

## Notes

### TX-100 reverse micelles as microreactors for alkaline hydrolysis of tris(2,2'-bipyridine) iron(II) complex

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Alkaline hydrolysis reaction of tris(2,2'-bipyridine)iron(II) complex with sodium hydroxide has been investigated in TX-100 reverse micelles using cyclohexane/water with hexanol as cosurfactant by spectrophotometric method. In reverse micellar medium, the reaction is first order with respect to each reactant. The effects of water pool size and surfactant concentration are investigated. The rate decreases as the [water]/[surfactant] molar ratio ( $W$ ) increases, but increases as surfactant concentration increases. Effect of both  $W$  and surfactant concentration are prominent at lower regions of  $W$ . The results are explained by considering the occurrence of two reactions at a measurable speed in reverse micellar medium, i.e., aqueous dissociation and alkaline hydrolysis reactions. Both these reactions in the reverse micellar medium are catalyzed. In the water pool, properties of water are such that at lower  $W$ , dissociation reaction is favorable, whereas at higher  $W$ , hydrolysis is favorable. Experimental results also conclude that dissociation occurs mainly at the interface and hydrolysis in the cavity of the water pool.

**Keywords:** Hydrolysis, Alkaline hydrolysis, Surfactants, Reverse micelles, Microreactors, Dissociation, Water pools, Micropolarity

Studies on different processes under characteristic conditions, known as restricted geometry conditions, that is, under conditions in which a given reactant or different reactants are forced to remain bound at the surface of some substrate, are of current interest. The restricted geometry conditions include phenomena such as heterogeneous catalysis<sup>1</sup>, enzymatic catalysis<sup>2,3</sup>, reactivity in micellar systems<sup>4</sup> and microemulsions<sup>5</sup>, trapping of substrates by polyelectrolyte<sup>6,7</sup>, conformational changes of DNA induced by the binding of solutes<sup>8</sup>, etc. Among the variety of restricted geometry conditions, reverse micelles have been assessed as a unique and versatile reaction medium for different kind of chemical reactions<sup>9-12</sup>. Usually three different compartments are available for the confinement of reactants in reverse micelles:

(i) the internal aqueous core or water pool, (ii) the micellar interface formed by a monolayer of surfactant molecules with their polar head groups oriented towards the water pool, and, (iii) the external bulk organic phase<sup>13-15</sup>. However, the key structural parameter of a reverse micelle is the [water]/[surfactant] molar ratio ( $W$ ), which determines the size, shape as well as the unique physicochemical properties of the entrapped water<sup>16-18</sup>. These nanoscopic water pools have proven useful as minireactors for various types of reactions.

Although several surfactants have been investigated, very few studies on reverse micelles have focused on systems utilizing the surfactant, TX-100. Kumar & Balasubramaniam<sup>19-21</sup> first characterized the reverse micelles of TX-100, *n*-hexanol and water in cyclohexane. Qi & Ma<sup>22</sup> have studied the microenvironment of this system by using absorption probes and established that three types of water are present in water pools. At low values of water-to-surfactant molar ratio ( $W$ ), water is utilised in solvation of ethylene oxide groups at the interface and is termed as primary bound water. With progressive increase in  $W$ , water is also involved in secondary hydration and is called secondary bound water. Free water in the water pool begins to appear at  $W > 5.3$  and with further increase in  $W$ , volume of free water increases. In reverse micellar medium, the properties of the entrapped water (water pool), e.g., micro-polarity, micro-viscosity, H-bonding potential, water activity, etc. are somewhat different from the bulk phase of water<sup>23-25</sup>. It is of interest to study how kinetics is modified with these changes. Kinetics of chemical reactions has seldom been studied in TX-100 reverse micellar systems<sup>26-28</sup>. Herein, we have studied the alkaline hydrolysis of tris(2,2'-bipyridine)iron (II) complex in TX-100 reverse micellar medium.

### Experimental

All reagents from Merck, India were used without further purification. Conductivity water from Millipore Synergy (India) with conductivity 2–4  $\mu\text{S cm}^{-1}$  at 303 K was used throughout the experiment. Fe(II) complex was synthesized and purified following the conventional method<sup>29</sup>. Freshly prepared NaOH solution was standardized against standard oxalic acid

solution for day to day experiments. Quartz cells (1.0 cm path length) from Hellma were used. All kinetic measurements were made using a thermostated Agilent 8453E Diode Array UV-visible spectrophotometer.

TX-100 reverse micelles were prepared following the procedure used by Qi & Ma<sup>22</sup>. TX-100 was first mixed with hexanol in a fixed ratio of 4:1 v/v to form a blend; which was then dissolved in a calculated volume of cyclohexane to form a clear solution. Adequate amount of aqueous solution of sodium hydroxide was then pipetted out into the clear TX-100 solution and shaken thoroughly. Finally, the aqueous solution of Fe complex was added with vigorous shaking to obtain a transparent and apparently homogeneous solution, which was considered to be the reverse micellar medium<sup>30</sup>. The reaction was initiated as soon as the Fe complex was added. Solutions of different surfactant concentrations were prepared by varying the amount of TX-100, maintaining the ratio of TX-100 to hexanol at 4:1 (v/v). At a particular surfactant concentration, W (water/surfactant) was varied by varying the total aqueous (Fe complex and NaOH) part, keeping the volume of hexanol constant. The concentration of complex and NaOH inside the water pool, i.e., the local concentration, was calculated considering the total volume of the added aqueous part. Concentrations of reactants were so calculated because they exist only in the water pool and not in the oil phase.

Kinetics of the reaction between Fe(II) complex and sodium hydroxide was studied spectrophotometrically under pseudo-first order condition with excess amount of hydroxide at 303 K. Before each kinetic run, all solutions were thermostated at the desired temperature. All experiments were performed by mixing the required volumes of thermostated reactants with proper dilution to the required volume in the quartz cell (1.0 cm path length). The reaction was initiated by adding requisite amount of Fe(II) complex to the reverse micellar solution. Absorbance of Fe(II) complex at 520 nm, decreased gradually with the progress of the reaction. Thus, the reaction was followed by measuring the absorbance change of Fe(II) complex at 520 nm<sup>31</sup>. Observed pseudo-first order rate constants ( $k_{obs}$ ) and their standard deviations were obtained by first order decay curve fitting using UV-vis Chemstation software

(G1115AA). The results were reproducible within  $\pm 3\%$  in replicate kinetic runs.

## Results and discussion

Alkaline hydrolysis reaction between Fe(II) complex  $[\text{Fe}(\text{bipyridine})_3]^{2+}$  and NaOH in aqueous medium follows overall second order kinetics; first order each in  $[\text{Fe}(\text{II})]$  and  $[\text{HO}^-]$ . The well established mechanism of this reaction has been shown in earlier reports<sup>32,33</sup>. Observed pseudo-first-order rate constant ( $k_{obs}$ ) of the reaction versus the initial sodium hydroxide concentration in aqueous medium maintaining all other variants constant, is shown in Fig. 1. Linear plot of  $k_{obs}$  versus  $[\text{OH}]_0$  shows a positive slope and a small positive intercept. Positive intercept in the linear plot of  $k_{obs}$  versus  $[\text{OH}]_0$  indicates that there are two paths that occur simultaneously; one is alkali dependent or alkaline hydrolysis and the other is alkali independent or aqueous dissociation path. The reported mechanism of this reaction is shown in Scheme 1.

Overall rate of the reaction is as follows:

$$\text{Rate} = -\frac{d[\text{Fe}(2,2'\text{-bpy})_3^{2+}]}{dt} = \{k_0 + k_1 K_1 [\text{OH}^-] + k_2 K_1 K_2 [\text{OH}^-]^2\} [\text{Fe}(2,2'\text{-bpy})_3^{2+}]$$

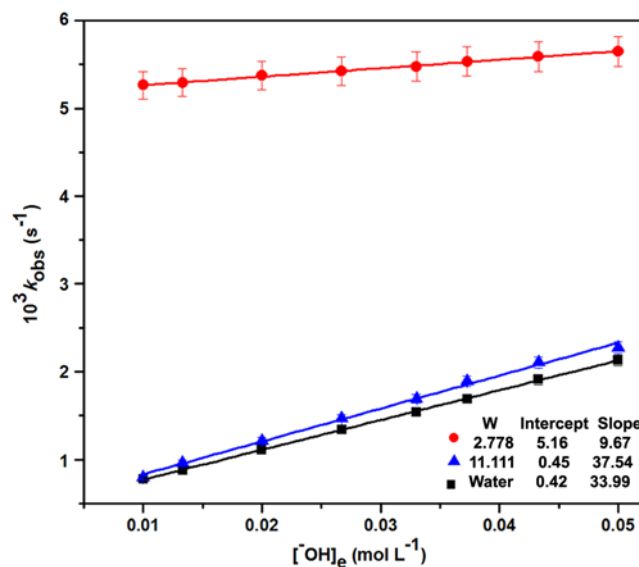
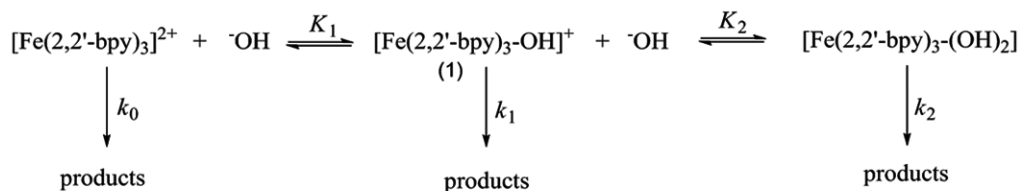


Fig. 1 – Variation of  $k_{obs}$  with NaOH at different sizes of water pools (W) in TX-100/hexanol/cyclohexane/water reverse micellar medium and in water.  $\{[\text{Fe}(\text{II})]_e = 0.56 \text{ mM}, [\text{TX-100}]_0 = 0.2 \text{ mol L}^{-1}$  at 303 K}.



Mechanism of the reaction in aqueous medium

Scheme 1

When  $[\text{OH}]_0 \gg [\text{Fe}(2,2'\text{-bpy})_3]_0$ , then  $[\text{OH}]_0$  remains almost constant during reaction.

Hence,

$$\text{Rate} = -\frac{d[\text{Fe}(2,2'\text{-bpy})_3^{2+}]}{dt} = k_{\text{obs}} \left[ \text{Fe}(2,2'\text{-bpy})_3^{2+} \right]$$

$$\text{where, } k_{\text{obs}} = k_0 + k_1 K_1 [\text{OH}^-] + k_2 K_1 K_2 [\text{OH}^-]^2$$

At lower concentrations of  $[\text{OH}]_0$ ,  $k_{\text{obs}} \approx k_0 + k_1 K_1 [\text{OH}]_0$ , (neglecting higher terms in the rate equation) where  $k_0$  is the intercept and  $k_1 K_1$  is the slope of the linear plot of  $k_{\text{obs}}$  versus  $[\text{OH}]_0$ .

Effects of both the Fe(II) complex and hydroxide ion on rate have also been studied in TX-100/1-hexanol/water reverse micelles in cyclohexane medium, and results reveal the same conclusion, that the order of the reaction is one with respect to each of the Fe(II) complex and hydroxide ion in TX-100 reverse micellar medium. Only the rate increases significantly as compared to that in aqueous medium. Being ionic in nature, both the reactants prefer to stay and react inside the water pool of reverse micelle instead of in the hydrophobic bulk environment. Hence, unlike in the aqueous medium, the reactants are locally concentrated in very tiny nanometer-sized cavities known as water pools in the reverse micellar medium. Increase in reactant concentration surely is the prime reason for rate enhancement. However, to know the additional effects of special properties of reverse micelles, local concentration of reactants were used. In aqueous medium, local concentration of reactants are same with their overall concentration due to the nonexistence of microheterogeneity in the medium.  $k_{\text{obs}}$  versus  $[\text{OH}]_e$  plot at a fixed value of  $W$  is shown in Fig. 1. It is clear from Fig. 1 that for a particular concentration of  $\text{OH}^-$ , rate is highly increased even when the effect of local concentration of  $\text{OH}^-$  is omitted. This increment is due to the special properties of water pools and to examine this we

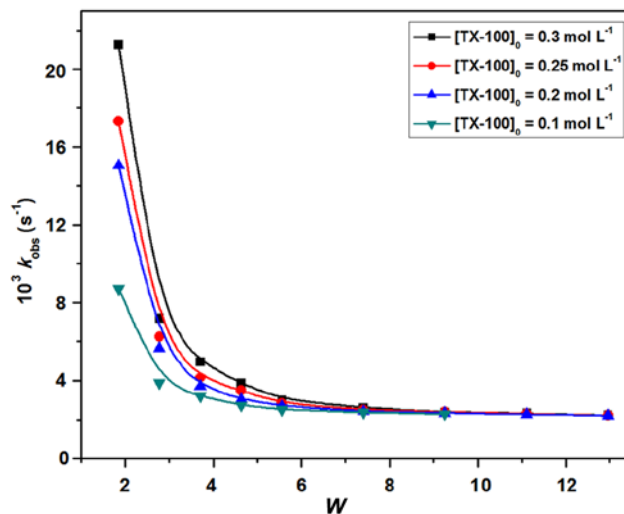


Fig. 2 – Variation of  $k_{\text{obs}}$  with the size of water pools ( $W$ ) at different concentration of TX-100 in TX-100/hexanol/cyclohexane/water reverse micellar medium.  $\{[\text{Fe(II)}]_e = 0.56 \text{ mM}, [\text{HO}^-]_e = 0.05 \text{ mol L}^{-1} \text{ at } 303 \text{ K}\}$ .

varied the concentration of TX-100 and  $W$ . Also, the linearity of this plot with a positive slope and intercept indicates the presence of both hydroxide dependent and an independent path.

Kinetics of alkaline hydrolysis of Fe (II) complex has been studied in a series of experiments in which the size of water pools has been varied ( $W = 1.852\text{--}12.963$ ), keeping the concentration of the surfactant TX-100 constant. Experimental results show that the reaction is catalyzed at all values of  $W$  in reverse micellar medium compared to that in aqueous medium with a continuous exponential decrease in the values of  $k_{\text{obs}}$  upon increasing the size of water pools (Fig. 2).

Owing to the ionic nature of reactants, the reactant molecules cannot stay in either the continuous oil phase or in the hydrophobic moiety of reverse micelles; rather they prefer to stay solvated inside the water pools. These increases the local concentration of the reactants inside the water pools. As a result, the rate of the reaction is much higher in the reverse micellar medium as compared to that in the aqueous medium for a similar concentration of reactants.

However, with increase in  $W$ , i.e., with increase in the size of the water pools, rate of the reaction decreases.

In spite of increasing local concentration of reactants, the nanocavity of water pools possesses several properties which are different from bulk water; such as decreased micropolarity, increased microviscosity, etc. Polarity of the entrapped water in water pools of TX-100 reverse micelles lies in between the polarity of isopropyl alcohol and methanol<sup>22</sup>. As the reaction under study takes place between two charged species, we expect an increased ion pairing between the reactants and hence an increment in rate in reverse micelles of low polarity. Moreover, in our previous study, the same reaction has been reported to be catalyzed in different alcohol-water systems<sup>31</sup>. However, as the water pool becomes larger, the confined water behaves like bulk water of higher polarity, thereby decreasing the rate, although the rate is not uniformly decreased at all values of  $W$ . Initially, at lower  $W$ , the rate decreases sharply then quite gradually, featuring an exponential decay of  $k_{obs}$  with  $W$ . This is because of the large difference in the properties of water at different  $W$ . Water present at lower  $W$  is mainly primary or secondary bound water and is used for the solvation of ethylene oxide groups of TX-100 molecules. When  $W$  is very small, there is no free water and only bound water and at  $W$  value of 5.3, free water is introduced into the water pool<sup>26</sup>. With further increase in  $W$ , the amount of free water or the size of water pool increases and starts behaving like bulk water. Nucleophilicity of this bound water is very high whereas, free water is mostly bulk like<sup>34,35</sup>. Sarkar *et al.*<sup>26</sup> studied the dissociation of the same complex and reported that the rate is very high at lower  $W$  and decreases with increase in  $W$ . They concluded that high nucleophilicity of this bound water is accountable for rate enhancement. As also shown in the present study, dissociation rate (obtained from the intercept of Fig. 1) of the complex is negligible in aqueous medium, but increases abruptly at lower  $W$  and with increase in  $W$ , it decreases gradually.

In presence of alkali, dissociation is not the only reaction; we have to consider the hydrolysis reaction also. Alkaline hydrolysis rate (obtained from the slope of Fig. 1) at lower  $W$ , is quite low, even less than in aqueous medium. At lower  $W$ , both the bound water and  $[HO^-]$  act as nucleophiles. Hence, it is likely that there is competition between the two. The experimental result confirms that bound water

prevails over the hydroxide ion. Concentration of  $[HO^-]$  is also negligible in comparison to bound water molecules. Hence, comparing both dissociation and hydrolysis reaction, it may be concluded that  $k_{obs}$  is basically the dissociation rate at lower  $W$ . This situation is quite different from that in CTAB reverse micellar medium<sup>36</sup>. In CTAB reverse micelles; even at lower  $W$ , hydrolysis rate constant contributes the most to  $k_{obs}$  and is always higher than aqueous medium. Hence, either the involvement of surfactant head group on increasing the nucleophilicity of bound water molecules or its involvement in the dissociation process increases the dissociation rate. With increase in  $W$ , free water is introduced into the water pool and increases the hydrolysis rate. Hence, at higher  $W$ , alkaline hydrolysis is the main reaction. With further increase in  $W$ , free water of water pool behaves like bulk water of higher polarity and the ion pairing between the reactants and also the hydrolysis rate decreases.

Alkaline hydrolysis of Fe(II) complex in TX-100 reverse micelles has also been studied at varying TX-100 concentration in the range of 0.1- 0.3 mol L<sup>-1</sup> for fixed values of  $W$  (Fig. 3). From this figure, it is clear that  $k_{obs}$  is catalyzed by the surfactant concentration and at a low value of  $W$  ( $W = 1.852$ ), surfactant concentration has a significant effect on the rate. Increase in TX-100 concentration at fixed  $W$  increases the micellar concentration and hence the area of the interface without changing the micellar composition or other properties. Moreover, at this

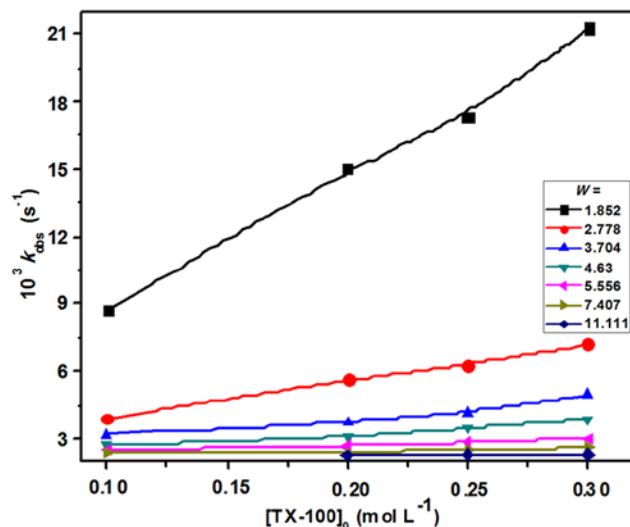


Fig. 3 – Variation of  $k_{obs}$  with TX-100 concentration at different  $W$  in TX-100/hexanol/cyclohexane/water reverse micellar medium.  $\{[Fe(II)]_e = 0.56 \text{ mM}, [HO^-]_e = 0.05 \text{ mol L}^{-1} \text{ at } 303 \text{ K}\}$ .

low  $W$ ,  $k_{obs}$  is solely guided by the dissociation rate and with increase in interfacial area, the fraction of high nucleophilic bound water increases. Hence, increase in rate with TX-100 concentration shows that at this low value of  $W$ , the reaction is taking place at the micellar interface. In fact, at such a low value of  $W$ , the size of the water pool is so small that the reaction position available for reaction is only the interface of the reverse micelles.

At a moderate value of  $W$  ( $W = 5.556$ ), the catalytic effect of [TX-100] is very less. Both the dissociation and alkaline hydrolysis reactions are taking place at this  $W$ . Also, both bound and free waters are present at this  $W$ . We know that bound water increases the dissociation rate. While the binding of Fe(II) complex by the interface is very small<sup>26</sup> and this transfers the complex from the interface to the water pool, some amount of complex is still there at the interface which contributes to the process of dissociation. Also, the nucleophile for hydrolysis reaction ( $\text{OH}^-$ ) being ionic, prefers to stay in the water pool rather than at the interface. Hence, it may be concluded that dissociation reaction is taking place mainly at the interface and is catalyzed by the surfactant, whereas the hydrolysis reaction occurs in the water pool and is independent of surfactant concentration. As a result,  $k_{obs}$  increases slightly with surfactant concentration at this  $W$ .

When  $W$  is increased from moderate to high values, dissociation reaction becomes negligible and  $k_{obs}$  is solely guided by the hydrolysis reaction. Since both the reactants preferably stay in the water pool, hydrolysis reaction is taking place mainly in the water pool and is independent of surfactant concentration. This is further supported by the fact that in CTAB reverse micellar medium, the reaction position for hydrolysis reaction is reported to be in the cavity of water pool<sup>36</sup>.

In the present study, alkaline hydrolysis of iron(II) complex in aqueous and TX-100 reverse micellar media follows overall second-order rate law, first order each in Fe(II) complex and  $[\text{OH}^-]$ . In TX-100 reverse micellar medium, two reactions occur simultaneously at measurable speed. One is alkaline hydrolysis and the other one is aqueous dissociation. Both the reactions are catalyzed in reverse micellar medium.  $k_{obs}$  decreases with  $W$  and increases with surfactant concentration. At lower  $W$ , dissociation is the leading reaction, whereas at higher  $W$ , hydrolysis is the leading reaction. In the water pool, all the water

present is bound water. High nucleophilicity of this bound water helps the water molecules to compete over  $[\text{OH}^-]$  and increases the dissociation rate. At moderate  $W$ , water in the water pool approaches bulk water and free water enters into the water pool. This free water loses its nucleophilicity, but its lower micropolarity and confinement of both the complex and  $[\text{HO}^-]$  into this tiny sized free water, increases the hydrolysis rate. With further increase in  $W$ , the size of the water pool becomes larger, hence the confined water behaves mostly like bulk water of higher polarity and thereby both the rates are decreased. Increased effect of surfactant concentration on rate is prominent at lower  $W$  and is almost independent at higher  $W$ . Increase in surfactant concentration increases the interfacial area of reverse micelles. This indicates that at lower  $W$  when dissociation is the dominating reaction, the reaction occurs at the interface of reverse micelles. Independence of rate on surfactant concentration at higher  $W$ , when hydrolysis is the main reaction, indicates that hydrolysis reaction occurs inside the cavity of the water pool.

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