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Kinetic studies on sodium dodecyl sulfate micelle inhibited reactions of triphenylmethyl carbocations with cyanide ion

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Abstract The kinetics of the decolorization reactions of triphenylmethane dyes (BG, MG and PRH) with the cyanide ion (nucleophile) were studied in the presence of anionic micelles of sodium dodecyl sulfate (SDS). The reactions follow pseudo-first order kinetics. The rate constant depends on surfactant concentration. SDS micelles inhibit the overall rate of the reaction between the dye carbocation with the nucleophile. Quantitative analysis of the micellar data obtained has been done by applying a positive cooperativity model of enzyme catalysis. For all the dyes under study, the value of n (index of cooperativity) has been found to be greater than one. The inhibitory effect has been explained in terms of hydrophobic and electrostatic interactions of various species present in the reaction systems.

Keywords Cyanide · Micelles · SDS · Dyes · Kinetics

Introduction

There has been growing interest in the studies of chemical reactions in the presence of micelle-forming surfactants [1–4]. 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, 5–9]. The surfactants possess both hydrophobic (non-polar) and hydrophilic (polar) regions in the same molecule [6, 7]. Also, an analogy has been drawn between enzyme catalysis and micellar catalysis. The physico-chemical properties are altered in micellar media leading to its numerous chemical,

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biological medicinal and technological applications. Surfactants have also been successfully utilized to improve existing analytical methods and to develop new analytical techniques. Micellar systems have also been employed to affect the rates of several organic and inorganic reactions [6, 7, 10–12].

The alkaline fading of triphenylmethane dyes has been extensively reported [13, 14] and investigations have also been carried out in the presence of various nucleophiles namely hydroxyl ions, sulfite ions, etc. [14, 15]. Photodegradation of dyes have been reported by utilizing various nanomaterials [16, 17]. 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. [18] 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 develop new analytical procedures for improving the spectrophotometric determination of cyanide ion in trace amounts [19, 20]. Such applicability is based upon the observation that CTAB micelles catalyze the nucleophilic addition reactions of cyanide ion with aromatic disulfides [19, 20] and quinine [20]. Bunton et al. have investigated the addition of cyanide ion to the various substrates by using a reactive counterion surfactant (CTACN—Cetyl trimethyl ammonium cyanide) [21]. In spite of all these findings about the synthetic and applicability of cyanide ion, due consideration has not been given to the systematic studies on the reaction kinetics of cyanide ion in micellar media.

This paper reports a systematic study of the kinetic effect of anionic micelles of sodium dodecyl sulfate (SDS) on the reaction of selected triphenylmethane carbocations with cyanide ion. The micellar inhibition has been attributed to the formation of functional micellar aggregates of various species present in the system. Furthermore, it has been successfully established that the positive cooperativity model of enzyme catalysis could be applied for the reaction under study.

Experimental

Materials

Sodium dodecyl sulfate (SDS) was procured from Sisco Chemical Industries, potassium cyanide from Loba-Chemie, brilliant green (BG), malachite green (MG), pararosaniline hydrochloride (PRH) from Central Drug House, disodium hydrogen orthophosphate and sodium hydroxide from Glaxo-Labs were analytical grade reagents. Double distilled water was used throughout the work for the preparation of solutions.

Methods

The kinetic investigations were studied spectrophotometrically by following the decolorization reactions on a Beckman DU-6 Spectrophotometer in the visible range while maintaining the temperature of the cell compartment at 25.0 ± 0.1 °C using a high precision refrigerated thermostatic bath (HAAKE). 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 632 nm (BG), 626 nm (MG) and 552 nm (PRH) in presence of SDS micelles. 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 dyes (MG, BG and PRH) exhibit maximum absorptions at 616, 624 and 546 nm. In the presence of 2×10^{-2} M SDS micelles, the absorption peak is shifted to 626, 632 and 552 nm (Table 1). The red shift of the λ_{max} value shows that SDS micelles bind with the substrate by incorporating the dye carbocations into the micelles [22]. Fig. 1 shows the normalized absorbance of the dye carbocations (MG, BG and PRH) in absence and presence of SDS micelles.

General mechanism of reaction of dyes with cyanide ion

The decolorization of dye carbocations 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 carbocation. The positive charge is delocalized over the whole molecule due to resonance stabilization of the molecule. The nucleophile (CN^-) attacks the dye carbocations forming colorless triarylleuconitrile compounds.

Fig. 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). The dye concentration was varied from 0.5 to 3×10^{-5} M at the fixed concentration of the nucleophile (2.64×10^{-2} M). The observed rate constant for MG, BG and PRH are 11.33 ± 0.11, 5.9 ± 0.11 and $7.74 \pm 0.12 \times 10^{-3}$ s^{-1}.

With an increase of the nucleophile concentration from 0.64 to 4.64×10^{-2} M at a fixed concentration of the dyes, the rate of the reaction increases linearly for each

Table 1 Absorbance maxima (λ_{max}) of dyes (BG, MG and PRH) in the absence and presence of SDS micelles

Sl. no.	Dye	λ_{max} (nm)	
		In the absence of surfactant	In the presence of SDS surfactant
1.	Malachite green (MG)	616	626
2.	Brilliant green (BG)	624	632
3.	Pararosaniline hydrochloride (PRH)	546	552

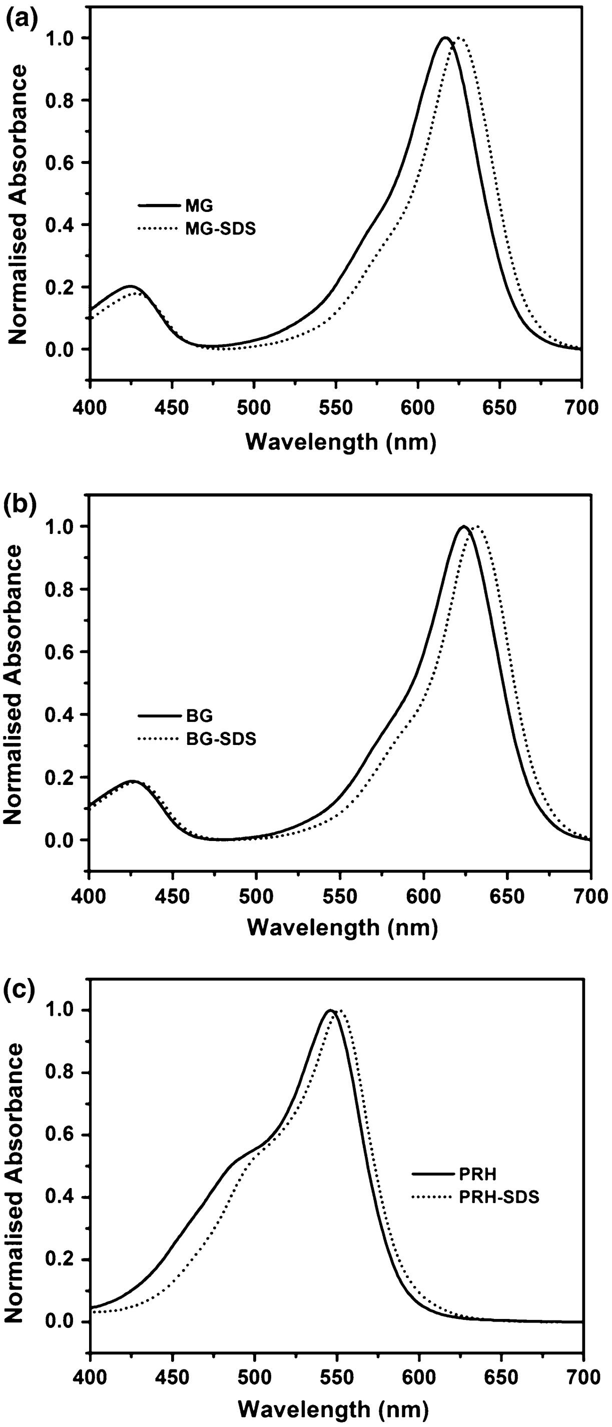
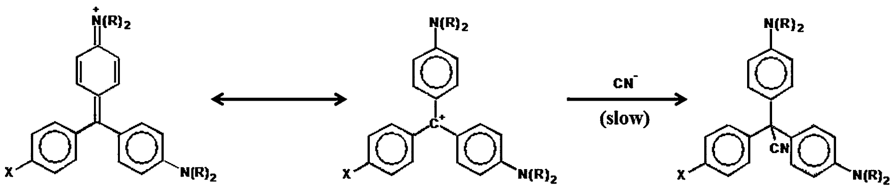


Fig. 1 Absorbance of dyes **a** MG, **b** BG and **c** PRH in absence and presence of SDS surfactant



Substrate (Dye)	**R**	**X**
Malachite Green (MG)	CH_3	H
Brilliant Green (BG)	CH_2CH_3	H
Pararosaniline hydrochloride (PRH)	H	NH_2

Fig. 2 Mechanism of the reactions between dye carbocations (MG^+, BG^+, PRH^+) with cyanide ion

of the reactions between the dye carbocation 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.

Effect of SDS surfactant on the rate of the reaction

Fig. 4 shows the effect of SDS on the rate of the reaction of the dyes (BG, MG and PRH) 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. A schematic representation for the interaction of the dye carbocation with the nucleophile in presence of SDS surfactant is shown in Scheme 1. The triphenylmethane dye substrates (which have hydrophobicity) producing carbonium ions have an electrophilic carbon at the centre to which the nucleophile (CN^-) attacks.

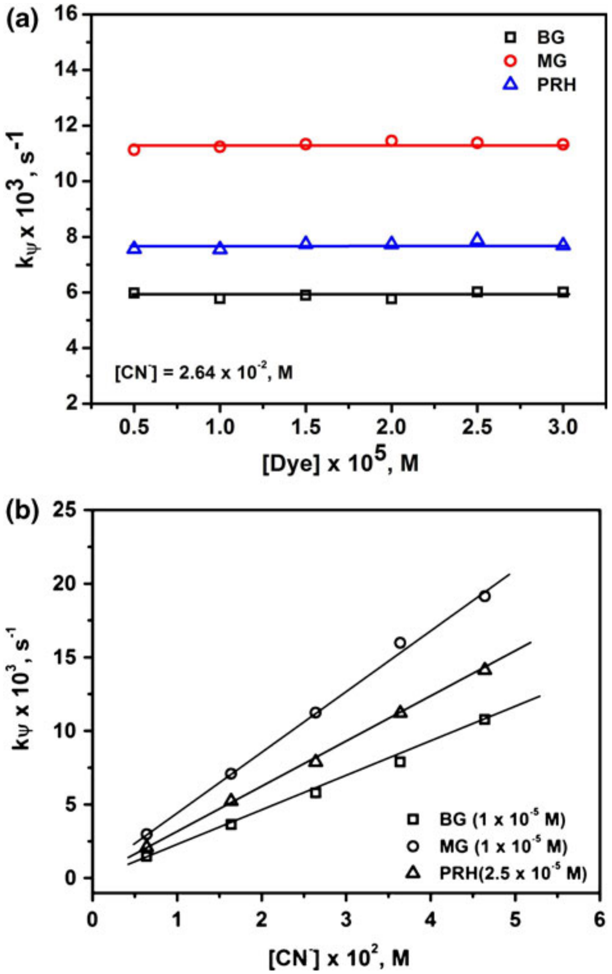


Fig. 3 Effect of concentration of **a** dye and **b** nucleophile on the rate constant of the reaction

The overall inhibition factor, k^{-}_{rel} (k_w/k_m) is found to be 29.9 for the reaction of BG with cyanide ion, where k_w and k_m is the rate constant at aqueous and micellar phase. For MG and PRH reactions, the overall inhibition factor, k^{-}_{rel} (k_w/k_m) is observed to be 5.08 and 10.88, respectively. The reason for the difference on the overall inhibition factor can be ascribed to the hydrophobicity factor. For the substrate BG, being more hydrophobic due to the presence of $-CH_2CH_3$, the substrate is solubilized into the hydrophobic core which further reduces the interaction with the nucleophile. The other substrates, MG and PRH are less hydrophobic, and therefore are preferably localized on the micellar surface, thus leading to the less inhibitory effect from the anionic SDS micelles. Thereby, the inhibitory effect of the anionic SDS micelles is more prominent in case of the substrate BG than the other two substrates.

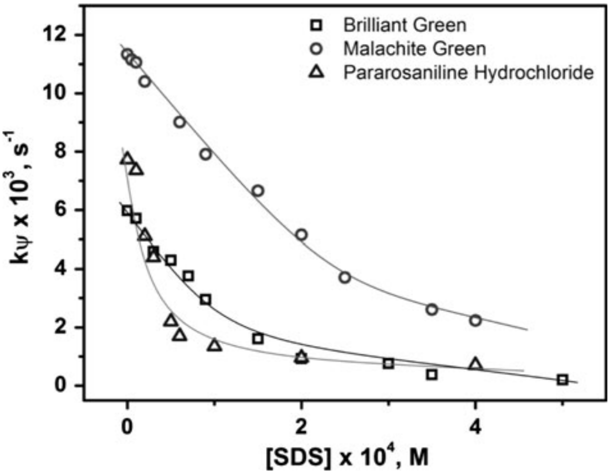
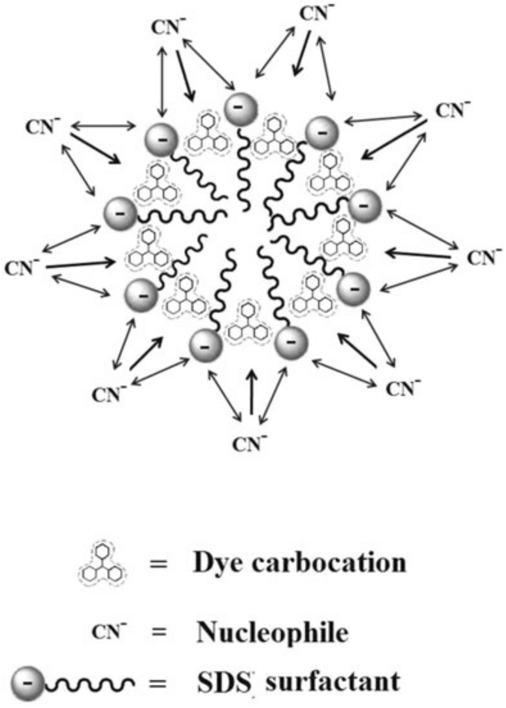


Fig. 4 Effect of SDS surfactant concentration on the rate constant of the reaction of dye carbocations (MG^+, BG^+, PRH^+) with cyanide ion

Scheme 1 Schematic diagram for the interaction of dye carbocation with the nucleophile in the presence of SDS micelles

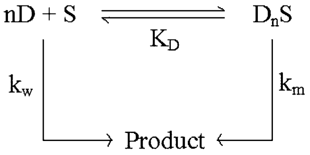


Quantitative analysis of micellar data

In order to understand the mechanism by which enzymes catalyze reactions, many efforts have been made in studying mechanism of simpler model chemical reactions

[23, 24]. Reactions catalyzed or inhibited by micelles have thus been viewed as models for enzyme catalyzed reactions [6, 7]. 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 [6, 7, 25–27].

A kinetic model analogous to the Hill Model, which describes the positive cooperativity in enzyme catalyzed reactions has been used for the quantitative analysis of micellar data [28, 29]. This assumes that a substrate, S (dye carbocation) and a number '*n*' of the surfactant (or detergent) molecules D, aggregate to form catalytically functional micellar aggregate D_nS, which may undergo reaction to yield products.



K_D is 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. For this reaction scheme, pseudo-first order rate constant k_Ψ is expressed as a function of concentration of the detergent D, by the following equation:

$$k_\Psi = \frac{k_m[D]^n + k_w K_D}{K_D + [D]^n} \tag{1}$$

This equation can be written in the following form,

$$\log\left[\frac{(K_\Psi - k_w)}{(k_m - k_\Psi)}\right] = n\log[D] - \log K_D \tag{2}$$

From Eq. 2, a plot of log $[(k_\Psi - k_w)/(k_m - k_\Psi)]$ versus log [D] should be linear with slope, *n* and intercept (−log K_D). The value of [D] or log [D] at this point of half maximal inhibition is designated as $[D]_{50}$ or log $[D]_{50}$ and when left hand of the Eq. 2 is zero, we have

$$\log[D]_{50} = \frac{\log K_D}{n} \tag{3}$$

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

The applicability of Eq. 2 was tested by using the micellar data for the dye carbocations (BG, MG and PRH) in an SDS micellar system as shown in Fig. 4. The Hill-type double log plots and the quantitative analysis according to Eqs. 2 and 3, for the reactions under study are shown in Fig. 5 and Table 2. The linear Hill-type plots show good correlation coefficient (R^2), values being 0.9756, 0.9951 and 0.9748 for various substrates BG, MG and PRH, respectively. It is found that the

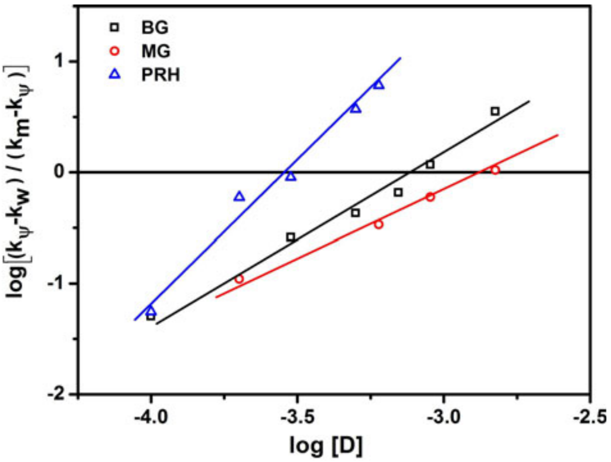


Fig. 5 Quantitative analysis of the effect of SDS surfactant on the reaction of dye carbocations (MG^+, BG^+, PRH^+) with CN^- ion, applying positive cooperativity model of enzyme catalysis (Hill-type plots)

Table 2 Values of parameters from Hill-type plots for SDS inhibited reaction of dye carbocations (BG^+, MG^+ and PRH^+) with nucleophile

Dye	No. of k_Ψ and D values used	Slope, *n* (index of cooperativity)	$[D]_{50}$	Intercept ($-\log k_D$)	K_D	Binding constant ($1/K_D$)
BG	5	1.5 ± 0.1	8.57×10^{-4}	4.6 ± 0.4	2.51×10^{-5}	3.98×10^{4}
MG	5	1.1 ± 0.1	1.39×10^{-3}	3.2 ± 0.2	6.31×10^{-4}	1.59×10^{3}
PRH	5	2.5 ± 0.2	2.75×10^{-4}	8.9 ± 0.7	1.26×10^{-9}	7.94×10^{8}

binding constant in the SDS micellar system are 3.98×10^4, 1.59×10^3 and 7.94×10^8 for the BG, MG and PRH dyes. It is to note that the value of n was found to be greater than one for all the dyes under study showing the positive cooperativity in the micellar system. The applicability of Piszkiewicz's cooperativity model has also been reported for other micellar reactions [30, 31]. For the reaction of dye carbocations with nucleophile, CN^- in the presence of SDS, inhibition was found to begin in the pre-micellar region.

Conclusions

The reactions of triphenylmethane dyes (BG, MG and PRH) with the nucleophile (cyanide ion) were studied in the SDS micellar systems. There is evidence of dye-surfactant interaction. The rate constant of the reaction shows linear dependence on nucleophile concentration, and is independent of dye concentration. SDS micelles inhibit the overall rate of the reaction. The positive cooperativity model of enzyme catalysis has been successfully applied for the quantitative analysis of the kinetic data in presence of micelles.

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