

Kinetics of Dissociation of *bis*(2,4,6-Tripyridyl-*s*-triazine)iron(II) and *tris*(2,2'-Bipyridyl)iron(II) in the presence of Triton X-100/Tween 80 Mixed Micellar Medium

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Surface tension studies were carried on the binary surfactant mixtures over a wide range of Triton X-100 mole fractions and total surfactant concentrations to obtain critical micellar concentration values. These values were used to determine the composition of the mixed micelles and the average interaction parameter (β) which contains all the interactions of the mixed surfactants. The method is based on Rubingh's theory using a Gauss-Newton iteration technique written in FORTRAN. The value of β was found to be -0.69 indicating synergistic behaviour *i.e.*, combined positive catalytic effect of both the surfactants on rates of reactions. Hence, the kinetics of dissociation of *bis*(2,4,6-tripyridyl-*s*-triazine)iron(II) ($[\text{Fe}(\text{tptz})_2]^{2+}$) and *tris*(2,2'-bipyridyl)iron(II) ($[\text{Fe}(\text{bipy})_3]^{2+}$) were studied in the presence of Triton X-100/Tween 80 mixed micellar medium. The reactions have been carried out in the presence of mixed micelles of Triton X-100/Tween 80 at various mole fractions of Triton X-100 ($\alpha_{\text{TX-100}} = [\text{Triton X-100}]/([\text{Triton X-100}] + [\text{Tween 80}])$) and at different total surfactant concentrations of Triton X-100 and Tween 80 ($C_t = [\text{Triton X-100}] + [\text{Tween 80}]$). The results show that as $\alpha_{\text{TX-100}}$ increases the rate increases for all values of C_t . Kinetic analysis has been carried out by using a simple pseudo phase model and binding constants were determined. These binding constants were found to be in agreement with the binding constants obtained spectrophotometrically.

Keywords: *s*-Triazine, Iron(II), 2,2'-Bipyridyl, Mixed surfactants, Triton X-100, Tween 80.

INTRODUCTION

Mixed normal micelles are defined as normal micelles formed from monomers of two different surfactants in aqueous solutions. These systems are used in all commercial applications because they can be produced at relatively lower cost compared to single pure surfactants and their performance can be improved compared to single surfactants. Since various types of combinations of surfactants are possible the composition and concentration of mixed surfactants can be optimized to produce different properties for various practical applications [1]. Physical properties of mixed micelles solutions are reported by different theoretical models such as Clint [2], Nagarajan [3], Attwood *et al.* [4], Puwada & Blankschtein [5], Munoz *et al.* [6] and Motomura *et al.* [7]. Up to now, various physico-chemical aspects such as CMC measurements [4,8], micelle composition and aggregation numbers [8,9] micelle demixing

and modeling [4,9] were studied in the presence of mixed micelles but very few studies on kinetics of unimolecular reactions in the presence of mixed micelles are reported in literature [6,10,11].

The study of dissociation of *tris*(2,2'-bipyridyl)iron(II) $[\text{Fe}(\text{bipy})_3]^{2+}$ and *tris*(1,10-phenanthroline)iron(II) $[\text{Fe}(\text{phen})_3]^{2+}$ and related complexes has been studied by several workers. Basolo *et al.* [12] reported a kinetic study of dissociation of $[\text{Fe}(\text{bipy})_3]^{2+}$ in aqueous medium in the presence of acid. They found that the dissociation of the complex is accelerated by H^+ ion, the rate reaching a limiting value at $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$. Sriramam *et al.* [13] also investigated the reaction in the aqueous acetic acid media including mineral acids and found a linear variation of rate with H^+ ion concentration reaching a limiting value. The reaction also has an acid-independent path. The solvent effect on the dissociation of $[\text{Fe}(\text{phen})_3]^{2+}$ and related complexes has been investigated in detail by Burgess *et al.*

[14,15]. Their results indicate an apolar periphery around the central metal ion, the greater solvation of this periphery in the transition state by the organic co-solvent being responsible for the acceleration of reaction in aqueous-organic media like *t*-butanol-water, DMSO-water mixtures in the absence of added acid. The dissociation kinetics of *bis*(2,4,6-tripyridyl-*s*-triazine)-iron(II) was studied by Pagenkoff and Margerum [16] using acid, EDTA and base. In case of the reaction with EDTA, one of the *bis*(2,4,6-tripyridyl-*s*-triazine) (tptz) ions dissociates completely before EDTA can react. On the other hand, hydrogen ion and hydroxide ion react directly with the complex to accelerate the dissociation.

Since, the micropolarity of micelles is much less compared to conventional aqueous medium and closer to that of organic solvent-water mixtures, it is interesting to investigate the kinetics of dissociation of these complexes in the presence of micelles and mixed micelles. Studies on the effect of non-ionic micelles like Triton X-100, Tween 80 and their combined effect on the rates of unimolecular reactions are very few. In view of this, the kinetic investigation of dissociation of $[\text{Fe}(\text{tptz})_2]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$ in the presence of pure Triton X-100, Tween 80 and mixed micelles of Triton X-100 and Tween 80 has been carried out.

EXPERIMENTAL

All solutions were prepared using double-distilled water and the chemicals used were of analytical reagent grade. Triton X-100 and Tween 80 were received from Merck, India and used without further purification. A solution of *bis*(2,4,6-tripyridyl-*s*-triazine)iron(II) ($[\text{Fe}(\text{tptz})_2]^{2+}$)/*tris*(2,2'-bipyridyl) iron(II) ($[\text{Fe}(\text{bipy})_3]^{2+}$) (0.01 mol dm⁻³) was prepared by mixing stoichiometric amounts of ferrous ammonium sulphate and tptz/bipy in water.

Kinetic studies: The dissociation of *bis*(2,4,6-tripyridyl-*s*-triazine)iron(II) and *tris*(2,2'-bipyridyl)iron(II) have been followed in the surfactant media by measuring the decrease in absorbance from time to time at 595 nm and 520 nm, respectively using a Shimadzu UV-1800 spectrophotometer maintained at constant temperature (27 ± 0.1 °C). Pseudo first order rate constants were determined from the plots of log (*A_t*) versus time (where *A_t* is the absorbance at time *t*). The kinetic data were the averages from triplicate runs with reproducibility ± 3%.

Product analysis: The dissociation of *bis*(2,4,6-tripyridyl-*s*-triazine)iron(II) and *tris*(2,2'-bipyridyl)iron(II) complexes has been established by the absence of absorbance of the complexes at λ_{max} = 595 nm and 520 nm, respectively, since the products of dissociation, Fe²⁺ and tptz (or bipy) have no absorbance. The molar absorptivity coefficient, ε₅₉₅ for *bis*(2,4,6-tripyridyl-*s*-triazine)iron(II) at 595 nm is 21,600 dm⁻³ mol⁻¹ cm⁻¹ and ε₅₂₀ for *tris*(2,2'-bipyridyl)iron(II) at 520 nm is 8,750 dm⁻³ mol⁻¹ cm⁻¹. To a product, ammonium thiocyanate was added and no red colour developed. The absence of Fe(III) was confirmed by ammonium thiocyanate test.

Determination of CMC of Triton X-100/Tween 80 mixed surfactants {C_{exp}}: Since, the CMC values change with experimental conditions, CMC's of mixed surfactants in the presence of 0.01 mol dm⁻³ NaCl were determined by measuring the

surface tension of the mixtures at different total surfactant concentrations (C_t) and at different mole fractions of Triton X-100 [α_{TX-100}].

RESULTS AND DISCUSSION

Determination of interaction parameter (β) and calculation of CMC of mixed surfactants: The pseudo-phase models, which have been developed to treat mixed micellization in binary surfactant mixtures, assume ideal mixing of the surfactants in the micelle and these models are quite successful in predicting the behaviour of both binary non-ionic and binary ionic mixtures of surfactants. But in the case of binary mixtures of non-ionic and ionic surfactants or of surfactants with different hydrophilic groups, significant deviations from the ideal model were observed. This led to the development of a pseudo-phase model where non-ideal mixing is treated using a regular solution approach developed by Rubingh and Jones [1]. The regular solution approach is used to determine the deviation from the ideality of mixed CMC values by using a single empirical parameter (β), which contains all the interactions involved in the mixed micelles. Considering the phase separation model for micellization, Rubingh and Jones [1] derived the following eqn.:

$$\frac{X_1^2 \ln \left(\frac{\alpha_1 C_{\text{exp}}}{X_1 C_1} \right)}{(1 - X_1)^2 [\ln(1 - \alpha_1) C_{\text{exp}} / (1 - X_1) C_2]} = 1 \quad (1)$$

where X₁ is the actual mole fraction of surfactant 1 in the mixed micelle. A computer program in FORTRAN based on Gauss-Newton iteration technique was developed for solving the eqn. 1 for X₁ given the values of C_{exp}, C₁, C₂ and α₁. Substitution of the value of X₁ into eqn. 1 gives the value of interaction parameter β for each mole fraction:

$$\beta = \frac{\ln[\alpha_1 C_{\text{exp}} / X_1 C_1]}{(1 - X_1)^2} \quad (2)$$

The value of β is a measure of the extent of interaction between the surfactants, negative values indicating synergism (unlike interactions, *i.e.* anionic-nonionic) and positive values antagonism. Interaction parameter (β) for Tween 80/Triton X-100 thus obtained is -0.69. Once the values of X₁ and β are known, f₁ and f₂ were calculated using the following expression:

$$f_1 = \exp[\beta(1 - X_1)^2] \text{ and } f_2 = \exp(\beta X_1^2) \quad (3)$$

C_{calc} is then calculated using eqn. 4:

$$\frac{1}{C_{\text{cal}}} = \frac{\alpha_1}{f_1 C_1} + \frac{(1 - \alpha_1)}{f_2 C_2} \quad (4)$$

From the values of f₁ and f₂, the total monomer concentration of two surfactants (C_{mon}) above the mixed CMC for a given total surfactant concentration (C_t) can be obtained from eqn. 5

$$C_{\text{mon}} = X_1 f_1 C_1 + (1 - X_1) f_2 C_2 \quad (5)$$

The total concentration of the micellized surfactants, C_M (= C_t - C_{mon}) is calculated and used in the analysis of kinetic data (Table-1).

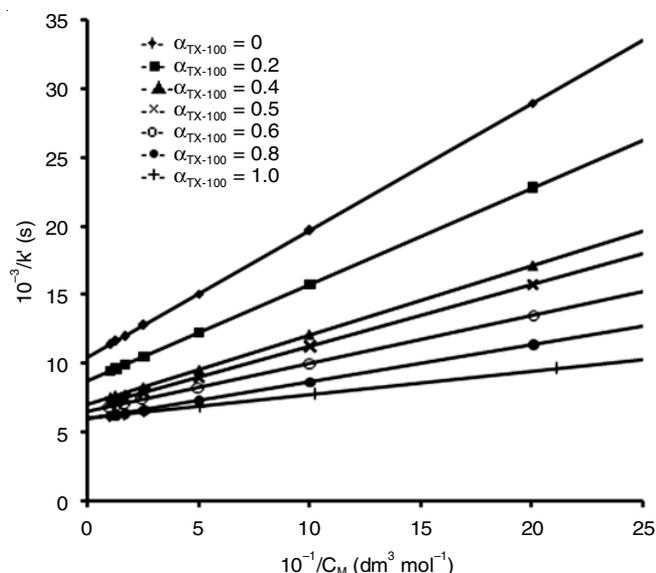


Fig. 3. Plot of $1/k'$ vs. $1/C_M$ at different mole fractions of Triton X-100 in dissociation of $[\text{Fe}(\text{bipy})_3]^{2+}$

TABLE-2
KINETIC PARAMETERS FOR DISSOCIATION OF
 $[\text{Fe}(\text{tpzt})_2]^{2+}$ AND $[\text{Fe}(\text{bipy})_3]^{2+}$ COMPLEXES

$\alpha_{\text{TX-100}}$	$[\text{Fe}(\text{tpzt})_2]^{2+}$		$[\text{Fe}(\text{bipy})_3]^{2+}$	
	$k_M \times 10^5$ (s^{-1})	K_S ($\text{dm}^3 \text{mol}^{-1}$)	$k_M \times 10^5$ (s^{-1})	K_S ($\text{dm}^3 \text{mol}^{-1}$)
0.0	17.5	8.12	9.55	113.8
0.2	19.6	8.82	11.4	125.4
0.4	25.6	9.55	14.2	140.1
0.5	26.4	10.8	14.8	151.3
0.6	55.2	14.7	15.4	187.5
0.8	58.9	24.7	16.7	226.1
1.0	108.0	30.1	17.2	338.0

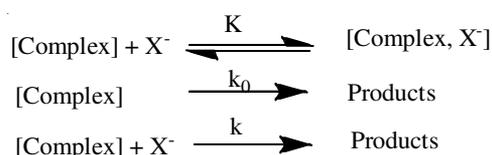
case of $[\text{Fe}(\text{tpzt})_2]^{2+}$. The lower value of K_S and higher value of k_M are in accordance with the stability constants of the complexes ($[\text{Fe}(\text{tpzt})_2]^{2+}$) (15.7); $[\text{Fe}(\text{bipy})_3]^{2+}$ (17.5).

Effect of synergism on kinetic parameters: Synergism is defined as an existing property in mixed surfactants system when a given property of the mixture can reach a more desirable value than that attained by either surfactant component of the mixture by itself. The values are given in Table-2 show that there is a continuous change in the mixed micellar characteristics from pure Triton X-100 to pure Tween 80 as the value of $\alpha_{\text{TX-100}}$ decreases from 1 to 0.

Consider the equation of $[\text{Fe}(\text{tpzt})_2]^{2+}$, when $\alpha_{\text{TX-100}}$ is 0, the value of K_S is 8.12 when $\alpha_{\text{TX-100}}$ is 1 it is 30.1. As $\alpha_{\text{TX-100}}$ decrease from 1 to 0, there is a continuous change in the value of K_S . But from $\alpha_{\text{TX-100}} = 0.5$ to $\alpha_{\text{TX-100}} = 0.2$, the values are comparable with K_S value obtained with pure Tween 80 micellar solution.

The values of K_S from $\alpha_{\text{TX-100}} = 0.2$ and $\alpha_{\text{TX-100}} = 0.5$ are expected to be much lower than the values obtained. These observations are attributed to synergism in these mixed micellar solutions. Similarly in the case of aequation of $[\text{Fe}(\text{bipy})_3]^{2+}$, the K_S value $\alpha_{\text{TX-100}} = 0.2$ to $\alpha_{\text{TX-100}} = 0.5$ are comparable with that of pure Tween 80 solution.

Effect of added anions: While the dissociation of $[\text{Fe}(\text{tpzt})_2]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$ in the presence of anions in aqueous medium is immeasurably slow and incomplete, the reactions proceed with appreciable rate in the presence of added ions in the presence of Triton X-100, Tween 80 and mixed micelles of Triton X-100/Tween 80. The results show that the pseudo first order rate constant k' , increases with increase in the concentration of the both Cl^- and Br^- and shows a limiting behaviour at high anion concentrations indicative of formation of ion pairs with the complexes. It is well known that dielectric constant of micellar medium is much less than in aqueous medium. Under these conditions ion pair is formed between each of these ions and the complex and the anion in the ion-pair exerts nucleophilic effect on the metal ligand bond aiding in dissociation. The kinetic results can be analyzed according to Fig. 4.



where $\text{Complex} = [\text{Fe}(\text{tpzt})_2]^{2+}/[\text{Fe}(\text{bipy})_3]^{2+}$ and $\text{X}^- = \text{Cl}^-$ or Br^-

Fig. 4. Rate law scheme

$$\text{Rate} = -\frac{d}{dt}[\text{Complex}] = k_0[\text{Complex}] + k[\text{Complex}, \text{X}^-] \quad (8)$$

where $[\text{Complex}] = [\text{Fe}(\text{tpzt})_2]^{2+}/[\text{Fe}(\text{bipy})_3]^{2+}$ and $\text{X}^- = \text{Cl}^-$ or Br^- ; K is the formation constant of $\{[\text{Fe}(\text{tpzt})_2]^{2+}, \text{X}^- \}/\{[\text{Fe}(\text{bipy})_3]^{2+}, \text{X}^- \}$; k_0 is the rate constant of the dissociation of complex $[\text{Fe}(\text{tpzt})_2]^{2+}/[\text{Fe}(\text{bipy})_3]^{2+}$ and k is the rate constant of the dissociation of ion-pair $[\text{Fe}(\text{tpzt})_2]^{2+}, \text{X}^- \}/[\text{Fe}(\text{bipy})_3]^{2+}, \text{X}^- \}$ at a given mole fraction of Triton X-100. Using equilibrium treatment, it can be shown that

$$K = \frac{[\text{Complex}, \text{X}^-]}{[\text{Complex}][\text{X}]_t} \quad (9)$$

where 't' indicates the initial concentration added and $[\text{X}]_t = [\text{X}] + [\text{Complex}, \text{X}^-]$

$$K = \frac{[\text{Complex}, \text{X}^-]}{\{[\text{Complex}]_t - [\text{Complex}, \text{X}^-]\}[\text{X}]_t} \quad (10)$$

$$[\text{Complex}, \text{X}^-] = \frac{K[\text{Complex}]_t[\text{X}]_t}{1 + K[\text{X}]_t} \quad (11)$$

$$\text{Rate} = k_0[\text{Complex}] + \frac{kK[\text{Complex}]_t[\text{X}]_t}{1 + K[\text{X}]_t} \quad (12)$$

The pseudo first order rate constant k' is equal to rate/ $[\text{Complex}, \text{X}^-]$

$$k' = k_0 + \frac{kK[\text{X}]_t}{1 + K[\text{X}]_t} \quad (13)$$

$$\frac{1}{k' - k_0} = \frac{1}{kK[\text{X}]_t} + \frac{1}{k} \quad (14)$$

TABLE-3
VALUES OF k AND K FOR Cl^- AND Br^- IONS ON DISSOCIATION OF $[\text{Fe}(\text{tptz})_2]^{2+}$ AND $[\text{Fe}(\text{bipy})_3]^{2+}$

[Anion]	$\alpha_{\text{TX-100}} = 0.0$		$\alpha_{\text{TX-100}} = 0.5$		$\alpha_{\text{TX-100}} = 1.0$		
	$k \times 10^5 \text{ (s}^{-1}\text{)}$	$K \times 10^{-2} \text{ (mol}^{-1} \text{ dm}^3\text{)}$	$k \times 10^5 \text{ (s}^{-1}\text{)}$	$K \times 10^{-2} \text{ (mol}^{-1} \text{ dm}^3\text{)}$	$k \times 10^5 \text{ (s}^{-1}\text{)}$	$K \times 10^{-2} \text{ (mol}^{-1} \text{ dm}^3\text{)}$	
$[\text{Fe}(\text{tptz})_2]^{2+}$	$[\text{Cl}^-]$	14.6	16.8	15.4	18.7	52.6	20.1
	$[\text{Br}^-]$	14.3	13.8	15.3	15.9	45.9	18.3
$[\text{Fe}(\text{bipy})_3]^{2+}$	$[\text{Cl}^-]$	8.25	10.3	8.43	13.4	8.61	15.1
	$[\text{Br}^-]$	7.21	9.47	7.66	12.2	8.07	14.9

In accordance with this equation, a plot of $1/(k' - k_0)$ vs. $1/[X]_t$ was found to be a straight line with a positive intercept (Figs. 5 & 6). Using the values of slope and intercept, the equilibrium constant (K) in the presence of Cl^- and Br^- has been calculated. The values in Table-3 show that the formation constant for the ion-pair is greater in the case of Cl^- compared to Br^- . A similar trend was observed by Tachiyashiki and Yamatera [18] in aqueous-alcohol mixtures where the dissociation of the complexes increases with increase in basicity of the anions, $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{SCN}^- < \text{OH}^- = \text{CN}^-$.

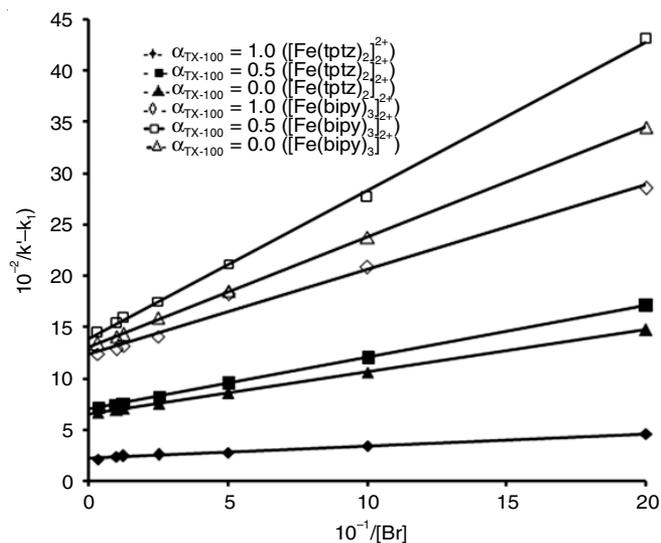


Fig. 5. $1/(k' - k_0)$ vs. $1/[\text{Br}^-]$ for dissociation of $[\text{Fe}(\text{tptz})_2]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$ at different mole fractions of Triton X-100 ($\alpha = 1.0, 0.5$ & 0)

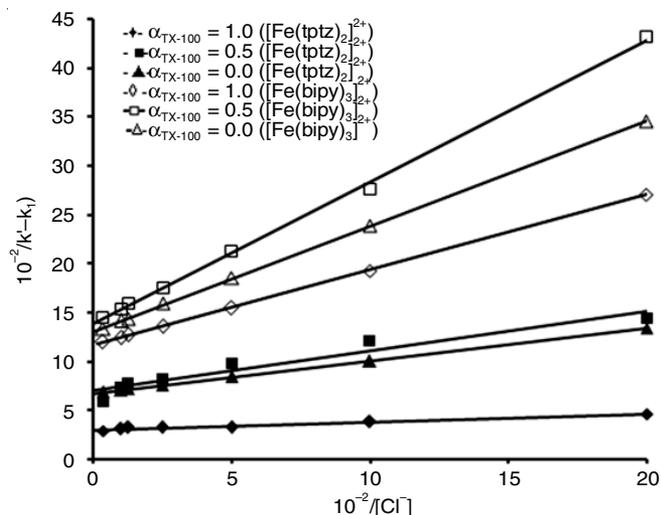


Fig. 6. $1/(k' - k_0)$ vs. $1/[\text{Cl}^-]$ for dissociation of $[\text{Fe}(\text{tptz})_2]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$ at different mole fractions of Triton X-100 ($\alpha = 1.0, 0.5$ & 0)

Conclusion

Micellization behaviour of Triton X-100/Tween 80 mixed surfactant solutions was studied by surface tension measurements at different mole ratios of Triton X-100. The CMC of the mixed surfactant system thus obtained was used to calculate the β interaction parameter. The β parameter was found to be -0.69 , which indicates synergistic effect. The catalytic property of the mixed micelles was investigated by carrying out the kinetics of dissociation of $[\text{Fe}(\text{tptz})_2]^{2+}$ and $[\text{Fe}(\text{bipy})_3]^{2+}$ in the presence of Triton X-100/Tween 80 mixed micellar medium. The kinetic studies showed that the rate constant change around twenty times on changing the mole fraction from 0.2 to 0.8 in the dissociation of $[\text{Fe}(\text{tptz})_2]^{2+}$ and change around two times on changing the mole fraction from 0.2 to 0.8 in the dissociation of $[\text{Fe}(\text{bipy})_3]^{2+}$.

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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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