Kinetics of the dissociation of tris(2,2'-bipyridyl)iron(II) and tris(1,10-phenanthroline)iron(II) in the reverse micelles of Tween-85 in cyclohexane

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Abstract : Dissociation of the aqueous complexes of tris(2,2'-bipyridyl) and tris(1,10-phenanthroline)iron(II) takes place with appreciable rate in the presence of reverse micelles of Tween-85 in cyclohexane-water mixtures. The rate of dissociation increases with increase in the concentration of Tween-85 at constant W (= [Water]/[Tween-85]) and decreases with increase in W at constant [Tween-85]. The results are in support of the mechanism envisasing the binding of the complex on the micellar interface, the micellar surface catalysing the dissociation of metal-ligand bond. The binding constants of the complexes on the micellar interface have been evaluated.

Keywords : Reverse micelles, [Tween-85], 2,2'-bipyridyl, 1,10-phenanthroline, kinetics of dissociation, binding constants.

Introduction

The reverse micellar systems have special properties which affect the kinetics of reactions taking place in their presence. The surfactant solubilizing water provides a medium with unique properties for reactions involving polar substrates[1]. In an attempt to investigate how reverse micelles affect the kinetics of dissociation reactions we have taken up the study of the aquation of transition metal complexes tris(2,2'-bipyridyl)iron(II), $[Fe(bipy)_3]^{2+}$ and tris(1,10-phenanthroline)iron(II), $[Fe(phen)_3]^{2+}$. These reactions are immeasurably slow in conventional aqueous medium in the absence of acid. Subba Rao *et al.*[2-4] investigated the dissociation of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in the water pools of reverse micelles of cetyl trimethyl ammonium bromide (CTAB) in hexane-chloroform-water mixtures. They found that the binding of the complex by the interface had been precluded in this cationic surfactant. Hence it is interesting to investigate the reaction in the presence of a non-ionic surfactant which does not repel the positively charged complex. In this direction the present authors have carried out these reactions in Tween-85-cyclohexane-water reverse micelles and reported the results in the present communication.

Results and discussion

The kinetics of the dissociation of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ complexes have been studied in the reverse micellar medium of Tween-85-cyclohexane-water in the absence of added acid. Kinetic runs have been carried out at pH 6.97, following the decrease in concentration of the complex by measuring its absorbance from time to time. Plot of log (absorbance) versus time has been found to be linear for at least 98% of the reaction, showing that the reaction obeys first order kinetics with respect to $[Fe(bipy)_3]^{2+}$ or $[Fe(phen)_3]^{2+}$.

Effect of variation of molar ratio, W, and concentration of Tween-85 :

To investigate the effect of variation of molar ratio, W (=[H_2O]/[Tween-85]) on rate, kinetic runs have been carried out varying the concentration of water keeping the concentration of Tween-85 and complex constant at constant temperature. The rate has been found to decrease with increase in W. Kinetic runs have also been carried out at different concentrations of Tween-85 keeping W and [complex] constant. The rate constant (k_{obs}) increased with increase in the concentration of Tween-85. Further, the change in the concentration of the complex has no effect on the value of k_{obs}. The kinetic study could not be

carried out at higher concentrations of Tween-85 (>0.056 mol dm^{-3}) and lower W (<6.94) because of the instability of the reverse micelle under these conditions. These results are presented in Tables 1 and 2. The water in the reverse micelle differs from bulk water in many physico-

M, S, MS and P represent micelle, substrate. micelle-substrate complex and product(s) respectively. K is the binding constant of the complex with reverse micelle, k_0 is rate constant of the reaction in the water pool of reverse micelle or at zero micellar concentration, k_M is the

Table 1. Effect of variation of W and [Tween-85] on the rate of dissociation of tris(1,10-phenanthroline)iron(II) in the reverse micelles of Tween-85-cyclohexane
[Fe(phen)$_3$]$^{2+}$ = 4.0 × 10^{-5} mol dm^{-3}; Temp. = 30.0 ± 0.1 °C

W	$10^4 × k_{obs}$ (s^{-1}) at [Tween-85] (mol dm^{-3})					$10^4 × k_0$ (s^{-1})	$10^{-2} × K$ (dm^3 mol^{-1})
	0.01	0.02	0.033	0.046	0.056		
6.94	6.75	7.40	8 54	9.90	11.36	6.17	19.25
13.8	6.13	6.66	7.57	8.77	9.80	5.68	16.44
16.6	5.49	5.81	6.53	7.29	8.00	5.14	14.11
20.8	4.97	5.29	5.74	6.36	6.84	4.71	11.85
23.6	4.71	4.97	5.37	5.78	6.21	4.49	10.94

Table 2. Effect of variation of W and [Tween-85] on the rate of dissociation of tris(2,2'-bipyridyl)iron(II) in the reverse micelles of Tween-85-cyclohexane
[Fe(bipy)$_3$]$^{2+}$ = 4.0 × 10^{-5} mol dm^{-3}; Temp. = 30.0 ± 0.1 °C

W	$10^4 × k_{obs}$ (s^{-1}) at [Tween-85] (mol dm^{-3})					$10^4 × k_0$ (s^{-1})	$10^{-2} × K$ (dm^3 mol^{-1})
	0.01	0.02	0.033	0.046	0.056		
6.94	4.80	5.34	6.17	7.29	8.47	4.62	17.00
13.8	4.42	4.80	5.55	6.41	7.24	4.23	15.10
16.6	4.18	4.54	5.05	5.61	6.17	4.06	14 01
20.8	3.90	4.11	4.46	4.90	5.26	3.77	10.26
23.6	3.73	4.09	4.23	4.51	4.85	3.63	9.95

chemical properties[5] (nuclophilicity, viscosity and polarity). When W increases at constant [Tween-85], the degree of hydration increases and the difference in properties of water pool and bulk water becomes less and less so that the rate of dissociation decreases[3]. As the concentration of Tween-85 increases at constant W, the dimensions of water pool remains constant but only the micellar concentration and the area of interface increase. This suggests the binding of the complex [Fe(bipy)$_3$]$^{2+}$ or [Fe(phen)$_3$]$^{2+}$ by micellar surface and the complex bound by the micelle undergoing dissociation with higher rate[6,7]. The analysis of the rate data has been carried out using pseudo-phase model for unimolecular reactions[8,9] which can be represented by the following Scheme.

$$M + S \xrightleftharpoons{K} MS$$
$$\downarrow k_0 \qquad \downarrow k_M$$
$$P \qquad P$$
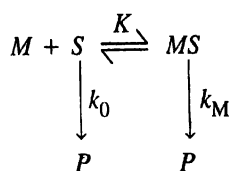
rate constant of the reaction taking place on the reverse micellar interface. This model gives the equation for the observed rate constant (k_{obs}) as

$$k_{obs} = \frac{k_0 + k_M K[M]}{1 + K[M]} \tag{1}$$

where $[M] = ([\text{Tween-85}] - \text{CMC})/N$

N = aggregation number and CMC = critical micellar concentration.

On rearranging eq. (1) we get

$$\frac{1}{k_{obs}} = \frac{1 + K[M]}{k_0 + k_M K[M]} \tag{2}$$

on neglecting the value of $k_M K[M]$ when compared to k_0, the eq. (2) takes the form

$$\frac{1}{k_{obs}} = \frac{1}{k_0} + \frac{K[M]}{k_0} \tag{3}$$

or

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$$\frac{1}{k_{obs}} = \frac{1}{k_0} + \frac{K([\text{Tween-85}] - \text{CMC})}{k_0.N} \quad (4)$$

as required by eq. (4) a plot of $1/k_{obs}$ versus ([Tween-85] – CMC) should be straight line, the slope of which should be $K/k_0.N$ and the intercept being $1/k_0$. The ratio of slope/intercept gives the value of K/N.

From the results in Tables 1 and 2 the plots of $1/k_{obs}$ versus ([Tween-85] – CMC) have been found to be straight lines. From this straight line the values of slope and intercept have been calculated. The CMC determined by the authors has been found to be 4.7×10^{-3} mol dm^{-3}. Assuming a value of 204 for aggregation number, N, based on the values reported by Bhattacharya et al.[10], the value of binding constant has been evaluated $K =$ (slope/intercept) N. It can be seen from the results in Tables 1 and 2 that the value of k_0 is nearer to the observed rate constant, k_{obs}, which implies that k_{obs} is primarily due to the contribution of k_0 and the value of k_M is very low and hence when compared to k_0 the value of k_M $K[M]$ can be neglected. k_0 which is the rate constant at zero micellar concentration can be considered to be the rate of dissociation of the complex in the water pool and expectedly, k_0 decreases with increase in W. The unique properties of water pool which get extenuated as W increases[3,9] are presumably responsible for the large acceleration of the dissociation of the complex in the reverse micelles[11]. The value of the binding constant, K has also been found to decrease with increase in W i.e. increase in water concentration and the volume of the water pool and this may also result in favourable partitioning of the complex in water pool and decrease in the concentration of micelle bound complex[12,13].

Interestingly the rate constant (k_{obs}) of $[\text{Fe(phen)}_3]^{2+}$ in Tween-85 reverse micellar medium is 60–90 times higher than that in the reverse micellar media made of cationic surfactant, CTAB[5], at identical concentrations of surfactants and the same W. The rate constant for the dissociation of $[\text{Fe(bipy)}_3]^{2+}$ in the presence of reverse micelles of Tween-85 is less than that of $[\text{Fe(phen)}_3]^{2+}$ under the same conditions inspite of the well known higher stability of the later complex. This can be explained by the more apolar nature of the 1,10-phenanthroline ligand than the 2,2'-bipyridyl and hence greater interaction with micelle of the Tween-85, higher binding constant.

Experimental

All solutions were prepared in doubly distilled water and chemicals used were of analytical reagent grade. Cyclohexane (Qualigens) was distilled before use. A 0.02 mol dm^{-3} solution of each tris(2,2'-bipyridyl)iron(II) and tris(1,10-phenanthroline)iron(II) were prepared by mixing stoichiometric amounts of ferrous ammonium sulphate (AnalaR, BDH) and 2,2'-bipyridyl (E. Merck) or 1,10-phenanthroline (E. Merck) solids in water. The pH of the solution was measured using a digital pH meter with an accuracy of 0.01 pH (Toshniwal, CL-46) and was found to be constant at 6.97 during the course of the reaction. Preparation of reverse micellar system and initiation of the reaction : Sigma-Aldrich sample of Tween-85 (poly oxyethylene (20) sorbitane trioleate) was used without further purification. A 0.01 mol dm^{-3} solution of Tween-85 was prepared by dissolving the required amount in cyclohexane. A known volume of (25–30 µL) of the complex was injected in the surfactant solution (10 ml) using a micro syringe. The mixture was shaken sufficiently to obtain a transparent and homogeneous solution that could be regarded as a reverse micelle[14,15]. The molar ratio, W, was varied in the range of 6.94 to 24.3. The reaction was monitored by measuring the absorbances of each of the complexes at 510 nm using Milton-Roy (Spectronic 1201) spectrophotometer with thermostated cell compartment. Pseudo-first order rate constants were obtained from slopes of log (absorbance) versus time plots. The kinetic data are the averages from triplicate runs with reproducibility of ±5%.

Determination of CMC : The authors determined the CMC of the reverse micelles of Tween-85-cyclohexane under the experimental conditions employed by adopting the procedure of Bhattacharya et al.[10]. The absorbance of the dye surfanine T at different concentrations of Tween-85-cyclohexane was measured at constant [Surfanine T] and W. From the intersection of the lines in the plot of absorbance (at 520 nm) versus [Tween-85], the CMC value was found to be 4.7×10^{-3} and it did not change with change in W.

Acknowledgement

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