Specific interactions of anions and pre-micelles in the alkaline fading of crystal violet carbocation

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HIGHLIGHTS

- Alkaline fading of CV carbocation in the pre-micellar region.
- Specific interactions of $Cl^-/Br^-/I^-/SO_4^{2-}$ with CV^+.
- Olson–Simonson model of ion pair formation.
- Pre-micellar aggregates of SDS/AOT, inhibition of reaction rate.
- Piszkiewicz co-operativity model of pre-micelle cluster.

GRAPHICAL ABSTRACT

The pre-micellar aggregates between the CV carbocation and the negatively charged surfactant monomers make it difficult for the entry of HO^- to the reaction center resulting in the inhibition of the alkaline fading of crystal violet. Electrostatic as well as hydrophobic interactions between CV^+ and anionic surfactant monomers play key role in the formation of pre-micellar aggregates.

ARTICLE INFO

ABSTRACT

The specific interactions of inorganic anions (Cl^-, Br^-, I^- and SO_4^{2-}) and pre-micelles in the alkaline fading of crystal violet carbocation (CV^+) have been studied in the temperature range 303–318 K. The pseudo-first order rate constant decreases with increasing the concentration of anions and ultimately reaches a limiting value. Cl^- and Br^- ions appear to exert simple salt effects on the reaction rate, while larger ion I^- and bivalent ion SO_4^{2-} exert some specific electrostatic interaction effects on the CV carbocation. This salt effect on the reaction rate has been rationalized in terms of Olson–Simonson (O–S) model of ion pair formation. The same reaction has been studied in the presence of two anionic surfactants, namely, sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) at concentrations well below their CMC. A sharp decrease in the rate constant with increasing surfactant concentration suggests a pre-micellar aggregation between the CV^+ ion and SDS/AOT monomers. The results have been explained using O–S model as well as Piszkiewicz cooperativity model. The single hydrocarbon tail in SDS binds favorably to the CV^+ in the pre-micelle whereas in AOT the presence of two hydrocarbon tails makes the binding less favorable due to some steric crowding. The cooperativity index (n) values in the pre-micelle cluster suggest the formation of a 1:1 and 1:2 dye-surfactant ion pair. In AOT pre-micelle the nucleophile HO^- gets easier access to the reaction center leading to a lower energy of activation and higher rate of reaction than those in case of SDS.

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1. Introduction

Self-organized assemblies such as micelles have created interests because of their importance in a number of fields such as pharmaceutical, environmental as well as biological systems [1–5]. These microdispersed systems often affect the rate of the reactions especially when the reactions take place at the interface of these media [6–9]. Micelles and reverse micelles are nowadays used to prepare nanoparticles of coinage metals such as copper, silver and gold which have strong catalytic effect on different reactions [10,11]. The fact that surface catalyzed reactions are comparable to the enzyme catalyzed reactions has drawn interests of many researchers in this direction [12,13]. The similar nature of these two types of reactions is mainly based on their similar structure containing hydrophobic core as well as polar group [12]. Micelles are often found to catalyze or inhibit the rates of different chemical reactions owing to electrostatic and hydrophobic interactions [14]. The accelerating effect of micelles has been attributed to the fact that micelles increase the local concentration of reactants [15]. However, the retarding effect may be explained owing to the adsorption of one reactant on the polar micellar surface and repulsion of the other by the same [15,16]. It may be worth to mention that in a number of instances, inhibiting/accelerating effects on reaction rates by different surfactants have also been observed [17–20] even at the pre-micellar region (surfactant concentrations much below CMC). The influence of surfactants in the pre-micellar region may arise due to the aggregation of the monomeric surfactant molecules with substrate to form pre-micelles [15].

Crystal violet (CV^+) is an important triarylmethane dye, chemically known as tris(4-(dimethylamino) phenyl) methylium chloride. It has antibacterial, antifungal and anthelmintic properties [21] and was previously used as a topical antiseptic. It is also used as a histological stain for classifying bacteria. Industrially it is used to dye paper and prepare printing inks [22]. Crystal violet is a highly colored compound due to its conjugative structures. On alkaline hydrolysis, the hydroxyl group becomes attached to the carbocation center, thereby destroying the conjugation and it is converted to the colorless carbinol compound (Scheme 1).

The interaction of crystal violet with other compounds, such as surfactants, is expected to be of great importance due to its wide applications. Dye-surfactant interactions are now a days being widely investigated [20,23,24]. Since crystal violet exists as a carbocation it may be expected that there will be interaction between CV^+ and anionic surfactants. Numerous attempts have been made to investigate the interactions of surfactants on the alkaline hydrolysis of CV^+ in the post micellar region [25–31]. As reported, the rate of alkaline hydrolysis of CV^+ was accelerated in the presence of cationic surfactants [25] and retarded by anionic surfactants [26,27]. The kinetics of the alkaline hydrolysis of CV^+ have also been investigated in micelles, reverse micelles and microemulsion of ionic and nonionic surfactants [28–30]. The same hydrolysis reaction was also studied in mixed system comprising α-cyclodextrin and a micelle-forming surfactant, cetyltrimethylammonium
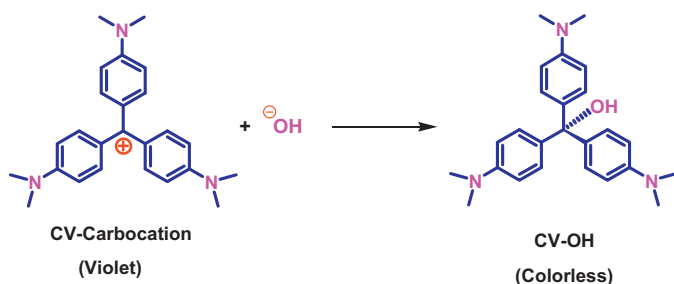
chloride (CTACl) [31]. In systems involving ionic dyes and charged surfactants, smaller species, known as dye-rich micelles or premicellar aggregates, are often formed before the formation of normal micelles [20,32–34]. The formation of ion pairs between the ionic dye and oppositely charged surfactant monomers through hydrophobic as well as electrostatic interactions leads to the formation of such pre-micelles [20,32,34]. Hence, the interaction in the pre-micellar region (where surfactant molecules remain as monomers or small surfactant assemblies) will not be the same as that operating in the post-micellar region and such interaction will possibly influence the reaction rate in a different manner. However there are only a few reports of studies involving such interactions in the pre-micellar region in the literature. As a consequence an attempt has been made to investigate the influence of a few anionic surfactants (at concentrations much below CMC) on the alkaline hydrolysis of CV^+. In addition, there is a possibility of interactions of inorganic anions with the CV carbocation during the hydrolysis of the latter this interaction may affect the reaction rate.

The present work deals with the investigation on the influence of anionic surfactants such as SDS and AOT in the pre-micellar region on the alkaline hydrolysis of crystal violet. The chemical structures of the surfactants are given in Scheme 2.

The pre-micellar kinetics have been explained using Piszkiewicz's model [15] and cooperativity indices (n) and the binding constants between the substrate and the surfactants have been evaluated. The influence of inorganic anions such as Cl^-, Br^-, I^- and SO_4^{2-} have also been studied in order to see the possible interactions between the carbocation (CV^+) and the anions in the alkaline fading of crystal violet and the values of rate constants and equilibrium constants have been determined and compared applying Olson–Simonson model [35].

2. Materials and methods

2.1. Materials

Crystal violet, sodium hydroxide (AR, SRL, India), surfactants aerosol OT (AOT) (extra pure, SRL, India), sodium dodecyl sulfate (SDS) (LOBA, India) and salts KCl, KBr, KI, K_2SO_4 (Merck, India) were used without further purification. For kinetic study, sodium hydroxide was freshly prepared in water and standardized against standard oxalic acid solution. Water from Millipore synergy was used throughout the experiment.

2.2. Absorption spectra of CV^+

Visible spectrum of crystal violet solution was recorded in the range 550–620 nm and λ_{max} was found at 592 nm (Fig. 1). Absorbances of crystal violet solution at the λ_{max} for six different concentrations ((1.6–9.6) $\times$ 10^{-5} M) of crystal violet were observed and plotted against [CV^+]. The plot was found to be a straight line passing through origin in accordance with Beer's law. The molar absorption coefficient was found to be 6983 M^{-1} cm^{-1}.

2.3. Kinetic measurements

The kinetic advancement of the reaction for alkaline fading of crystal violet in the presence of different salts (KCl, KBr, KI and K_2SO_4) as well as surfactants (SDS and AOT) was monitored by noting the absorbance (A) at 592 nm. The pseudo-first order condition ([OH^-] $\gg$ [CV^+]) was maintained during all the kinetic runs. The experimental observations were carried out in a UV–visible Shimadzu 1800 spectrophotometer with a Peltier controlled thermostated cell compartment. The plots of ln$A$ (A = absorbance) *versus* 'time' were linear (Fig. 2) and the pseudo first order rate constants (k_{obs} or k_ψ), evaluated from such plots, were reproducible to within

Scheme 1. Alkaline hydrolysis of crystal violet carbocation.