Catalysis in SDS and CTAB micellar media: Kinetics of base hydrolysis of Bis(2,4,6-tripyridyl-s-triazine) iron (II)

Leela Kumari B.[1], Shyamala P.[1*] and Nagalakshmi K.V.[2]
1. Department of Chemistry, Andhra University, Visakhapatnam - 530003, Andhra Pradesh, INDIA
2. Department of Chemistry, Gayatri Vidya Parishad college of Engineering (Autonomous), Madhurawada, Visakhapatnam, AP, 530048, INDIA
*shyamalapulipaka06@gmail.com

Abstract

Kinetics of the hydrolysis of $[Fe(tptz)_2]^{2+}$ *in the presence of NaOH has been studied in two different types of micellar media: SDS anionic and CTAB cationic. The reaction was found to be much faster in both the micellar media compared to aqueous medium* ($k_{SDS} = 102.2 X10^{-4}\ mol^{-1}dm^3s^{-1}$, $k_{CTAB} = 43.92\ X\ 10^{-4}\ mol^{-1}dm^3s^{-1}$, $k_{aq} = 0.115\ X10^{-4}\ mol^{-1}dm^3s^{-1}$)*. The reaction obeys first order kinetics with respect to both the reactants in both the media.*

The rate constant versus surfactant profile shows a maximum in both cases which is characteristic of a bimolecular micelle catalyzed reaction. The kinetic behaviour has been accounted for by using the Berezin model.

Keywords: $[Fe(tptz)_2]^{2+}$, hydrolysis, micelles, SDS, CTAB.

Introduction

Replacement of organic solvents with better ecofriendly solvents is a common target for all chemical reactions. Water as an alternate solvent has many advantages: non-flammable, abundant, economical, large heat capacity, high polarity, improved productivity and selectivity etc. Surfactants acts as mediators between water and sparingly soluble substrates and catalysts. Micellar mediated reactions are not only a "new solution to old problems" but the simplest and most promising strategies to overcome solubilisation problems. A better understanding of the surfactant is still deserved. Micellar catalysis by surfactants has become a subject of great significance as it provides organized microenvironment[18]. It is well established that the presence of micelles brings about acceleration of reaction by 10 to100 times, in a few cases 10^3 to 10^4 times[3,5,11,14].

Catalysis or inhibition of chemical reactions in solutions is due to binding of the reactants. Excellent reviews of micellar catalysis include those of Berizin et al[1], Romsted[13], Mittal and Fendler[8]. Several factors are responsible for micellar catalysis. In ion- neutral molecule reactions micelles with sign opposite to that of the reactive ion are catalytically active[16]. However, the reacting ion and neutral substrate must be bound by the micelle in close proximity. Since ions are adsorbed on the stern layer of the micelle, the substrate also should be adsorbed around this region for the catalysis to be observed[2,10,17]. In the case of cation- anion reactions, the ionic surfactants in general have inhibitory effect though cation-cation or anion-anion reactions are catalysed by surfactant of opposite charge.

The environment of the micellar phase has influence on the reaction in many ways[6,7]. The micelles produce concentration effects in micellar phase. According to Romsted[13], if the binding constant is large, the reactant concentration with in the micelle can be 100 to 1000 times greater than in the bulk.

Material and Methods

$[Fe(tptz)_2]^{2+}$ was prepared by taking iron(II) and tptz in the ratio 1:2. 0.01 mol dm^{-3} of bis(2,4,6-tripyridyl-s-triazine)iron(II) prepared by taking a mixture of 0.284 gm of ferrous ammonium sulphate (Qualigens) and 0.625 gm of 2,4,6-tripyridyl-s-triazine (TPTZ) (Sigma, India) in 100 ml double distilled water[9]. 0.1 mol dm^{-3} sodium hydroxide (Qualigens, AnalaR) solution was prepared and standardized against oxalic acid. SDS and CTAB were obtained from Merck.

Surface tension measurements were used to determine the CMC's of SDS, CTAB using a stalagmometer maintaining an ionic strength, μ of 0.5 mol dm^{-3} and were found to be 2.2×10^{-3} mol dm^{-3} and 1.2×10^{-3} mol dm^{-3} respectively. $[Fe(tptz)_2]^{2+}$ has maximum absorbance at 598 nm. The reaction was followed by measuring the absorbance of $[Fe(tptz)_2]^{2+}$ which decreases with time. A double beam spectrophotometer (Shimadzu UV-1800 make) was used for the purpose. Duplicate runs were performed and averages were reported.

Spectrophotometric determination of the binding constant: To determine the binding constant of $[Fe(tptz)_2]^{2+}$ with SDS, spectra of $[Fe(tptz)_2]^{2+}$ have been determined in the presence of SDS concentrations varying from 0.0 to 80 x 10^{-3} mol dm^{-3}. Significance changes in the absorbance of $[Fe(tptz)_2]^{2+}$ have been observed (Fig. 1) and from the values of absorbance at 598nm, the binding constant, $K^I[Fe(tptz)_2]^{2+}$ has been determined using the equation (1):

$$\frac{1}{(A_s\text{-}A_w)} = \frac{1}{(A_m\text{-}A_w)}\left(1 + \frac{1}{K'_{[Fe(tptz)_2]^{2+}}\ C}\right) \qquad (1)$$

In this equation, A_W is the absorbances in the absence of surfactant, A_m is limiting absorbance upon complete incorporation into the micellar phase, A_S is absorbance in the presence of SDS and C is equal to [SDS] - CMC. The values of $1/(A_W - A_S)$ have been calculated for different concentrations of SDS and are presented in table 1. A plot of $1/(A_W - A_S)$ versus (1/C) has been found to be linear (Fig. 2) and from the ratio of intercept to slope of this plot, the value of $K^I[Fe(tptz)_2]^{2+}$ has been calculated to be 9.72 mol dm^{-3}.

Results and Discussion

The plots of log(absorbance) vs time were linear up to 80% of the reaction in the presence of CTAB/SDS, and under the conditions [NaOH] >> $[Fe(tptz)_2]^{2+}$. Pseudo first order rate constants (k) were calculated from the slopes of these linear plots[12,19]. CTAB/SDS increases the rate of the reaction (table 2). Under identical conditions, the rate constant values in SDS, CTAB, aqueous medium are 102.2 X10^{-4} $mol^{-1}dm^3 s^{-1}$, 43.92 X 10^{-4} $mol^{-1}dm^3s^{-1}$, 0.115 X10^{-4} $mol^{-1}dm^3s^{-1}$ respectively. The present reaction is bimolecular and like all bimolecular reactions, a maximum was obtained in the rate-surfactant profile (Fig. 3). Two opposing factors have been identified as the cause of the maximum. The amount of reactant molecules entering the micelle grows as micelle concentration rises, and this is what causes the catalysis.

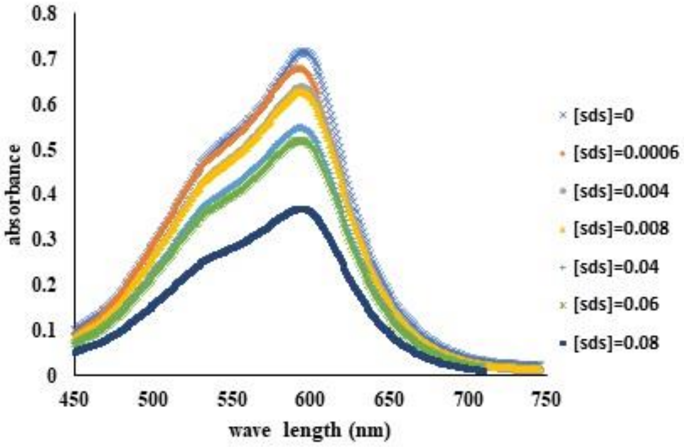

Fig. 1: Effect of [SDS] on the spectrum of $[Fe(tptz)_2]^{2+}$

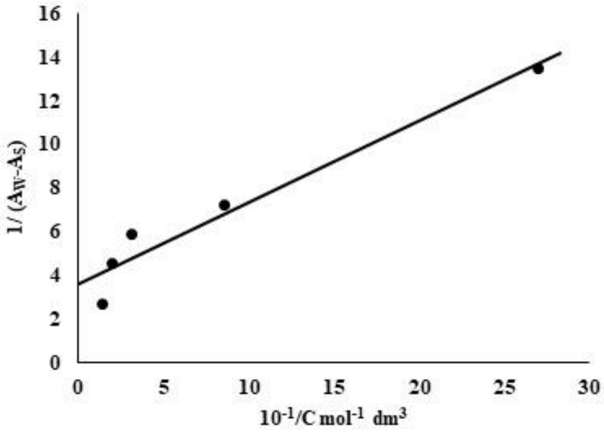

Fig. 2: Plot for the determination of binding constant of $[Fe(tptz)_2]^{2+}$ in SDS from spectral data.

Table 1
Absorbance data of $[Fe(tptz)_2]^{2+}$ at different SDS concentrations.
$[Fe(tptz)_2]^{2+}$ =2.0 x10^{-5} mol dm^{-3}, μ = 0.5 mol dm^{-3}

[SDS] X 10^3	Absorbance (A_S)	$1/(A_W-A_S)$	1/C mol^{-1} dm^3
0.0	0.713	-	-
10.0	0.620	10.75	625.00
20.0	0.574	7.19	82.60
40.0	0.542	5.84	31.64
60.0	0.515	5.05	19.37
80.0	0.366	2.88	13.96

However, as the micelle concentration rises, a saturation is reached, and any additional growth in the micellar phase has a dilution impact which lowers the rate. To explain the effect of rate on surfactant, Berezin's pseudo model has been used. Berezin's rate equation can be expressed as follows:

$$k = \frac{\left(k_M P_{OH^-} P_{[Fe(tptz)_2]^{2+}} + K'_M P_{OH^-} + K''_M P_{[Fe(tptz)_2]^{2+}}\right) C\bar{V} + k_W(1-C\bar{V})}{\left(1+K_{OH^-} C\right)\left(1+K_{[Fe(tptz)_2]^{2+}} C\right)} \qquad (2)$$

where $\bar{V}$ is the molar volume of a micelle and k and P are the binding constants and partition coefficients in this equation. The rate constants for the reaction between micelle-bound NaOH and $[Fe(tptz)_2]^{2+}$ present in the aqueous phase are represented by k_M and k_W respectively. K_M' represents the rate constants of the reaction between micelle- bound NaOH and $[Fe(tptz)_2]^{2+}$ present in the aqueous phase, and K_M'' is for the reverse situation. C is equal to CMC minus the surfactant concentration. In case of CTAB micelle negatively charged OH^- is strongly bound to positively charged micelle and $[Fe(tptz)_2]^{2+}$ is repelled. As a result, K_M'' and K_W can be disregarded. Under these circumstances, equation (2) is altered to:

$$k = \frac{\bar{K}_M K_{OH^-} + K'_M}{\left(1+K_{OH^-} C\right)} \qquad \text{Where } \bar{K}_M = \frac{k_M}{\bar{V}}$$

$$\frac{1}{k} = \frac{1}{\left(\bar{K}_M K_{OH^-} + K'_M\right)} + \frac{K_{OH^-} C}{\left(\bar{K}_M K_{OH^-} + K'_M\right)} \qquad (3)$$

According to equation (3), a plot of 1/k vs C was found to be linear with a positive intercept (Fig. 4). The binding constant of NaOH obtained from the intercept and slope was found to be 40.30 $mol^{-1}dm^3$ (Fig. 4).

Table 2
Effect of [CTAB] and [SDS] on base hydrolysis of $[Fe(tptz)_2]^{2+}$ reaction.
$[Fe(tptz)_2]^{2+}$ = 4 x10^{-5} mol dm^{-3}, [NaOH] =2 X10^{-4} mol dm^{-3}, μ = 0.5 mol dm^{-3}

[CTAB]X10^3 mol dm^{-3}	k x10^4 mol^{-1} dm^3 s^{-1}	[SDS]X10^3 mol dm^{-3}	k x10^4 mol^{-1} dm^3 s^{-1}
0.0	0.115	0.0	0.115
0.6	0.614	0.6	1.420
1.0	2.725	1.0	1.688
4.0	10.97	4.0	1.727
8.0	20.11	8.0	1.804
12.0	23.98	12.0	9.864
16.0	43.35	16.0	11.476
20.0	34.92	20.0	102.2
40.0	29.28	40.0	79.19
60.0	13.05	60.0	70.312
80.0	9.8	80.0	66.324

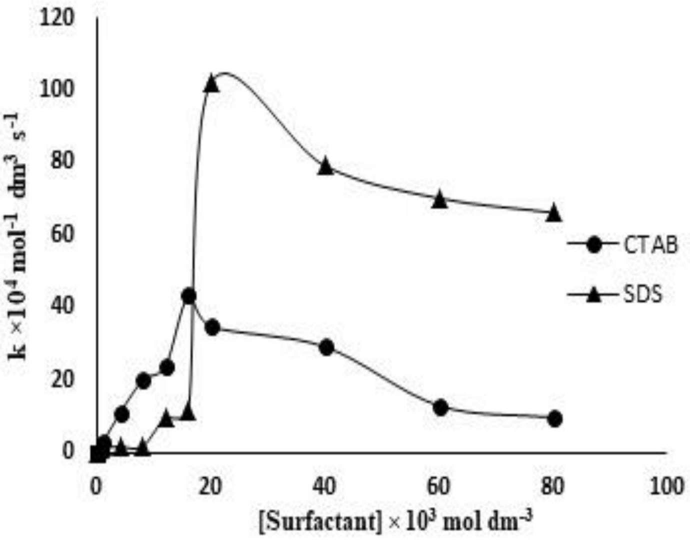

Fig. 3: Plot of k versus [surfactant].$[Fe(tptz)_2]^{2+}$ = 4 x10^{-5}mol dm^{-3}, [NaOH] =2 X10^{-4} mol dm^{-3}, μ = 0.5 mol dm^{-3}

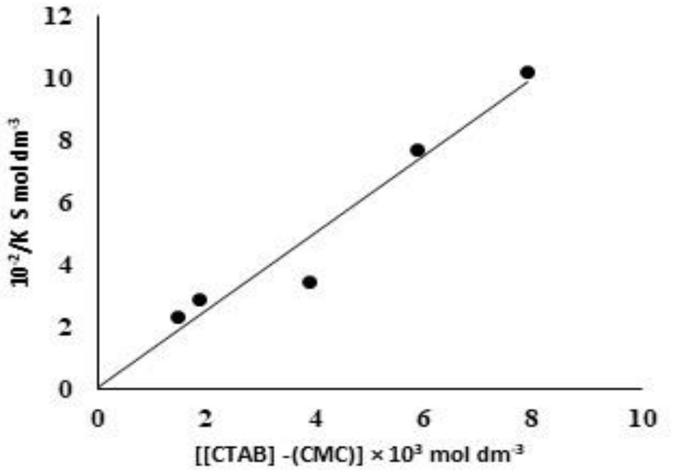

Fig. 4: Plot of 1/ k versus [CTAB]-CMC. $[Fe(tptz)_2]^{2+} = 4 \times 10^{-5}$ mol dm^{-3}, [NaOH] =2 X10^{-4} mol dm^{-3}, μ = 0.5 mol dm^{-3}

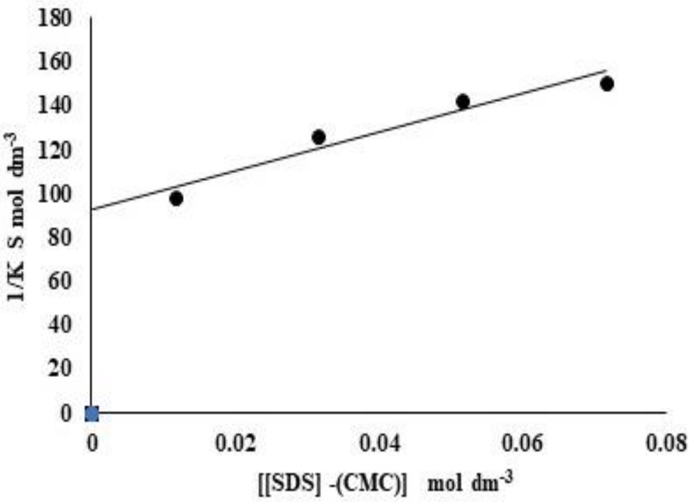

Fig. 5: Plot of 1/ k versus [SDS]-CMC . $[Fe(tptz)_2]^{2+} = 4 \times 10^{-5}$ mol dm^{-3}, [NaOH] =2 X10^{-4} mol dm^{-3}, μ = 0.5 mol dm^{-3}

The partition coefficient P, for each substrate with the micellar phase and water is given as $P = e^{-\Delta\mu/RT}$ where Δμ is the standard chemical potential (For CTAB, P = 280). For CTAB micelles, the surfactant's molar volume[4] V is equivalent to 0.14 mol^{-3} dm^3. As a result, the binding constant, k_{OH^-} , has the value Pv = 39.2 and is of the same order as k_{OH^-} from equation (3).

In case of SDS, $[Fe(tptz)_2]^{2+}$ is strongly bound to the negatively charged micelle and OH$^-$ is repelled by SDS micelle. As a result, K_M'' and K_W can be disregarded. Under these circumstances, equation (2) is altered to

$$\frac{1}{k} = \frac{1}{\left(\bar{K}_M K_{[Fe(tptz)_2]^{2+}} + K'_M\right)} + \frac{K_{[Fe(tptz)_2]^{2+}}\, C}{\left(\bar{K}_M K_{[Fe(tptz)_2]^{2+}} + K'_M\right)}$$

$$k = \frac{\bar{k}_M K_{[Fe(tptz)_2]^{2+}} + k'_M}{1 + K_{[Fe(tptz)_2]^{2+}}\, C} \quad \text{Where } \bar{k}_M = \frac{k_M}{V} \qquad (4)$$

From equation (4), a plot of 1/k vs C is linear with a positive intercept (fig.5). The value of $K_{[Fe(tptz)2]2+}$ has been calculated from the slope and intercept and was found to be 9.42 mol dm^{-3}. It can be seen that binding constant obtained from the kinetic data is in good agreement with the binding constant obtained from the spectrophotometric data (Fig. 2).

Conclusion

- The reaction is accelerated around 890 times in SDS and 375 times in CTAB compared to aqueous medium under identical conditions.
- The analysis of kinetic data has been carried out using the Berezin approach. Accordingly, the binding constant was calculated and it was found that the binding constant determined from kinetic data is in good agreement with the binding constant calculated from spectroscopic data.

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