

Effect of Cationic/Anionic Mixed Micelles on Reaction Kinetics of Alkaline Hydrolysis of Crystal Violet

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Kinetics of alkaline hydrolysis of crystal violet, a triphenylmethane dye in the micellar environment of cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfonate (SDS) and binary mixtures of these surfactants was studied. The regression parameters, together with rate constants and binding constants were obtained by analyzing the rate surfactant profiles using cooperativity model. It was observed that the reaction was catalyzed by both surfactants. The catalytic factor increased by 10 times in SDS and 38 times in CTAB indicating that binding of crystal violet to the micellar surface is stronger in pure CTAB than SDS but the strength drastically reduced in the mixtures of the surfactants. Reduction of binding constant became more important as the mole fraction of CTAB was improved in the mixture. The kinetic data were investigated using Piskiewicz model and Raghavan-Srinivasan model. The data obtained from the models were in good agreement with the experimental values.

Keywords: Crystal violet, Pseudo-phase, Mixed Micelles, Piskiewicz's model.

INTRODUCTION

Mixed surfactants are engaged in a broad range of real-time applications including improved food [1-3], cosmetic production [4], oil recovery [5,6], detergency [7,8], textiles [9] and paint production [10]. It is observed that in certain cases, mixed surfactant systems give rise to improved performance compared to single component systems [11-13]. Further, micellar systems include the ability to modify chemical reactivity. Equilibrium constants and reaction rates in micellar media can vary from the values in aqueous medium. The rates of chemical reactions are recognized to be changed or customized by self-organized assemblies such as micelles. Results from such investigations offered proof that surfactant aggregates can be employed in controlling the rate of chemical reactions and as probes for examining reaction mechanisms [14]. Mixed micellar systems are of considerable industrial importance due to several reasons, synergism exhibited by surfactant mixtures in their physico-chemical properties and better performance compared to pure surfactants. Recently, there have been several efforts to model and understand the structural and physico-chemical aspects of mixed micelles [15,16].

Hydrolysis reactions have also served as a model for comparisons of the effects of micellar medium. Established by the mechanisms derived from these hydrolytic processes, one assume that the properties of micelles together with lower confined water concentration in the micellar stern region, polarity of the micelles and the confined charge in micellar stern region resulting from partial counter-ion binding engage a significant role in the catalysis or inhibition of these processes [2,3]. Kinetic studies in these systems could be construed on the basis of the pseudo phase model [3,5] that permits us to explain a significant number of kinetic results [8-10], with straight-forward postulation of reaction distribution among two pseudo-phases.

Triphenylmethane dyes, like crystal violet (CV), brilliant green (BG) and malachite green (MG) correspond to a group of synthetic dyes of analytical and commercial importance. Several applications benefit from the range, intensity and light fastness of colour displayed by these dyes. Further, these dyes are employed as colorants in the cosmetic, food, textile and ink industries, as stable absorbers as indicators in spectrophotometric determinations of surfactants, in histological stains, laser mode locking, reagents in protein assays, metal ions and pesticides [17,18].

The hydrolysis of crystal violet dye and its derivatives have been widely investigated in aqueous medium [1,19]. Moreover, the hydrolysis of crystal violet in alkaline medium along with micelles, reverse micelles and micro emulsions of CTAB have already been reported [20,21]. The effect of solvent on the kinetics of alkaline hydrolysis of crystal violet and several other related investigations has been done in various aqueous-organic mixtures like 2-butoxyethanol and water [22-26] but hydrolysis of crystal violet in mixed micelles have not been reported yet. Micellar solutions have become important in pharmaceutical and drug delivery formulations [27]. Hence, it is essential to get an understanding on the kinetics of the hydrolysis in mixed micelles.

EXPERIMENTAL

Crystal violet (CV) (98 %), cetyltrimethylammonium bromide (CTAB, 99 %), sodium dodecyl sulfonate (SDS, 99 %) and sodium hydroxide (99 %) were purchased from Sigma-Aldrich and used as received. All the solutions were prepared with tripled distilled water.

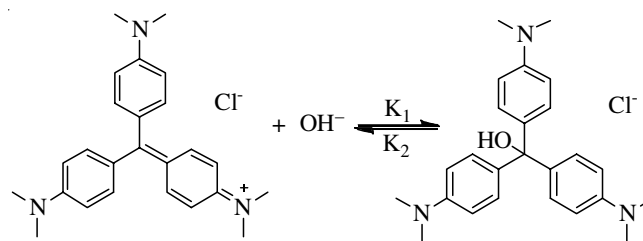
Determination of critical micelle concentration: The critical micelle concentration (CMC) of surfactants and their binary combinations were determined by conductivity method. The specific conductance of various solutions was measured as a function of concentration. The breakpoint in the conductivity-concentration profile was taken as CMC. The concentration of crystal violet in the solution was kept at 1.5×10^{-5} M and 0.001 M NaOH was used throughout the studies. All the measurements were carried out at 298 K. The CMC of mixed surfactants containing SDS and CTAB were measured at the different mole fraction of CTAB surfactant.

Conductance measurement was made using a conductivity meter (Aqualytic conductivity meter SD320 CON, with the sensor to read the temperature, cell constant = $0.475 \text{ cm}^{-1} \pm 1.5 \%$) with a dipped type electrode. The meter was calibrated with a standard KCl solution.

Kinetic measurements: Kinetic studies were conducted keeping the temperature constant at 298.0 ± 0.1 K by monitoring the change in the absorbance of dye as a function of time at the wavelength of maximum absorption (λ_{max}) at 585, 580, 590 and 585 nm in pure water, pure CTAB, pure SDS, and CTAB + SDS, respectively. The fading of dye by hydroxide ion in the presence of CTAB and its binary mixtures with SDS were carried out at 585 nm. The absorbance was observed on UV-visible spectrophotometer (Perkin-Elmer 330 UV-visible spectrophotometer). The kinetic experiments were checked under the pseudo first order conditions, $[\text{OH}^-] \gg [\text{CV}^+]$. The kinetics were examined under pseudo-first-order conditions with the hydroxide concentration ($0.0010 \text{ mol dm}^{-3}$) in excess compared to that of crystal violet concentration ($1.5 \times 10^{-5} \text{ mol dm}^{-3}$) by a factor of more than 200. The rate constants, k_{obs} (s^{-1}), were calculated from the slopes of $\ln(A_t - A_\infty)$ against the plots for time; where A_t is the absorbance at time t and A_∞ is the absorbance at the end of reaction, respectively. The kinetic profiles for pseudo-first order reactions were always linear for most part of the reaction. The reproducibility was checked by running each kinetic experiment at least twice and the rate constants were found to be reproducible within a precision of $\pm 5 \%$ [1].

RESULTS AND DISCUSSION

The effect of surfactant on the rate constant in the hydrolysis reaction depends on the addition of surfactant to the solution of substrate successively that may lead to the formation of micellar aggregates, which bring about the distribution of substrate among aqueous phase and aggregates. The most probable location of substrate in the micellar pseudo-phase is the stern layer of micelles of ionic surfactants. The interaction of substrate with surfactant molecules or ions and aggregates are indicated by the change of reaction rate on the addition of surfactant. Further, the cation of crystal violet may react with OH^- ions in the presence of surfactant, in aqueous phase and in dye-surfactant aggregates (**Scheme-I**).



Scheme-I: Hydrolysis of crystal violet in the presence of $[\text{OH}^-]$

The change in the concentration of the total surfactant is directly related to the degree of dye binding by aggregates. In these environments, the rate constant determined experimentally is an effective or observed value that depends on the rate constants of processes in each phase and on the local concentrations of the reacting ions [28].

Further, in case of base hydrolysis of crystal violet the ionic surfactants, $[\text{OH}^-]$ ions are distributed among bulk phase and the micellar pseudo-phase, where the cationic dye is localized on the surface. At a constant total concentration of hydroxide ions in solution, the $[\text{OH}^-]$ value on the surface of cationic micelles will be higher and the surface of anionic micelles will be lower due to the electrostatic interactions.

In case of SDS surfactant in pre-micellar region, the rate constant is a little bit high due to the interaction between the dye and the surfactant resulting in the formation of ionic pairs. There is a deviation in the rate constant on further addition of SDS. This could be due to the destruction of ionic pairs as a result of interaction of cationic dye with several surfactant anions. Moreover, there is no change in the rate constant as observed in Fig. 1. But for cationic surfactant (CTAB), the reaction rate increased despite the charge of dye and surfactant ion was same. This indicated that the binding of dye may not be due to the hydrophobicity of dye compared to SDS.

The n value shown in Table-1 also support that interaction in the system is not only dye-micelle interaction. If the interaction is only dye-micelle interaction then the n value will be constant. As shown in Table-1, the n value of CTAB increases as the mole fraction of CTAB increases, while that of SDS decreases. This suggests that the dye interacts with OH^- ion in the stern layer of micelle better in CTAB aggregate.

The influence of cationic/non-ionic mixed micelles on the alkaline hydrolysis of CV^+ was determined using different mole fractions of CTAB in SDS in $0.001 \text{ mol dm}^{-3}$ of OH^- .

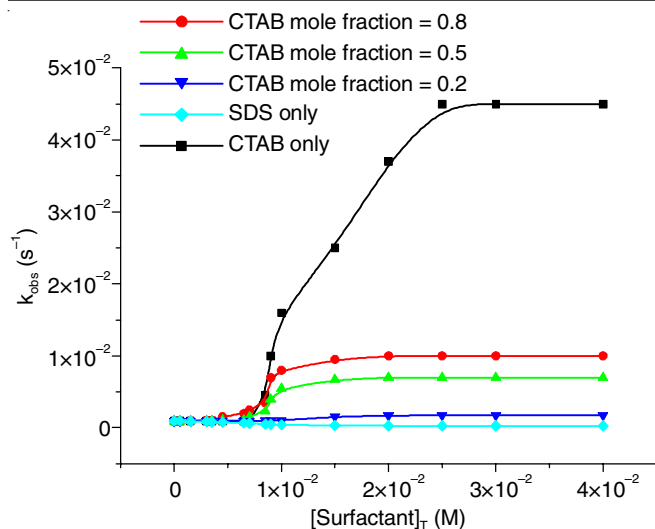


Fig. 1. Relationship of the observed rate constant, k_{obs} with the surfactant concentration for the alkaline hydrolysis of $1.5 \times 10^{-5} \text{ mol dm}^{-3}$ CV^+ on total surfactant concentration, $[\text{Surfactant}]_T$ at 298 K for CTAB + SDS

TABLE-1
KINETIC PARAMETERS OBTAINED FROM THE REGRESSION FIT OF eqn. 4 FOR THE ALKALINE HYDROLYSIS OF CV^+ IN CTAB + SDS MIXTURES AT 298 K, $[\text{NaOH}] = 0.001 \text{ M}$

α	$k_m \times 10^2 \text{ (s}^{-1}\text{)}$	n	$K_D \text{ (M)}$	k_m/k_w
0.0	0.03	1.14	5.73×10^{-5}	27.78
0.2	0.17	1.08	6.61×10^{-5}	188.89
0.5	0.70	1.13	5.34×10^{-5}	777.78
0.8	1.00	2.05	2.50×10^{-6}	1111.11
1.0	4.50	3.76	9.79×10^{-9}	1689.23

α = Mole fraction of CTAB

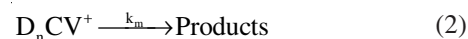
The difference in observed rate constant (k_{obs}) as a function of mole fraction of CTAB is shown in Fig. 1. When the concentration of the surfactants was below that of CMC, the k_{obs} decreased for SDS, while it was constant for CTAB. As soon as the surfactant concentration surpassed the CMC, the k_{obs} increased drastically for a small increment in the CTAB concentration. The K_{obs} reached a maximum value and further increase in surfactant did not alter the K_{obs} after saturation point. The data indicated that there is catalytic action in both surfactants. This may be attributed to the different interactions operating in the case of both substrate CV^+ and OH^- ion. The surfactants are attracted to the micellar surface with different partition constants due to electrostatic and hydrophobic interactions [1].

The fascinating feature of rate-surfactant concentration contour is the improved catalysis by CTAB in comparison with that of SDS. The rate of reaction is faster in CTAB than in SDS. This is corroborated by an increase in rate as the mole fraction of CTAB is increased in the mixtures. The electron donating methyl groups of CTAB stabilizes crystal violet more than SDS which have no such groups in its structure. Hence crystal violet binds strongly with CTAB than SDS.

There is no significant rate enhancement up to 6.71 mM as shown in Fig. 1. The onset of micellization was observed above this concentration; there is a radical change in the reaction rate around 9.0 mM. This observation indicates that pre-micellar activity is not significant in the observed rate enhancement of

CTAB as well as the mixture but for SDS there is a decrease in rate for the reaction.

The alkaline fading of CV^+ in the presence of surfactants and their mixtures was explained in terms of modified Piskiewicz model [29,30]. According to this model, substrate molecule, CV^+ , associates with n molecules of surfactant to form a critical micelle D_nCV , which may react as follows:



In the above equations, k_w and k_m are the rate constants in bulk aqueous and micellar phases, respectively. K_D is the dissociation constant between the CV^+ and the micelle. The model gives the following rate equation:

$$\log \left(\frac{(k_{obs} - k_w)}{(k_m - k_{obs})} \right) = n \log [D]_t - \log k_D \quad (4)$$

where K_D is the dissociation constant of micellized surfactant substrate compound back to its components and $[D]_t$ is the total surfactant concentration. Here, k_w is the rate constant in bulk aqueous in the absence of surfactant, and k_m is the rate constant in the presence of surfactant with maximum amount of surfactant concentration within the given range and if reaction is inhibited by adding surfactant, $k_m = 0$, n is known as the cooperativity index and is a measure of the association of additional surfactant molecules to an aggregate in the whole surfactant concentration range [31].

Table-1 showed that n values show positive cooperativity in the used concentration range of CTAB, SDS and their binary mixtures. Table-1 also shows that the catalytic factor k_m/k_w , increases with the rise in mole fraction of CTAB in the mixture. The values of K_{CV^+} are in a good conformity with $1/K_D$ obtained from Piskiewicz's model. The low value of K_{OH^-} also suggests that OH^- ion is solely present in the aqueous phase.

The surfactant-substrate binding constant is listed in Table-2. The surfactant-substrate binding constant $1/K_D$ is greater in pure CTAB than pure SDS. The substrate, therefore, binds more strongly with CTAB than SDS. The dependence of catalytic factor on the mole fraction of CTAB in mixture is depicted in Fig. 2. The distribution of both CV^+ and OH^- ion in aqueous and micellar pseudo-phases is considered by Raghvan and Srinivasan model. This model assumes that substrate CV^+ associates with surfactant aggregates to form an aggregated complex D_nCV^+ to which the hydroxide binds to give a ternary complex $\text{D}_n\text{CV}^+\text{OH}^-$. The ternary complex may react by pathways 7 and 8.

TABLE-2
BINDING PARAMETERS OBTAINED FROM THE REGRESSION FIT OF eqn. 9 FOR CTAB + SDS MIXTURES AT 298 K, $[\text{NaOH}] = 0.001 \text{ M}$

α	K_{CV^+}	K_{OH^-}	$1/K_D$
0.0	1.81×10^4	0.89	1.75×10^4
0.2	1.56×10^4	0.89	1.51×10^4
0.5	1.91×10^4	0.90	1.87×10^4
0.8	4.05×10^4	1.00	4.00×10^5
1.0	1.06×10^8	1.00	1.02×10^8

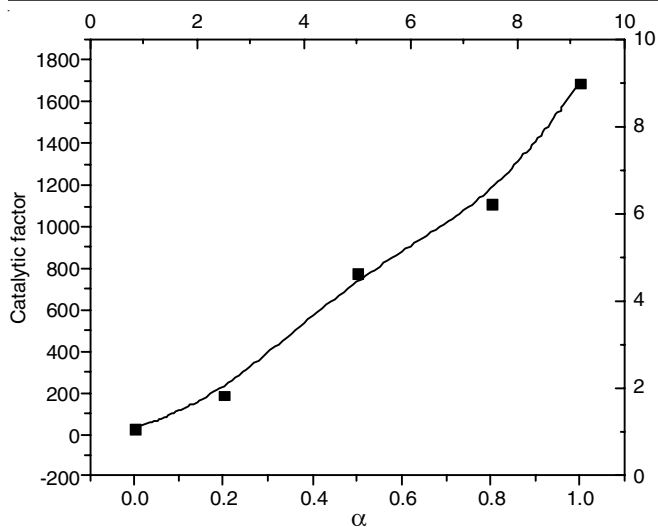
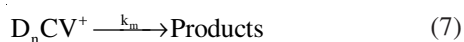


Fig. 2. Variation of the catalytic factor (k_m/k_w) with the mole fraction (α) for the alkaline hydrolysis of CV at 25 °C



According to this model, the observed rate constant in the presence of surfactant is given by the equation:

$$k_{\text{obs}} = \frac{k_w + k_m K_{CV^+} K_{OH^-} [D]^n}{1 + K_{CV^+} [D]^n \{1 + K_{OH^-} [S]_T\}} \quad (9)$$

In eqn. 9, K_{CV^+} and K_{OH^-} are the binding constants of CV^+ and OH^- ions, respectively. The values of K_{CV^+} and K_{OH^-} are obtained using eqn. 9 with the experimental values of k_w , k_m and n value is obtained from the Pizkiewicz model using eqn. 4 and are tabulated in Table-2. The determined values of K_{CV^+} are in good conformity with $1/K_D$ obtained from Pizkiewicz's model. The lower values of K_{OH^-} proposed that OH^- ion is solely present in the bulk aqueous phase; this idea is in good agreement with that of the literature value [32-34]. Hence, above results suggest that the reaction takes place between crystal violet solubilized inside the micelle and the OH^- ion residing at the Stern layer, with the composition of mixed micelle significantly influencing the extent of incorporation of the substrate within the micelle [1,35].

Conclusion

The catalytic factor for the hydrolysis of crystal violet due to $[OH^-]$ increased from 28 for pure SDS to 1700 for pure CTAB when the surfactant was changed from SDS to CTAB. The studies showed that the binding of OH^- to the micellar surface is stronger in CTAB than in SDS. Further, it is also observed that the strength of binding considerably reduced in surfactant mixtures. The enhancement of the rate is because of lowering of repulsions due to electrostatic interactions between CTAB head groups and the substrate, thus facilitating micellar ionization (counter ion binding decreases leading to increasing in rate). In contrast, the reaction is much slower in SDS compared

to aqueous medium because the proximity of hydrophilic hydroxyl ion to crystal violet is prevented by SDS. Hence, the substrate crystal violet, being positively charged, binds more to the hydroxyl head group of CTAB than SDS, leading to a more substantial rate acceleration observed in CTAB than in SDS. The change in rate constant with the variation of concentration of surfactants is due to the distribution of reagents between aqueous and micellar phases and the changing of their properties based on the micro-environment. The rate of reaction is increased in CTAB micelles but in SDS micellar solution it drops significantly in magnitude. These results are in good conformity with both the Pizkiewicz model and its modified model proposed by Raghavan and Srinivasan.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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