

Dynamics of CTAB micelle mediated reaction of fuchsin degradation in alkaline medium

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Abstract. Cetyltrimethylammonium bromide (CTAB) micelles catalyzed the degradation of fuchsin in the entire surfactant concentration range investigated. The pseudo first order rate constants increased with CTAB concentrations. However, there was a decrease in the rate constant at higher concentrations of CTAB. Increase in the rate constant was attributed to the incorporation of fuchsin and hydroxide ion in the stern layer of the CTAB micelles. The kinetics involved the removal of the π -conjugation in fuchsin due to its attack by hydroxide ion on the central C atom of the planar ring which led to the formation of carbinol. The reaction showed first order each to fuchsin and OH⁻. Menger-Portnoy and Piszkievicz cooperative models were used to explain the micellar and kinetic effects.

Keywords: cetyltrimethylammonium bromide (CTAB); fuchsin; sodium hydroxide; potassium nitrate; pseudo-phase model.

1. Introduction

Fuchsin (rosaniline hydrochloride) is a synthetic cationic triphenylmethane dye used in the detection of acid-fast bacilli and also find application in textile industries [1].

Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant which influences a lot of reactions by shifting the acid-base equilibria [2]. CTAB has been reported to catalyze the reaction between dipeptide glycyl-alanine and ninhydrin [3] and the catalytic role of CTAB in chemical reactions have been attributed to the hydrophobic/electrostatic interactions [4]. Gemini surfactants have also been reported to accelerate the hydrolysis of carboxylate and phosphate esters using hydroxamate ion [5] and Raghvan and Srinivasan model have been used to determine the binding constant of the oxidation reaction between aminoalcohols and N-bromosuccinimide in the presence of CTAB [6]. Furthermore, the effect of CTAB micelles on the kinetics of the oxidation of oxalic acid by chromium (VI) have been investigated [7]. The pre-micellar environment of CTAB have been reported to strongly inhibit the oxidation of D-dextrose by diperiodatoargentate (III) [8]. CTAB have been found to retard the hydrolysis of imines in alkaline medium [9]. The catalytic effect of CTAB on chemical reactions was also reported for the permanganate oxidation of D-glucose in sulfuric acid and the association of permanganate with the cationic head group of CTAB was suggested and pseudo phase model proposed by Menger and Portnoy as modified by Benton was used to explain the oxidation reaction [10]. The catalytic activity of CTAB on the oxidation of ethylenediaminetetraacetic acid (EDTA) by permanganate ion in alkaline medium have been

attributed to the incorporation/ association/ solubilization of permanganate ion, reactive species of the EDTA and OH⁻ in the stern layer by Menger-Portnoy model [11]. The catalytic effect of CTAB on alkaline hydrolysis of triflusal decreases upon addition of electrolyte [12]. Moreover, the catalytic effect of CTAB on the oxidation of D-mannose by cerium (IV) in sulfuric acid has been explained via Menger-Portnoy model [13]. In this paper, investigation on the kinetics of the reaction of alkaline hydrolysis of fuchsin was studied in the presence of a cationic surfactant CTAB at concentrations above critical micelle concentration (CMC).

2. Experimental

2.1. Reagents

The chemicals, *i.e.* fuchsin, cetyltrimethylammonium bromide (CH₃(CH₂)₁₅N(Br)(CH₃)₃, CTAB), sodium hydroxide (NaOH) and potassium nitrate (KNO₃) were all analar grade. Four times distilled water was used for the preparation of all the stock solutions.

2.2. Kinetic measurements

Stock solutions of fuchsin, CTAB, NaOH and KNO₃ were placed in a water bath for 30 minutes before the kinetic runs.

The hydrolytic reaction between fuchsin and OH⁻ was performed in cationic surfactant, CTAB under pseudo first order conditions by maintaining a large excess of [OH⁻] over the concentration of fuchsin. Requisite amount of the reactants from the stock solutions were introduced into a 1 cm quartz cuvette and progress of the reaction was monitored by following the decrease in the fuchsin concentration using a double beam Unicam-1800 Shimadzu spectrophotometer equipped with a thermo-regulated cell compartment and

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spectral data processing facilities at 546.5 nm. The rate constant was evaluated from the slope of the plot of ln absorbance versus time.

3. Results and discussion

3.1. Effect of CTAB concentration

The kinetics of the reaction was investigated at different initial concentrations of CTAB at fixed concentrations of fuchsin, NaOH and KNO₃, at 298K and the observed rate constants in aqueous and micellar media (Table 1). The table shows the catalytic property of CTAB on the reaction.

Table 1. Effect of CTAB concentration

10 ² [CTAB]/M	10 ³ k _{obs} /s ⁻¹
0	4.65
0.50	6.00
0.90	7.00
1.00	7.70
1.50	9.00
2.00	9.85
2.50	10.52
3.00	12.25
4.00	14.76
4.50	14.71
5.00	14.04

[Fuchsin] = 1x10⁻⁵ M; [NaOH] = 4x 10⁻⁴ M μ 0.05M; T = 298K

The kinetics of different initial concentrations of OH⁻ at fixed concentrations of fuchsin, KNO₃ and CTAB at 298 K was investigated. Increase in observed pseudo first order rate constant with increase in [OH⁻] was observed (Figure 1). The slope of the plot of log k_{obs} versus log[OH⁻] was 1, indicating a first order dependence on [OH⁻] in the presence of CTAB.

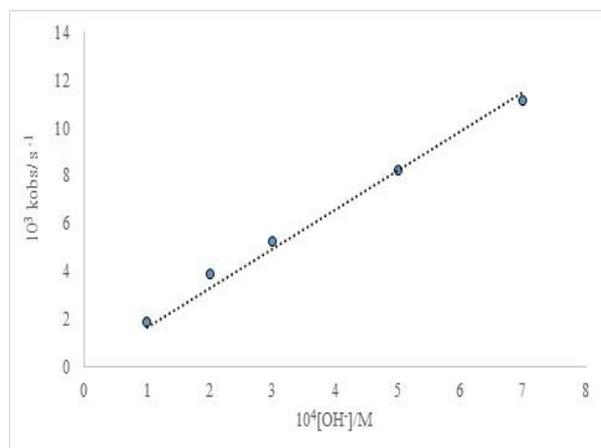


Figure 1. Plot of k_{obs} versus [OH⁻].

3.2. Effect of fuchsin concentration

This was accomplished by varying the concentrations of fuchsin at fixed concentrations of CTAB, KNO₃ and OH⁻ at 298 K. The observed pseudo first order rate constant increased with increase in [Fuchsin] (Figure 2). Moreover, slope of a plot of log-log plot of the pseudo-first order rate constants and [Fuchsin] gave 1, implying a first order dependence on [Fuchsin] in the presence of CTAB.

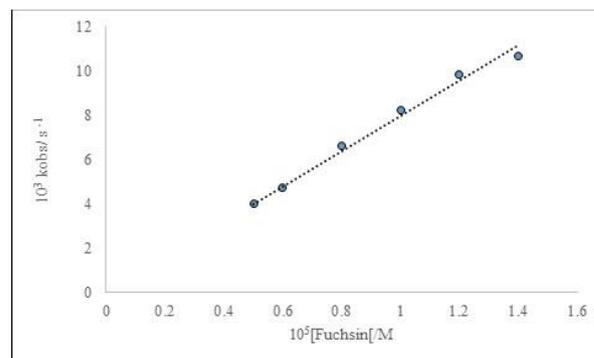


Figure 2. Plot of k_{obs} versus [Fuchsin].

3.3. Effect of temperature

Activation parameters of the reaction were obtained from temperature dependent study at fixed concentrations of Fuchsin, NaOH and KNO₃ and varying the temperature of the reaction mixture. The thermodynamic parameters were evaluated from the slope and intercept of the Eyring's plot and are shown in Table 2.

$$\log k = \log A - \frac{E_a}{2.303RT} \quad (1)$$

$$\ln \left(\frac{k}{T} \right) = \frac{-\Delta H^\ddagger}{RT} + \ln \left(\frac{k'}{h} \right) + \left(\frac{\Delta S^\ddagger}{R} \right) \quad (2)$$

$$\ln \left(\frac{k'}{h} \right) = 23.76 \quad (3)$$

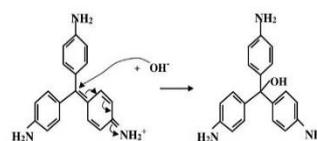
$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

Table 2. Activation parameters.

Substrate	ΔH^\ddagger (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
Fuchsin	25.29	0.199	84.59

3.4. Mechanism in micellar media

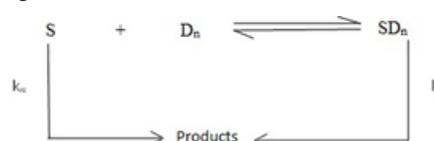
The observed kinetic and spectral data support same mechanism of reaction in absence or presence of CTAB. The reaction involved attack by OH⁻ on the central carbon atom in planar ring of fuchsin, leading to the removal of π conjugation in fuchsin, hence, the formation of carbinol (Scheme 1).



Scheme 1. Hydrolytic process

3.5. Rate law

Menger-Portnoy model. This model accounts for the partitioning of fuchsin between aqueous and micellar pseudo-phase (Scheme 2).



Scheme 2. Menger-Portnoy model (D_n= micellar CTAB surfactant; S = free substrate (fuchsin); SD_n= associated substrate).

The observed rate constant, k_{ψ} is given as:

$$k_{\psi} = \frac{(k_w + k_m K_s [D]^n)}{(1 + K_s [D]^n)} \quad (5)$$

where: k_{ψ} = observed rate constant at a given surfactant concentration; k_w = pseudo first order rate constants in aqueous phase; k_m = pseudo first order rate constants in micellar phase; K_s = binding constant of the substrate with the surfactant, $[D]^n$ = concentration of the micellar surfactant = $([D]_T - \text{CMC})$. CMC value of CTAB in the aqueous reaction mixture was $8.75 \times 10^{-4} \text{ mol dm}^{-3}$ [14].

Equation 1 can be re-arranged to give:

$$\frac{1}{(k_{\psi} - k_w)} = \frac{1}{(k_m - k_w)} + \frac{1}{(k_m - k_w) K_s [D]^n} \quad (6)$$

In the present study the plot of $\frac{1}{(k_{\psi} - k_w)}$ versus $\frac{1}{[D]^n}$ is linear with positive slope of $\frac{1}{(k_m - k_w) K_s}$ and intercept $\frac{1}{(k_m - k_w)}$ showing the validity of Menger-Portnoy's model to the degradation reaction.

k_m was $3.56 \times 10^{-2} \text{ s}^{-1}$ and K_s was $10.86 \text{ mol dm}^{-3}$ as obtained from the intercept and slope of Fig. 3.

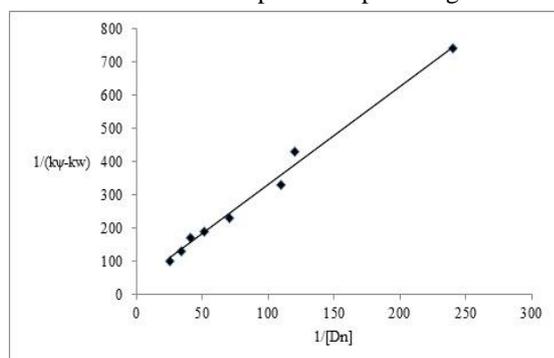
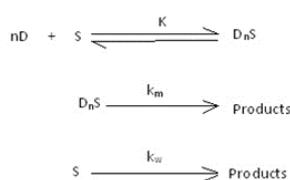


Figure 3. Validity of Menger-Portnoy's model

Piszkiewicz cooperative model. Piszkiewicz cooperative model is likened to the Hill model used in enzyme catalyzed reaction. Herein, fuchsin and sodium dodecyl sulphate form the reactive micelles (Scheme 3).



Scheme 3. Piszkiewicz cooperative model.

Piszkiewicz cooperative model shows that:

$$k_{\psi} = k_m [D]^n + \frac{K_D k_w}{K_D + [D]^n} \quad (7)$$

Re-arranging Equation 7:

$$\log \frac{(k_{\psi} - k_w)}{(k_m - k_{\psi})} = n \log [D] - \log K_D \quad (8)$$

where: K_D = dissociation constant of micellized substrate back to its free component; K = association constant of the micelle-substrate complex.

Applying Equation 4 and using the earlier obtained value of k_m in Menger-Portnoy's model, the plot of $\log \frac{(k_{\psi} - k_w)}{(k_m - k_{\psi})}$ versus $\log [D]$ show linear for this reaction.

n and K_D were determined respectively from the slope and intercept as 1.09 and 6.60×10^{-2} .

The value of n obtained in the present study indicates the formation of catalytically active sub-micellar aggregates. Since $n > 1$, it indicates positive cooperativity which implies that binding of the first molecule of the substrate allows for the binding of subsequent molecules. Furthermore, the value of n is far than the aggregation number (20-100) of the surfactants which indicate the formation of catalytically productive sub-micellar aggregates [15]. The linear plot supports the positive cooperativity between fuchsin and micelle to form reactive micelles which indicates that the substrate, fuchsin molecules are included into the micellar phase.

The solubilize may be entrapped in the hydrocarbon core of the micelle or be adsorbed on the surface of the micelle at the stern layer. The micellar interior is not steric rigid and consequently a solubilized substrate is relatively mobile [16, 17]. Micellar catalysis occurs as a result of difference in the rate of reaction of substrate in micellar phase and in the bulk solution and the distribution of the substrate between these two phases. The change in rate could be attributed to electrostatic and hydrophobic interaction between the micellar phase and the reactants, transition state and the products. It can also be due to the structure of the surrounding water in some cases [18]. Catalytic activity of CTAB on the hydrolysis reaction is due to the electrostatic attraction between the positively charged head group of CTAB and the hydroxyl group and fuchsin being preferably partitioned in the micellar pseudo-phase of CTAB by hydrophobic interaction. Basically, the effect of ionic micelle on the reaction rate of bimolecular reaction is attributed to the association of reactants due to electrostatic or hydrophobic interactions [18].

Furthermore, CTAB being a cationic surfactant would stabilize the hydroxide ion in solution. However, in some cases hydrophobic interactions are much stronger than the electrostatic attractions [19]. Micelles are able to influence the reaction rate by decreasing the reactants entropy as reactants have the tendency to bind on micelles [20, 21]. The reaction rate increases as the hydroxide ion binds stronger with the surfactant and displaces the bromine ions from the Gouy-Chapman layer. The overall reaction is dependent on the repartition of the hydroxide ions between the micelles and bulk solution. In this study, the activation free energy is small due to the hydrophobic interaction between the positively charged CTAB and fuchsin. Therefore, the catalytic effect of CTAB is best explained by the hydrophobic interactions between CTAB and fuchsin, which supersedes the unfavorable columbic attractions. The gradual decrease in the reaction rate at high CTAB concentration was observed. Furthermore, as the concentration of CTAB is further increased, the electrostatic repulsion between the micellar head groups and the positively charged fuchsin increases thereby discouraging further solubilization of fuchsin in the micellar core. It is the reduction of the concentration of fuchsin in the micellar core that causes a gradual decrease in the rate of hydrolysis. However, another

explanation for the decrease in rate constant at high CTAB concentration could be due to the change in solubilization as a result of change in the structural orientation of the micelle possibly from the normal sphere to rod like shape at high CTAB concentrations.

4. Conclusions

The rate constants were enhanced within the CTAB concentrations investigated. However, at high concentrations of CTAB, retardation in rate was observed. Furthermore, the negative value of change in entropy of activation revealed an association mechanism and that the reactant molecules associates in a rigid activated state in micellar medium with less degree of freedom. The relatively high positive values of change in enthalpy of activation and change in Gibbs free energy of activation suggests highly solvated transition state. Removal of dyes from industrial effluent has become worrisome for textile factories. Hence the study of dye breakdown in the presence of surfactant would ascertain novel methods of removing contaminants present in effluents from textile industries. Since fuchsin degradation is catalyzed by small concentrations of CTAB, this hydrolytic reaction can be used to mop up contaminants present in industrial effluents from textile industries.

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Conflict of interest

Authors declare no conflict of interest.

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