical Industries, potassium cyanide from Loba-Chemie, malachite green (MG), from Central Drug House, disodium hydrogen orthophosphate and sodium hydroxide from Glaxo-Labs were analytical grade reagents. Sodium nitrate, sodium chloride and sodium fluoride were obtained from SISCO Chemical Industries. Doubly distilled water was used for the preparation of solutions.

Methods

All the kinetic investigations were carried out by following the decolorisation reactions on a Beckmann DU-6 Spectrophotometer in the visible range while maintaining the temperature of the cell compartment at 25° ± 0.1°C using a high precision refrigerated thermostatic bath (HAAKE). The reactions were monitored by observing the change in absorbance as a function of time at the absorption maxima (626 nm) in the "Time Drive" mode. Slopes and rate constants were calculated from the straight line plots by linear regression method. The pH of the solution was maintained at 9.5.

Results and Discussion:

The triphenylmethane carbonium ion (MG^+) exhibits absorption maxima at 616 nm in aqueous medium. In presence of both the micellar solutions (2×10^{-2} M CTAB and 5×10^{-4} M SDS) , the absorption maxima is shifted to nm 626 nm. This bathochromic shift is an evidence that the micelles bind with the substrate by incorporating the carbocations into the micelles [26].

General mechanism of reaction of dyes with cyanide ion

The decolorization of carbonium ion (MG^+) by cyanide (CN^-) ion was monitored by observing the change in the absorbance as a function of time at the respective absorption maxima. The general reaction mechanism is shown in Fig.2. In the initial step, the substrate dye ionizes in an aqueous solution giving a positively charged dye carbonium ion. The positive charge is delocalized over the whole molecule due to resonance stabilization of the molecule. The nucleophile (CN^-) attacks the dye carbonium ions forming colorless triarylleuconitrile compounds.

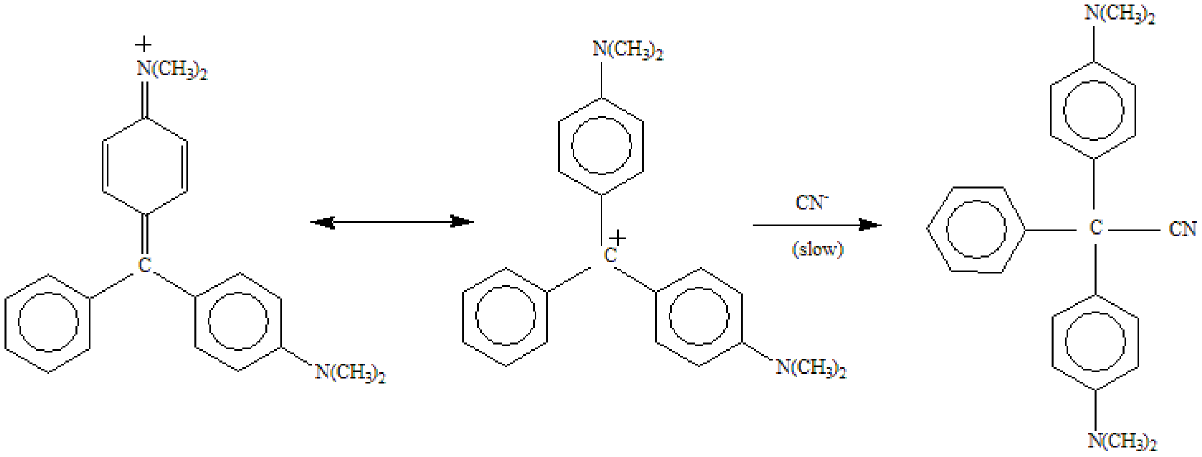


Fig.2: Mechanism of the reaction between Malachite green (MG) carbonium ion with Cyanide ion

"Figure 3" shows the effect of the dye and nucleophile concentration on the rate of the reaction. There is no observable change on the rate of the reaction with the increase of the dye concentration (Fig. 3a).

With an increase of the nucleophile concentration from 5×10^{-1} M to 4.64×10^{-2} M at a fixed concentration of the dyes, the rate of the reaction increases linearly for each of the reactions between the dye carbonium ion and cyanide ion (Fig. 3b). The above results indicate that the rate of the reaction follows pseudo-first order reaction with respect to the nucleophile. The reactions of the dye carbocations with the cyanide ion were carried out at pH 9.5. The pK_a value of hydrocyanic acid (HCN) is 9.21 and therefore, it was necessary to work at a pH more than 9.21, whereby appreciable nucleophile concentration would be available for the reaction. The hydroxyl ion also reacts and decolorizes these dyes in solution, and reaction rates with the hydroxyl ions are also affected by surfactants. So, an appropriate pH and buffer system (Na_2HPO_4 and NaOH) is selected at which the rates of reactions due to the hydroxyl ion is negligible as compared to the cyanide ion under the given conditions.

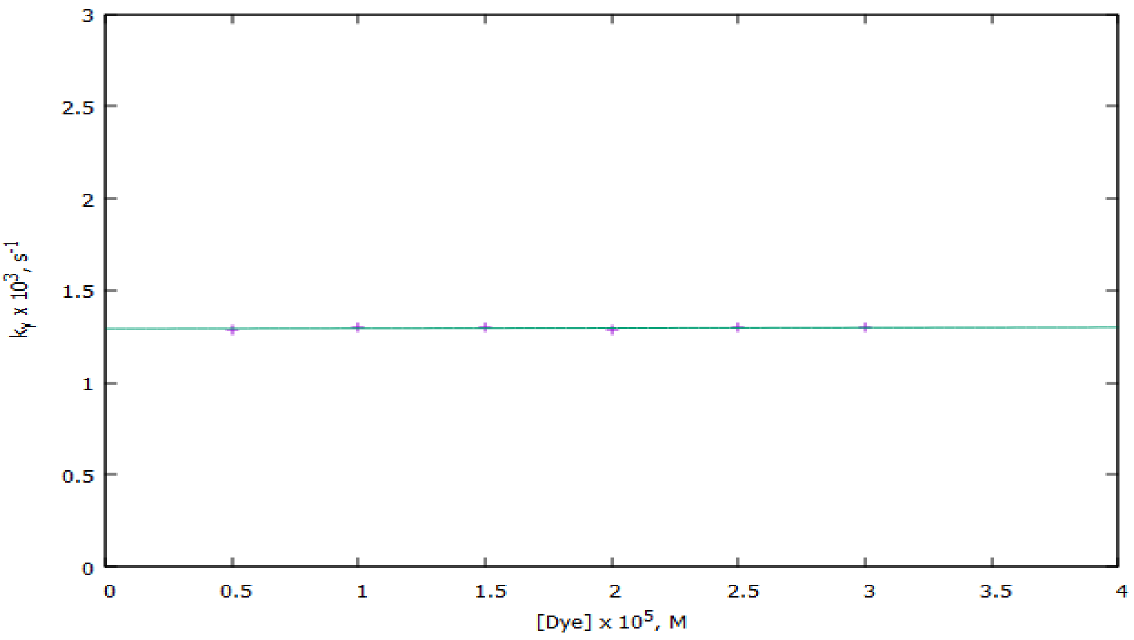


Fig.3(a): Effect of concentration of carbonium ion on the rate constant of the reaction of dye carbonium ion with cyanide ion.

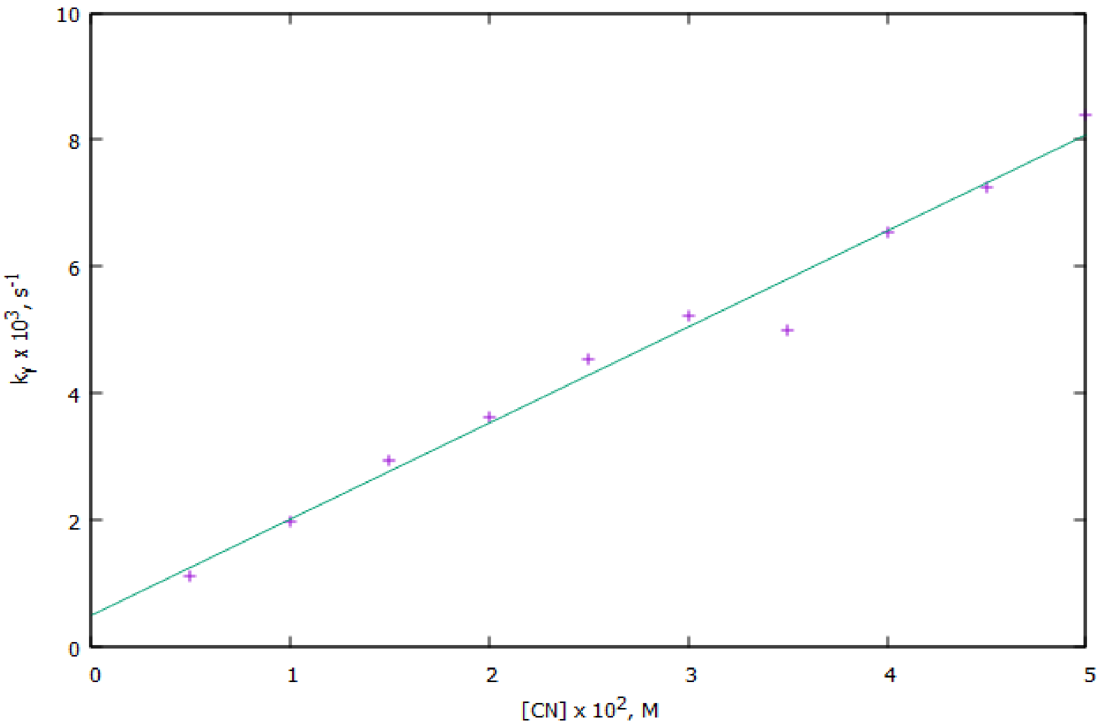


Fig.3(b): Effect of concentration of nucleophile on the rate constant of the reaction of dye carbonium ion with cyanide ion.

Effect of CTAB surfactant on the rate of the reaction

"Figure 4" shows the effect of CTAB on the rate of the reaction of the dye (MG) carbonium ion with cyanide ion. The rate constant exhibits increasing trend with the increase of the CTAB concentration initially and becomes nearly saturated at higher concentration. The catalytic effect of CTAB micelles can be explained by considering both the electrostatic and hydrophobic interactions which are operating simultaneously in the reaction systems. The reagent CN^-, being negatively charged has favourable attractive interaction with the positively charged CTAB micellar aggregate which contains hydrophobic substrate. Thus, approach of CN^- is facilitated towards the substrate and the local concentration of cyanide ion increases around the micellar aggregate, leading to the catalytic effect by CTAB. The variation of the pseudo-first order rate constant as a function of CTAB concentration is shown in Fig. 4. The overall catalysis factor k^+_{rel} ($=k_m / k_w$ where k_m is the rate constant in micellar phase and k_w is the rate constant in the absence of the surfactant) for MG^+ was found to be 16. The triphenylmethane dye substrates (which have hydrophobicity) producing carbonium ions have an electrophilic carbon at the centre to which the nucleophile (CN^-) attacks.

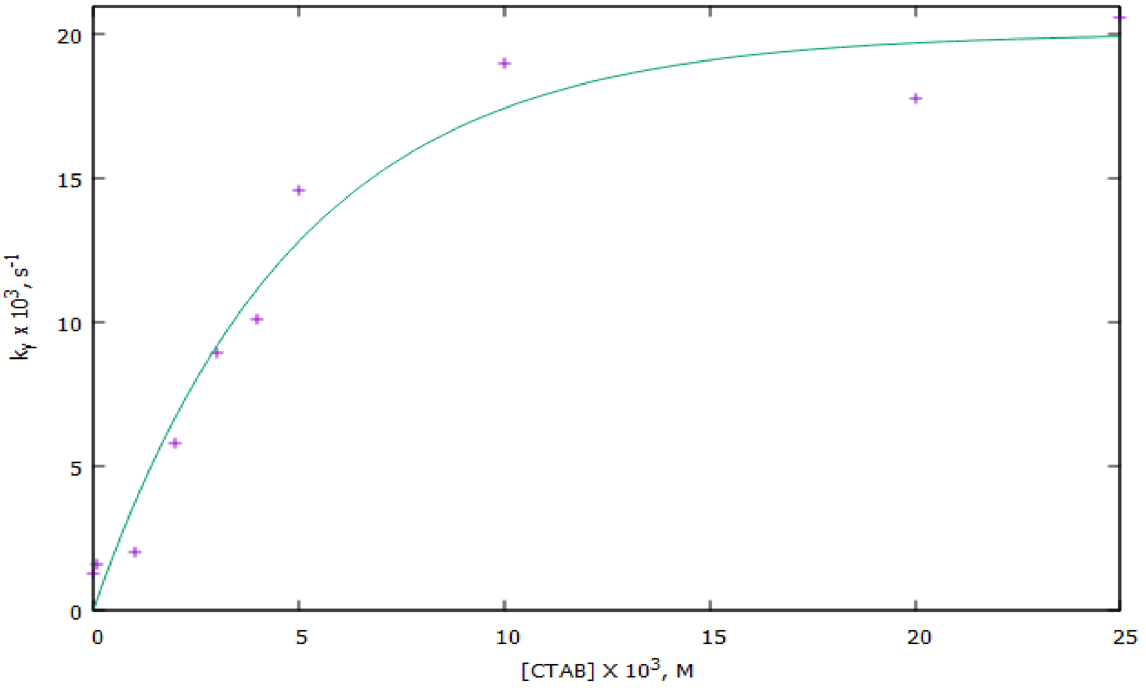


Fig. 4: Effect of CTAB micelles concentration on the rate constant of Malachite green (MG^+) carbonium ion with cyanide ion.

Effect of SDS surfactant on the rate of the reaction

"Figure 5" the effect of SDS on the rate of the reaction of the dyes (MG) carbonium ion with cyanide ion. The rate constant exhibits a decreasing trend with the increase of the SDS concentration initially and becomes nearly saturated at higher concentration. As both the hydrophobic and electrostatic interactions between the substrate (dye carbocation) and anionic SDS micelles are favorable to each other, the dye carbocation are strongly bound to the SDS micelles. The core SDS micelles are hydrocarbon-like and due to the high hydrophobicity of the dye carbocation, it is solubilized into the micellar aggregate. It is also favored by the electrostatic interaction between the positively charged dye carbocation and negatively charged SDS micelles. The nucleophile CN^-, which lacks hydrophobicity and bearing charge similar to that of SDS micellar surface (or head group) is excluded from the micellar aggregates containing the dye carbocation. Thus, in the presence of SDS micelles, an inhibitory effect is observed due to non-approachability of the nucleophile to the strongly bound dye carbocation in the negatively charged SDS aggregate. The overall inhibition factor k^-_{rel} ($=k_m / k_w$ where k_m is the rate constant in micellar phase and k_w is the rate constant in the absence of the surfactant) for MG^+ was found to be 5.

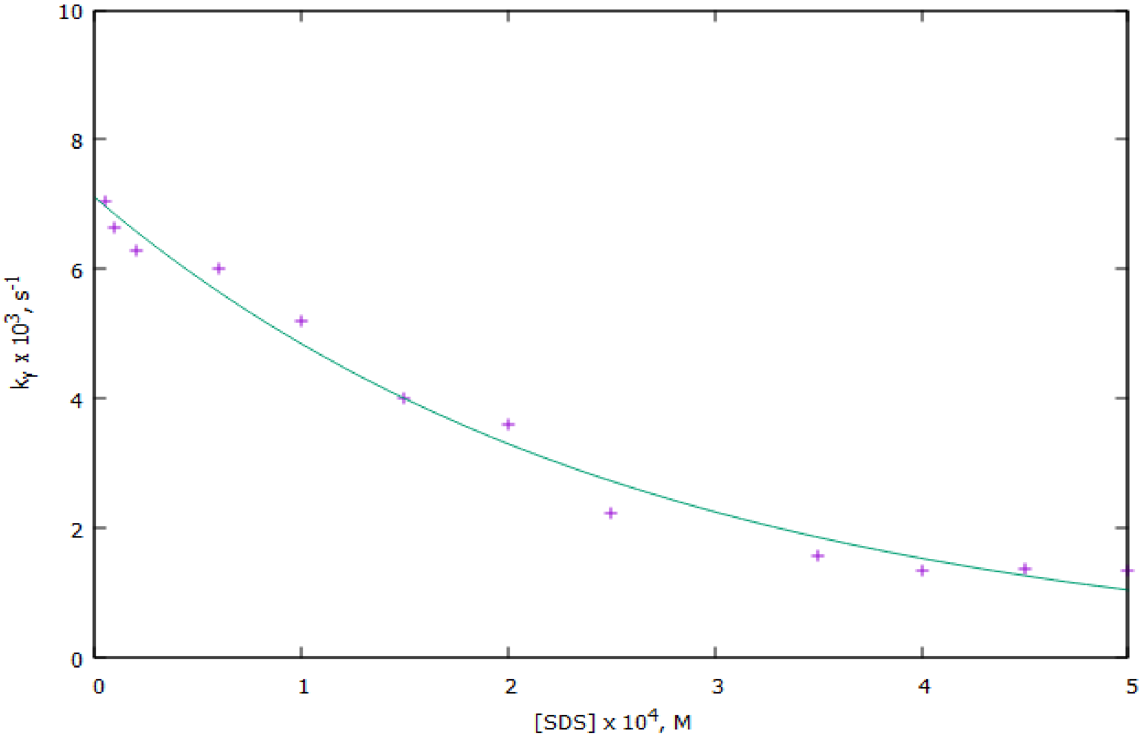


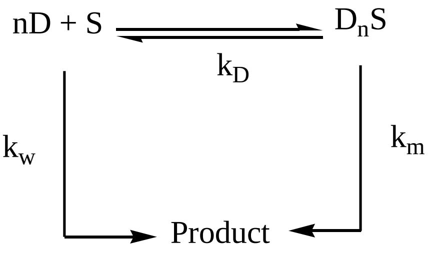
Fig. 5: Effect of SDS micelles concentration on the rate constant on the reaction of Malachite green (MG^+) carbonium ion with cyanide ion.

Quantitative analysis of micellar data

In order to understand the mechanism by which enzymes catalyze reactions, many efforts have been made in studying mechanism of simpler model chemical reactions [27,28]. Reactions catalyzed or inhibited by micelles have thus been viewed as models for enzyme catalyzed reactions [2,4]. This analogy, though far from perfect, is based on the observation that micelles and enzymes are structurally and functionally similar. Both micelles and enzymes have hydrophobic cores with polar regions on their surfaces. Both bind substrate in a non-covalent manner. The kinetics of micellar catalysis also resembles that of enzyme catalysis as described in various investigations [2, 4, 29-31].

A kinetic model analogous to the Hill Model which describes the positive cooperativity in enzyme catalysed reactions, has been used for a quantitative analysis of the micellar data. With reference to enzymes, positive cooperativity or homotropic interaction is defined as a stimulation (or inhibition) of the interaction of additional molecule(s) of a substrate with an enzyme as a result of interaction of the first molecule(s) of the substrate with the enzyme.

This model suitable for micellar reactions and analogous to the Hill Model has been developed by Piszkiewicz [29, 30]. Thus by analogy, with reference to micellar catalysis, cooperativity is defined as a 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 (the dye carbocation in our case) and a number n of the surfactant (or the detergent) molecules D, aggregate to form the catalytically functional micellar aggregate D_nS, which may undergo reaction to yield products. Such aggregation may be represented by the following scheme 1.



Scheme 1

K_D is the dissociation constant of the micelle substrate complex (its reciprocal may give the binding constant), k_m and k_w are the rates of the reactions in the micellar and the bulk (aqueous) phases, respectively. For this reaction scheme the pseudo-first order rate constant k is expressed as a function of the concentration of the detergent D, by the equation (1).

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

This equation may be written in the following form

$$\log \frac{k_\psi - k_w}{k_m - k_\psi} = n\log\,[D] - \log k_D \qquad (2)$$

According to the equation (2), a plot of log $[(k_\psi - k_w) / k_m - k_w)]$ versus log [D] should be linear with slope, n and intercept (- log k_D). Further if we take

$$k_\psi = \frac{k_m + k_w}{2}$$

the left hand side of the equation (2) becomes zero, i.e., log $[(k_\psi - k_w) / (k_m - k_\psi)] = 0$ the catalysis shows one half of its effect on the rate constant.

The value of [D] or log [D] at this point of half maximal catalysis is designated as $[D]_{50}$ or $\log[D]_{50}$ and when the left hand side of the equation (2) is zero, we have

$$\log[D]_{50} = \frac{\log k_D}{n}$$

Thus, in this model, slope (n) of the double log plot describes the stoichiometry of the reaction scheme 1. The value of n > 1 reflects positive cooperativity.

The applicability of the treatment given by equation (2) was tested using micellar data of the dye carbonium ion in CTAB and SDS system as shown in Fig.4 (CTAB) and Fig. 5 (SDS). The Hill type double log plots and the quantitative analysis according to equation (2) for the reaction under study is shown in Fig. 6 and Table 1. It is note that the value of "n" is found to be greater than 1 showing the evidence of positive cooperativity in the reaction system; the applicability of Piszkiewicz's cooperativity model has also been tested for many other micellar reactions [29-31]. For the reaction of dye carbonium ion with nucleophile, CN^- , in presence of micelles, catalysis and inhibition was found to begin in the pre-micellar region.

Table 1: Values of parameters from Hill type plots (Fig. 7) according to eqn. 2 applying Piezkiewicz's model for CTAB cataysed and SDS inhibited reaction of malachite green carbonium ion (MG^+) with CN^-

Micelles	No. of k_ψ and D values used	Slope (Index of cooperativity)	$[D]_{50}$	Intercept (-log k_D)	K_D	Binding constant
CTAB	6	1.47 ± 0.01	3.56×10^{-3}	3.6 ± 0.04	2.51×10^{-4}	3.9×10^{3}
SDS	5	1.59 ± 0.11	1.54×10^{-4}	6.26 ± 0.45	8.7×10^{-7}	1.1×10^{8}

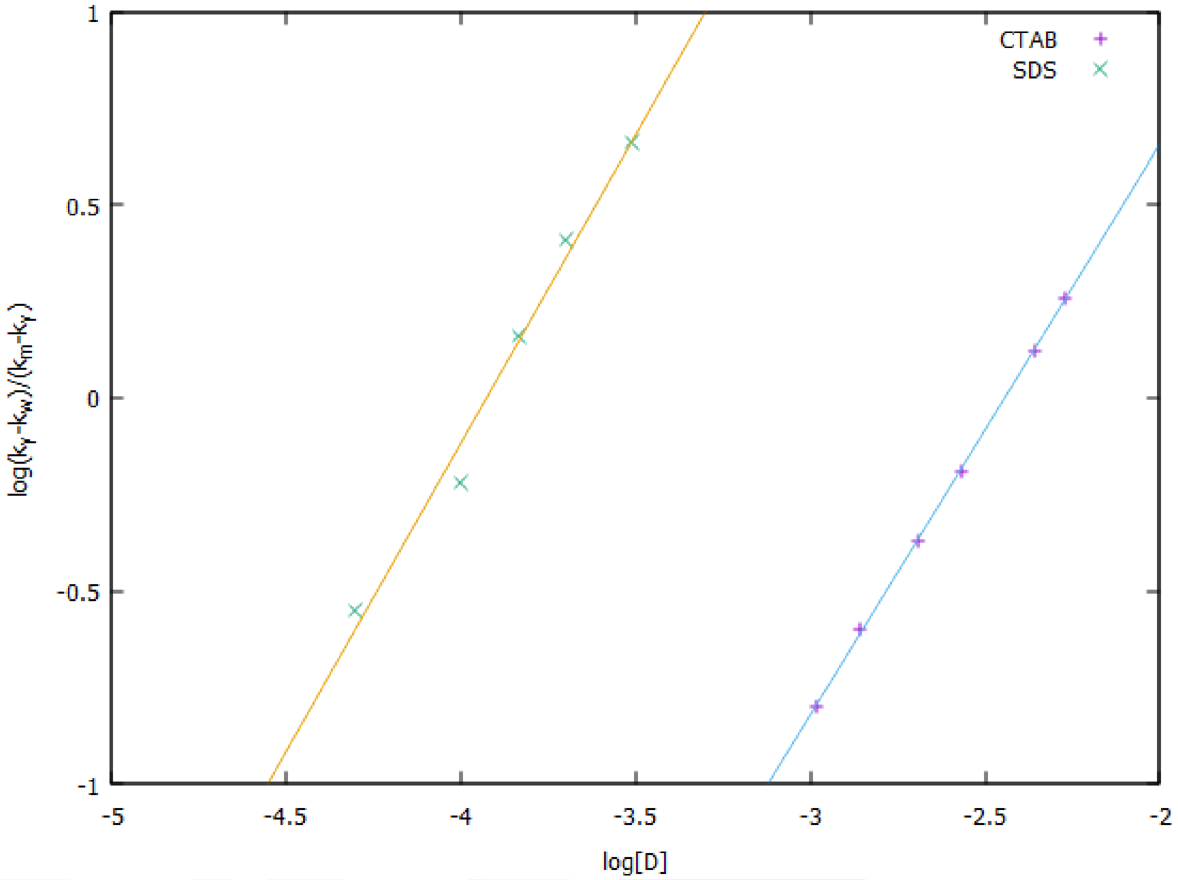


Fig. 6: Quantitative analysis of the effect of micelles of CTAB and SDS onr the reaction between MG^+ and CN^- showing positive coorperativity model of enzyme catalysis (Hill-type plots)

Effect of Counterions

The effect of added counter ions on the CTAB catalysed reaction of MG^+ with CN^- was investigated by varying the concentration of electrolytes. Counter ion is the ion having charge opposite to that of micellar surface. All the added counter ions X^- = NO_3^-, CI^- and F^-, exhibited inhibitory effects on the rate in the presence of CTAB in fig. 7. The added counter ions reduce the extent of overall catalysis earlier caused by the CTAB micelles, in the following order: $NO_3^- > CI^- > F^-$.

Thus, the anions having large size and low charge density have more influence since they can partly neutralise the micellar charge more effectively. The results closely parallel to lyotropic series [32,33]which represents salt effects on precipitation and denaturation processes of proteins.

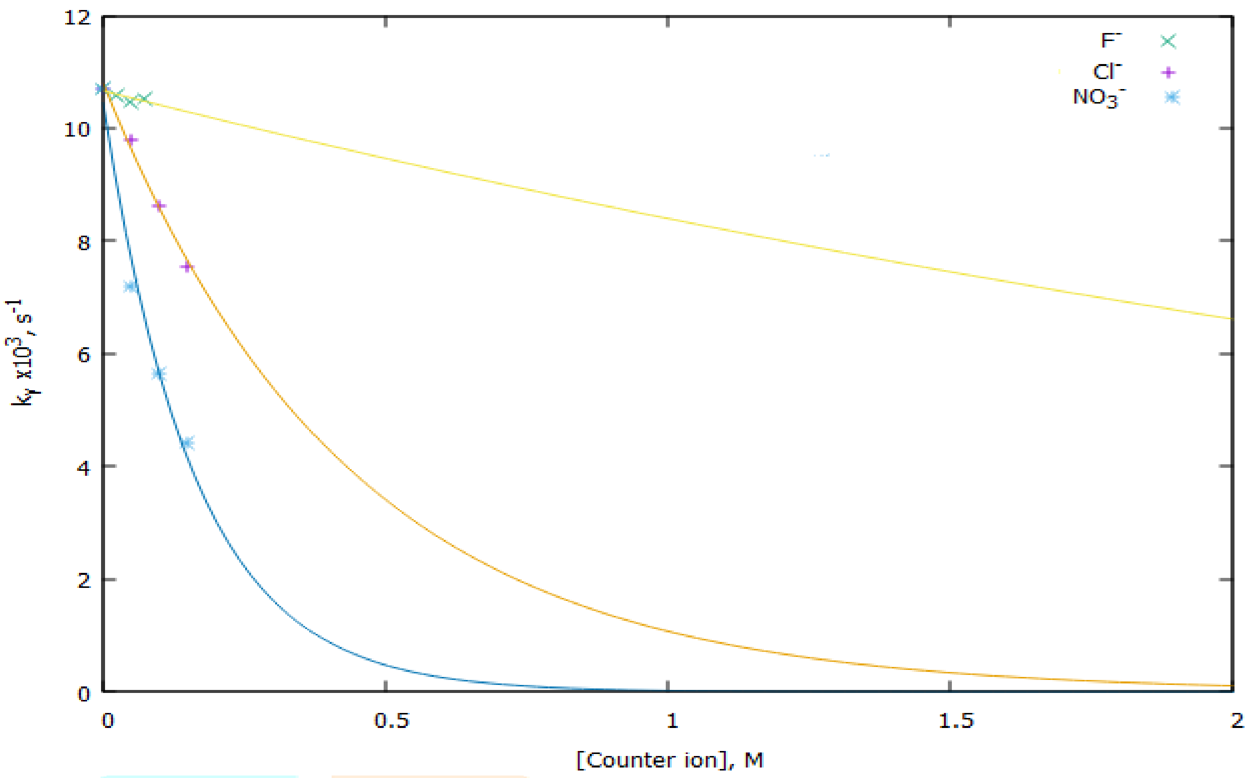


Fig. 7: Effect of added counter ions on the rate constant for CTAB catalysed reaction of MG^+ with CN^-.

Conclusion

The present study successfully demonstrated the addition reaction of nucleophile with carbonium ion in presence of micelles. There is evidence of interaction of carbonium ion with surfactants. The rate constant of the reaction shows linear dependence on nucleophile concentration and is independent of carbonium ion concentration. CTAB micelles catalyses the overall rate of the reaction and SDS micelles inhibit the overall reaction. The positive cooperativity model of enzyme catalysis has been successfully applied for quantitative analysis of the kinetic data in presence of micelles. The counter ions having large size and low charge density reduces the extent of overall CTAB catalysed reaction.

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