KINETICS OF $[Co(tpy)_2]^{2+}$ DISSOCIATION IN AOT/HEPTANE AND CTAB/CHLOROFORM/HEXANE REVERSE MICELLES: A COMPARATIVE STUDY

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ABSTRACT

A comparative study of the kinetic study of dissociation of $[Co(tpy)_2]^{2+}$ was carried out in two distinct reverse micellar environments, namely AOT/heptane and CTAB/hexane/chloroform. The observed reaction rates were significantly higher in the reverse micellar media compared to an aqueous medium, where the reaction was notably slow and incomplete {$k_{CTAB} = 6.9\times10^{-5}\ s^{-1} < k_{AOT} = 31.5\times10^{-3}\ s^{-1}$}. The enhanced reaction rate in reverse micelles was explained in terms of the lower dielectric constant of water present in the reverse micelles. Analysis revealed that, the rate of reaction decreases with increasing the W {= $[H_2O]/[surfactant]$}in both the reverse micellar media. The reaction rate increases with the concentration of the anionic surfactant (AOT) but independent of the concentration of the cationic surfactant (CTAB). The dependence of rate of reaction on surfactant concentration in the case of AOT has been explained on the basis of electrostatic interactions between electro positively charged complex $[Co(tpy)_2]^{2+}$ and charge of anionic micellar interface.

Keywords: *reverse micelles, cobalt(II) terpyridine complex, dissociation kinetics, AOT, CTAB.*

INTRODUCTION

The kinetics of metal ligand dissociation reactions are strongly influenced by the dielectric constant of the reaction medium. Numerous studies on coordination complexes have demonstrated that a decrease in solvent polarity significantly accelerates dissociation processes by preferential stabilization of the dissociative transition state relative to the more highly solvated ground state [1 - 3]. Dissociation reactions of polypyridyl metal complexes, such as tris(2,2′-bipyridyl)iron(II) and related systems, have been shown to proceed more rapidly in aqueous–organic solvent mixtures than in pure aqueous media, highlighting the importance of solvent dielectric properties in governing reaction kinetics [4 - 6]. Investigations into solvent effects have further revealed that the kinetic stability of bis-terpyridine complexes of iron(II) and cobalt(II) is highly sensitive to medium composition, with enhanced dissociation rates observed in organic solvents and aqueous - organic mixtures of lower dielectric constant compared to water [7, 8]. Similar acceleration of metal - ligand dissociation and racemization reactions has been reported in microemulsion systems, where the reaction medium possesses dielectric properties intermediate between those of water and organic solvents [9]. These rate enhancements have been attributed to reduced electrostatic stabilization of the intact complex and improved solvation of the apolar regions of the transition state in low-dielectric environments.

These observations collectively establish low-dielectric media as effective environments for promoting

metal ligand dissociation reactions. In this context, reverse micelles offer a unique nanoconfined reaction medium in which water is solubilized within a nonpolar continuous phase, resulting in water pools with physicochemical properties markedly different from bulk water [10]. Such systems provide an excellent platform for probing dielectric and microenvironmental effects on coordination reaction kinetics.

Reverse micelles are thermodynamically stable surfactant aggregates formed in nonpolar solvents, capable of solubilizing small amounts of water within nanosized polar cores. Among commonly employed reverse micellar systems, aerosol-OT (AOT) forms anionic reverse micelles in hydrocarbons such as heptane, while cetyltrimethylammonium bromide (CTAB) forms cationic reverse micelles in mixed organic solvents such as chloroform/hexane. The water solubilized in the polar cavity of reverse micelles is called water pool and is expressed by the parameter W (= $[H_2O]$/[surfactant]) [11 - 13]. Water confined within reverse micelles exhibits physicochemical properties markedly different from bulk water. In AOT reverse micelles at low water loading (W ≈ 2 - 4), water exists predominantly as highly structured interfacial water strongly bound to sulfonate head groups [14, 15]. Similarly, in CTAB reverse micelles at low water content (W ≈ 2 - 6), water is largely confined to the interfacial region and is strongly associated with the quaternary ammonium head groups, resulting in a highly restricted, low-dielectric microenvironment [16 - 20]. Such confined environments are known to induce significant rate acceleration in reverse micellar and microemulsion systems.

In view of the pronounced influence of dielectric constant and microenvironment on metal–ligand dissociation kinetics, the present study investigates the dissociation behavior of the bis-terpyridine cobalt(II) complex, $[Co(tpy)_2]^{2+}$, in reverse micellar media. A comparative kinetic analysis is carried out in AOT/heptane (anionic) and CTAB/chloroform/hexane (cationic) systems to elucidate the role of surfactant charge, water loading (W), and confined low-dielectric water pools on the dissociation kinetics. The reactivity in reverse micelles is further compared with that in conventional aqueous medium, and the observed rate enhancements are rationalized in terms of dielectric effects, electrostatic interactions, and micellar microenvironment.

EXPERIMENTAL

Materials

All solutions were prepared using doubly distilled water and chemicals of analytical grade were used. Heptane, hexane, and chloroform were used after distillation. The stock solution of cetyl trimethyl ammonium bromide (CTAB) was prepared by dissolving 9.111 g of CTAB in a 250 mL chloroform-hexane mixture (in a 3 : 2 volume ratio), resulting in a concentration of 0.1 mol dm^{-3}. Similarly, solutions of 0.2 and 0.3 mol dm^{-3} were also prepared. The stock solution of aerosol-OT (AOT) was obtained by dissolving 11.11 g of AOT in 250 mL of hexane, yielding a concentration of 0.1 mol dm^{-3}. Correspondingly, solutions of 0.2 and 0.3 mol dm^{-3} were prepared. A 0.04 mol dm^{-3} solution of bis (2,2';6',2''terpyridyl) cobalt (II) was made by mixing 0.1095 g of $CoCl_2 .6H_2O$ and 0.2 g of terpyridine in 10 mL of water.

Experimental method

0.04 mL of $[Co(tpy)_2]^{2+}$ solution (0.04 mol dm^{-3}) was introduced into 10 mL of 0.1 mol dm^{-3} AOT solution using a micropipette. The mixture was vigorously shaken until a clear solution was obtained. The variable 'W' was adjusted within the range of 4.44 to 12.2 in subsequent experiments. Absorbance measurements of $[Co(tpy)_2]^{+2}$ were consistently carried out at 450 nm wavelength using a Shimadzu UV 1800 spectrophotometer. Log(absorbance) vs time plots showed excellent linearity, indicating first order kinetics with respect to $[Co(tpy)_2]^{+2}$. To ensure reliability, triplicate runs were consistently performed, and averages were calculated.

RESULTS AND DISCUSSION

The dissociation of the $[Co(tpy)_2]^{2+}$ complex is notably slow without the presence of acid and does not reach completion in an aqueous medium. However, in the presence of AOT and CTAB reverse micelles, the reaction achieves completion even without added acid and is markedly accelerated. The doubly positively charged $[Co(tpy)_2]^{2+}$ complex is confined within the water pool of the reverse micelles, and its aquation follows simple first-order kinetics. The log(absorbance) versus time plots exhibit linearity for at least 98 % of the reaction (Fig. 1).

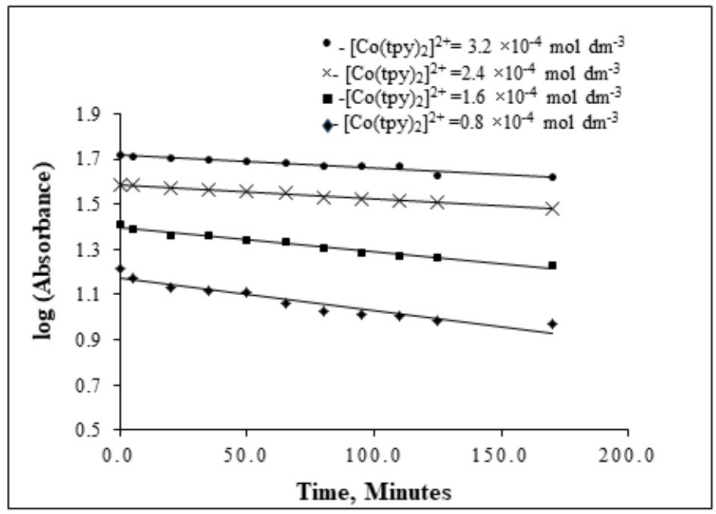


Fig. 1. Plots of log (Absorbance) vs. time.

The accelerated reaction rate observed in reverse micelles compared to conventional aqueous media can be attributed to two factors. Firstly, the higher solubility of terpyridyl in the organic phase relative to water favours the partitioning of terpyridyl into the organic phase, leading to a significant decrease in the overall process's free energy. Secondly, the water pool of reverse micelles is distinctly less polar than the aqueous medium. Goto et al. reported that the micro-polarity of the water pool in CTAB reverse micelles is comparable to that of methanol (W = 1 - 10), while the micro-polarity of the water pool in AOT reverse micelles falls between water and methanol. Studies have reported that the dissociation of metal complexes occurs more rapidly in the presence of organic cosolvents, as the transition state involving metal complexes is more favourable in organic solvents with a lower dielectric constant compared to water. As reverse micelles exhibit lower dielectric constants, low activity, limited mobility, modified pH and high nucleophilicity compared to conventional aqueous solutions, the rates of reactions are faster within the reverse micelles. Based on the experimental results, the dissociation mechanism is proposed in Fig. 2.

Effect of molar ratio (W) and concentration of AOT on dissociation of $[Co(tpy)_2]^{2+}$

The first order rate constant, k, decreases with increase in molar ratio (W = $[H_2O]$/[AOT]) at constant [AOT] (Table 1). The decrease in rate with increase in W at constant [AOT] must therefore be due to attenuation of the special properties of the water, the lower dielectric constant. At constant W, with increase in AOT concentration, the first order rate constant increases this study has been carried out in detailed manner at different values of W (3.33, 4.44, 6.66, 8.88 and 12.2). The effect of [AOT] has been explained quantitatively using the

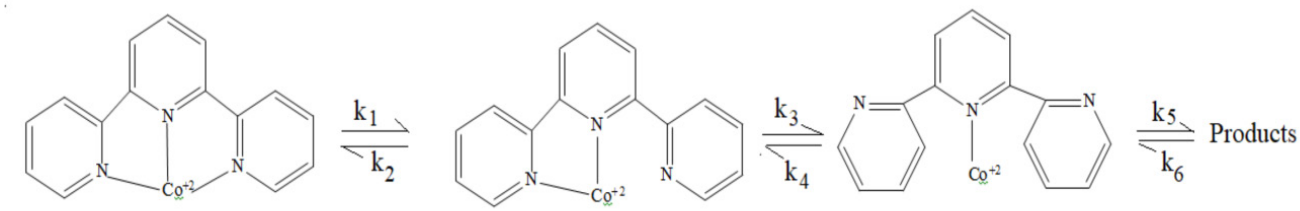
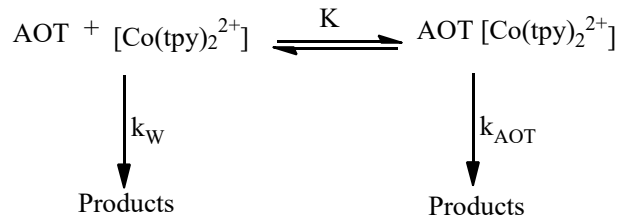


Fig. 2. Mechanism of dissociation of $[Co(tpy)]^{+2}$.

Berezin's pseudo-phase model [18, 21].

According to Berezin's pseudo-phase model, for a unimolecular reaction:



where K is the binding constant of the complex with reverse micelle.

This model gives the equation for the observed rate constant as presented in the Eq. (1 - 3):

$$k = \frac{k_W + k_{AOT}\,K[AOT]}{1 + K[AOT]} \quad (1)$$

$$\frac{1}{k} = \frac{1 + K[AOT]}{k_W + k_{AOT}\,K[AOT]}\ ;\ k_W \ll k_{AOT} \quad (2)$$

$$\frac{1}{k} = \frac{1}{k_{AOT}\,K[AOT]} + \frac{1}{k_{AOT}} \quad (3)$$

According to above equation 1/ k verses 1/[AOT] was found to be linear, showing that the validity of proposed Berezin's pseudo-phase model to reverse micelles (Fig. 3). The binding constant of $[Co(tpy)_2]^{2+}$ can be calculated from slope of the above plot and it was found to be 21.455 at W = 4.44 and 6.541 at W = 12.2

Table 1. Effect of W and [AOT] on observed first order rate constant (k) at $[Co(tpy)_2]^{2+} = 1.6\times10^{-4}$ mol dm^{-3}; T = 304K.

[AOT], mol dm^{-3}	W	k×10^3, s^{-1}
0.1	3.33	11.7
	4.44	10.5
	6.66	7.8
	8.88	11.9
	12.2	5.9
0.2	3.33	19.8
	4.44	17.9
	6.66	16.1
	8.88	15.4
	12.2	14.7
0.3	3.33	31.5
	4.44	29.5
	6.66	27.1
	8.88	21.6
	12.2	21.4

Effect of molar ratio (W) and concentration of CTAB On dissociation of $[Co(tpy)_2]^{2+}$

To investigate the effect of variation of the mole ratio, (W = $[H_2O]$/ [CTAB]) on rate, kinetic runs were

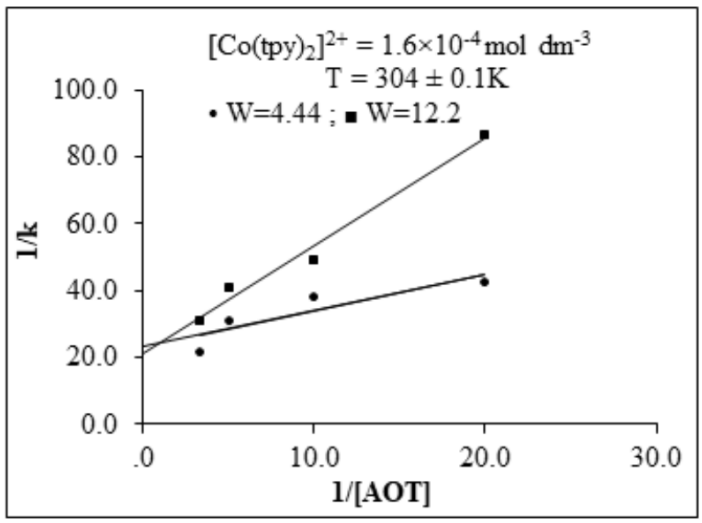


Fig. 3. A plot of 1/k vs 1/[AOT].

carried out by varying the concentration of water (which is the concentration with respect to the total volume of the system, CTAB, hexane and chloroform), but keeping the overall concentration of CTAB and $[Co(tpy)_2]^{2+}$ constant at 0.1 mol dm^{-3} and 1.6×10^{-4} mol dm^{-3} respectively. Series of runs were repeated at different overall concentrations of CTAB. First order rate constant, k, decreases with increase in molar ratio (W = $[H_2O]$/ [CTAB]) at constant [CTAB] (Table 2). The decrease in rate with increase in W at constant [CTAB] must therefore be due to attenuation of the special properties of the water pool like the lower dielectric constant. At high W, the entrapped water behaves like bulk water. And there is no change in k with change in concentration of CTAB at the same value of the mole ratio, W. The reason of dependence of rate on surfactant concentration is different in both the surfactants.

Effect of added anions on rate

In the water pool of the reverse micelle, the equilibrium constants have appreciable values to produce discernible effect on rate in their presence whereas such an effect is absent in the aqueous medium where the formation constants of the ion pairs have very small values due to high dielectric constant of the medium. The results indicate greater effect of more basic SCN^- compared to Cl^-. To study the effect of added anions on the rate of dissociation, kinetic runs were carried out in the presence of Cl^- and SCN^- ions at different concentrations in the range (5.0 - 100.0) × 10^{-4} mol dm^{-3} but keeping the concentrations of CTAB and $[Co(tpy)_2]^{2+}$ and W constant. First order rate constants, k, evaluated from the plots of log A_t versus time are presented in Table 3 and Table 4. The results show that k increases with increase in $[Cl^-]$ and $[SCN^-]$ and

Table 2. Effect of W and [CTAB] on observed first order rate constant (k) at $[Co(tpy)_2]^{2+}$ = 1.6×10^{-4} mol dm^{-3}; T = 304K.

[CTAB], mol dm^{-3}	W	$k\times10^5$, s^{-1}
0.1	3.33	6.91
	4.44	3.07
	6.66	2.68
	8.88	1.91
	12.2	1.02
0.2	3.33	6.43
	4.44	3.07
	6.66	2.54
	8.88	2.02
	12.2	2.61
0.3	3.33	5.94
	4.44	2.32
	6.66	1.91
	8.88	1.84
	12.2	1.42
0.4	3.33	5.92
	4.44	2.25
	6.66	1.84
	8.88	1.82
	12.2	2.02

Table 3. Effect of variation of $[Cl^-]$ at $[Co(tpy)_2]^{2+}$ = 1.6×10^{-4} mol dm^{-3}, [CTAB] = 0.1 mol dm^{-3} W = 6.66; T = 304 ± 0.1 K.

$10^4\times[Cl^-]_{o,}$ mol dm^{-3}	$10^2\times[Cl^-]_{e,}$ mol dm^{-3}	$k\times10^5$, s^{-1}
0.0	0.00	3.0
5.0	4.05	3.2
10.0	8.10	3.8
50.0	40.50	4.9
75.0	60.75	10.0
100.0	81.00	11.1

Table 4. Effect of variation of $[SCN^-]$ at $[Co(tpy)_2]^{2+}$ = 1.6×10^{-4} mol dm^{-3}, [CTAB] = 0.1 mol dm^{-3} W = 6.66; T = 304 ± 0.1 K.

$10^4\times[SCN^-]_{o,}$ mol dm^{-3}	$10^2\times[SCN^-]_{e,}$ mol dm^{-3}	$k\times10^5$, s^{-1}
0.0	0.00	2.303
5.0	4.05	12.28
10.0	8.10	15.35
20.0	16.20	18.45
30.0	24.30	20.72
50.0	40.50	21.87

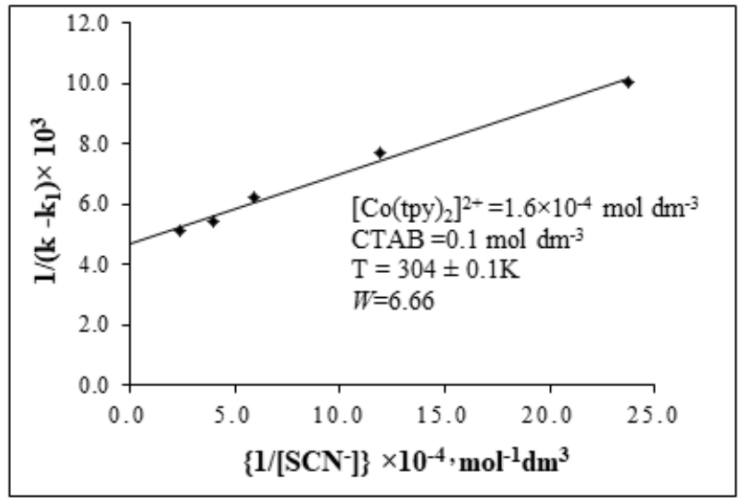


Fig. 4. A plot of 1/ (k'-k_1) versus 1/[SCN^-].

the accelerating effect is greater in the case of [SCN^-]. These ions have pronounced accelerating effect on the dissociation in the presence of the reverse micelle.

$$\text{Rate} = k_1[Co(tpy)_2^{2+}, Br^-] + \frac{k_2K[Co(tpy)_2^{2+}, Br^-][X^-]_t}{[Br^-]_t + K[X^-]_t} \quad (4)$$

The pseudo first order rate constant, k is equal to rate/ $[Co(tpy)_2^{2+}, Br^-]_t$ (Eq. (5)):

$$\frac{1}{k - k_1} = \frac{[Br^-]_t}{k_2K[X^-]_t} + \frac{1}{k_2} \quad (5)$$

A plot of 1/ (k'-k_1) versus 1/$[X^-]_t$ is a straight line with a positive intercept (Fig. 4). Using the values of the slope and intercept, the equilibrium constants, K in the presence of SCN^- and Cl^- have been determined. In the case of SCN^-, the value of the equilibrium constant, K is 20.3314 at W = 6.66. For Cl^-, K is 1.89 at W = 6.66. Also, the value of K is more at low W than at high W. This is because the ion pair formation is favored at low dielectric constant i.e., low W.

CONCLUSIONS

- The dissociation kinetics of the bis-terpyridine cobalt(II) complex, $Co[(tpy)_2]^{2+}$ were investigated in AOT/heptane, CTAB/chloroform/hexane reverse micellar systems and aqueous medium; the reaction is extremely slow and incomplete in water, but rapid and complete in both reverse micellar environments.
- The enhanced dissociation rates in reverse micelles are attributed to the lower dielectric constant and modified properties of confined water pools.
- In both reverse micellar systems, the rate decreases with increasing water loading (W), indicating a reduction in structured interfacial water at higher W values.
- In AOT reverse micelles, the dissociation rate increases with surfactant concentration due to electrostatic attraction between the cationic complex and the anionic micellar interface. Berezin's pseudo-phase model is applied to the AOT system and determined binding constants.
- In CTAB reverse micelles, the dissociation rate is independent of surfactant concentration at constant W.
- Addition of anions significantly accelerates the dissociation, with SCN^- exhibiting a stronger effect than Cl^-. Overall, reverse micelles act as efficient nanoreactors for controlling metal-ligand dissociation kinetics.

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Authors' contributions

L.B carried out the experimental work and data collection. S.P conceived the research idea, supervised the work and contributed to data interpretation. V.K assisted in data analysis, preparation of the manuscript.

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