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Kinetics of oxidation of $[Fe(phen)_3]^{+2}$ by persulphate: catalysis in the water pools of CTAB reverse micelles

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The kinetics of oxidation of $[Fe(phen)_3]^{2+}$ by persulphate was carried out in water pools of CTAB/chloroform/hexane reverse micelles. The reaction obeys first-order kinetics with respect to each of the reactants. In the reverse micellar medium, the reaction was found to be around fifty times faster compared to aqueous medium under identical experimental conditions. The pronounced acceleration is accounted for by the lower micropolarity of the reverse micelles, which facilitates the ion-pair formation between oppositely charged ions. The effect of variation of *W* {*W* = $[H_2O]$/ [CTAB]} at constant [CTAB] and variation of [CTAB] at fixed *W* was studied. At a fixed concentration of CTAB, the second-order rate constant of the reaction increases with increasing value of *W* and is independent of the concentration of CTAB at constant *W.*

Keywords: Kinetics, Oxidation, Ferroin, Persulphate, Reverse micelles, Water pools**.**

INTRODUCTION

The reverse micelles formed spontaneously in organic solvents are thermodynamically stable and have been characterized by various techniques. The solubilized water present in the polar cavity of reverse micelles is called "water pool". This water pool has unique properties like lower dielectric constant, i.e. micropolarity, higher viscosity, lower thermodynamic activity of water, higher ionic strength (in the case of reverse micelles made of ionic surfactants) and altered nucleophilicity compared to water in the conventional aqueous media [1-5]. These anomalous properties of the water pool are dependent on the *W* parameter, *W* = ($[H_2O]$/[surfactant]) and as the value of *W* increases, the properties approach that of ordinary water. Since the water pool has different properties compared to ordinary water, the rates of reactions and mechanisms can be expected to be different [6-10]. Another advantage of reverse micelles is that they are good solvents for both hydrophobic and hydrophilic reactants and therefore, appear to be useful media for studying reactions involving different types of reactants [11,12].

Earlier we have reported reactions taking place in the presence of reverse micelles and have given a quantitative assessment for the change in special properties with change in *W* and the observed kinetic results were quantitatively explained using Berezin pseudo phase model [13-15]. It has been reported that the lower dielectric constant of the water pool enhances the ion-pair formation and reactions involving formation of ion pairs between reactants may provide a basis for understanding the nature of bound water in the reverse micelles [16,17]. With this objective, oxidation of $[Fe(phen)_3]^{2+}$ by persulphate was chosen, which is very well known in aqueous and in various solvent mixtures [18,19].

EXPERIMENTAL

All solutions were prepared in double distilled water. Chemicals used were of analytical grade. Tris (1,10-phenanthroline) iron(II) complex (0.02 mol dm^{-3}) was prepared by mixing stoichiometric amounts (1:3) of ferrous ammonium sulphate (Merck, India) and 1,10-phenanthroline (Merck, India) in water. A stock solution of sodium persulphate (0.2 mol dm^{-3}) was freshly prepared by using sodium persulphate (Merck, India)

Chloroform and hexane were double distilled before use. CTAB (cetyltrimethylammonium bromide) purchased from Sigma was used without further purification. Reverse micellar solutions of CTAB (0.1 mol dm^{-3}, 0.2 mol dm^{-3} and 0.3 mol dm^{-3}) were prepared by dissolving requisite amounts of CTAB in chloroform-hexane (3:2 v/v) mixtures.

Preparation of reverse micellar medium and initiation of the reaction

$[Fe(phen)_3]^{2+}$ (0.02 ml, 0.02 mol dm^{-3}) was injected into 10 ml of 0.1 mol dm^{-3} CTAB solution using a micropipette. Persulphate solution (0.02 ml, 0.2 mol dm^{-3}) was then added to initiate the reaction.

The reaction mixture was shaken vigorously to obtain a transparent and homogeneous solution that

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can be regarded as a reverse micellar system. The molar ratio of [water] to [CTAB], i.e. *W*, was varied in the range from 2.22 to 16.6.

Kinetic measurement

The kinetic study of the oxidation of [Fe(phen)$_3$]$^{2+}$ by persulphate was carried out using a Shimadzu UV-1800 double beam spectrophotometer by measuring the decrease in absorbance of [Fe(phen)$_3$]$^{2+}$ at a wavelength of 510 nm. The reaction was carried out under pseudo first-order conditions, [$S_2O_8^{2-}$] >> [[Fe(phen)$_3$]$^{2+}$]. The concentration of [Fe(phen)$_3$]$^{2+}$ was 4×10^{-5} mol dm^{-3}. Persulphate was varied from 4.0×10^{-4} to 36.0×10^{-4} mol dm^{-3}. In all cases good linear plots were obtained for log (absorbance) *versus* time indicating first-order kinetics with respect to [Fe(phen)$_3$]$^{2+}$. The kinetic data are the averages from duplicate runs with reproducibility better than ±3%.

Calculation of effective concentration

When reactants are in the water pool they are confined to a small volume leading to a concentration effect. In the case of unimolecular reactions taking place in the water pools of the reverse micelles, the measured first-order rate constants can be compared directly with the rate constant of a reaction in aqueous medium. However, in the case of bimolecular reactions taking place in the water pools of the reverse micelles, the calculation of second-order rate constant involves the consideration of the effective concentration of the reactants. The effective concentration of a reactant in the water pool is calculated by dividing the overall concentration by the volume fraction of solubilized water. Volume fraction, *f*, is the volume of aqueous phase in the water pool divided by the total volume of the solution [20]. The volume fractions lie in the range from 4.00 to 36.0×10^{-3} for 0.1 mol dm^{-3} CTAB. For example, if the concentration of CTAB is 0.1 mol dm^{-3} and $W = 3.33$, then $f = (0.06/10.0)$. If $[S_2O_8^{2-}]_{\text{overall}} = 4.0\times10^{-4}$, then $[S_2O_8^{2-}]_{\text{effective}} = [S_2O_8^{2-}]_{\text{overall}}/f\} = \{4.0\times10^{-4}/0.006\} = 0.066$ mol dm^{-3}. From now onwards, the subscript 'o' is used to represent overall concentration and subscript 'e' to represent effective concentrations.

RESULTS AND DISCUSSION

The kinetics of the reaction was investigated in CTAB reverse micelles under pseudo first-order conditions, varying the overall concentration of persulphate in the range from 4.0×10^{-4} to 36.0×10^{-4} mol dm^{-3} and keeping the {Fe(phen)$_3$}$^{2+}$ complex at 4.0×10^{-5} mol dm^{-3}, thus isolating the complex. The reaction obeys first-order kinetics with respect to {Fe(phen)$_3$}$^{2+}$ as shown by the linear plots of log (A_t) *versus* time (Fig. 1). A plot of pseudo first-order rate constant, k' *versus* $[S_2O_8^{2-}]_o$ was found to be linear passing through the origin indicating first-order kinetics with respect to $S_2O_8^{2-}$ (Fig. 2). Based on the observed results in the CTAB reverse micellar medium, the following mechanism (Scheme 1) is proposed in CTAB reverse micelles:

$$[\mathrm{Fe(phen)_3}]^{2+} + S_2O_8^{2-} \rightleftharpoons [\mathrm{Fe(phen)_3}^{2+}, S_2O_8^{2-}]$$

$$[\mathrm{Fe(phen)_3}^{2+}, S_2O_8^{2-}] \xrightarrow{\text{slow}} [\mathrm{Fe(phen)_3}]^{3+} + 2\,SO_4^{2-}$$

Scheme 1.

The reaction was markedly catalyzed in the presence of CTAB reverse micelles and the second-order rate constant was found to be greater than that in aqueous medium by around fifty times under identical experimental conditions (Table 1).

Table 1. Comparison of rate constants in the aqueous medium and in the presence of reverse micelles (0.1 mol dm^{-3} CTAB) at the same ionic strength (μ). $[\mathrm{Fe(phen)_3}]_o^{2+} = 4\times10^{-5}$ mol dm^{-3}; $[S_2O_8^{2-}]_o = 4\times10^{-4}$ mol dm^{-3}; T = 304 K

μ (mol dm^{-3})	$k_{2\text{aq.med}}\times10^3$ (mol^{-1} dm^3 sec^{-1})	$k_{2(\text{rev mic})}\times10^3$ (mol^{-1} dm^3 sec^{-1})
3.33	7.06	52.4
12.5	0.621	28.0

The acceleration in reverse micelles is due to the fact that the water pool of a reverse micelle is distinctly less polar [21,22] than the aqueous medium and favours ion-pair formation of the complex with persulphate and facilitates the reaction between opposite charges.

Effect of variation of W on rate

The second-order rate constant increases with increasing *W* at constant CTAB concentration and is independent of CTAB concentration at constant *W* (Table 2). At constant CTAB concentration, an increase in *W* results in an increase in dielectric constant and a decrease in ionic strength of the medium. These two have opposing effects on the reaction. If there is only the effect of the dielectric constant, then the rate should decrease with *W*. If the ionic strength effect alone exists, there should be an increase in rate with increase in *W* since low ionic strength favours cation-anion reaction. Therefore, the rate constant is a resultant effect of these two factors. The increase in second-order rate constant k_2 with *W* implies that the effect of decrease in ionic strength on the rate is more pronounced than the increase in dielectric constant of the medium. Therefore, the increase in the rate of reaction with *W* is due to decrease in ionic strength. Hence, the effect of *W* was assessed in terms of ionic strength relating the rate constant k_2.

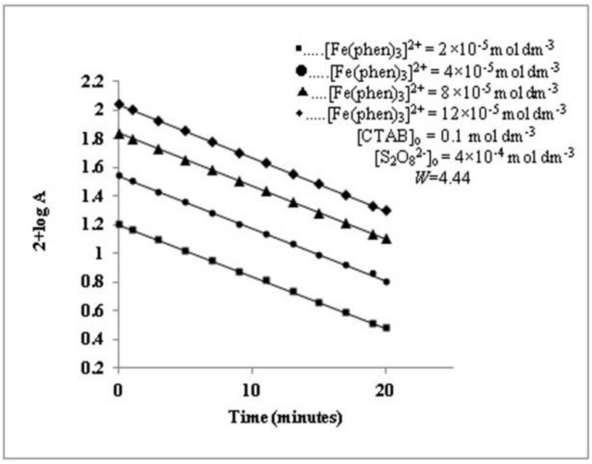

Fig. 1. Plots of log (A_t) *vs* time at different concentrations of $[Fe(phen)_3]^{2+}$; [CTAB] = 0.1 mol dm^{-3}, $[S_2O_8{}^{2-}] = 4.0\times10^{-4}$ mol dm^{-3} *W*= 4.44; T = 304 ± 0.1 K. $[Fe(phen)_3]^{2+}$ = 2.0×10^{-5} mol dm^{-3}; $[Fe(phen)_3]^{2+}$ = 4.0×10^{-5} mol dm^{-3}; $[Fe(phen)_3]^{2+}$ = 8.0×10^{-5} mol dm^{-3}; $[Fe(phen)_3]^{2+}$ =12.0×10^{-5} mol dm^{-3}

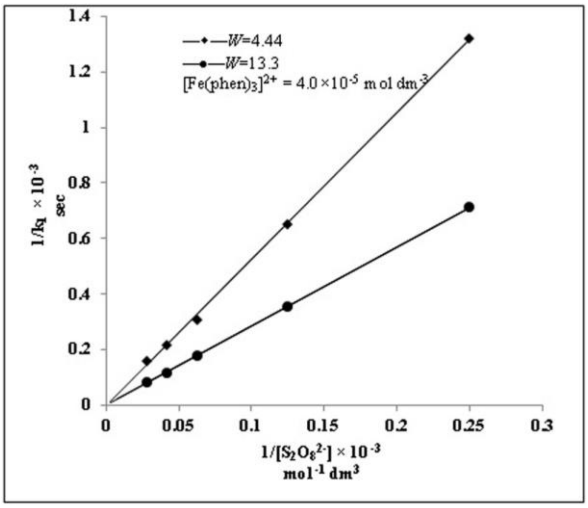

Fig. 2. Plots of $1/k_2$ *vs* $1/[S_2O_8^{2-}]$; $[Fe(phen)_3]^{2+}$ = 4.0×10^{-5} mol dm^{-3}; [CTAB] = 0.1 mol dm^{-3}; T = 304 ±0.1 K; *W*=4.44, *W*=13.3.

The ionic strength, μ, at each *W* was equated to the effective concentration of bromide ion $[Br^-]_e$ in the water pool.

$$\log k_2 \quad = \log k_2^o + \frac{2\,A\,Z_A\,Z_B\,\sqrt{\mu}}{1+\sqrt{\mu}} + B'\mu \,\ldots\ldots\ldots (1)$$

$$\log k_2 \quad = \log k_2^o - \frac{4\,\sqrt{\mu}}{1+\sqrt{\mu}} + B'[Br^-]_e \,\ldots\ldots\ldots\ldots (2)$$

where A is equal to 0.503, Z_A & Z_B are +2 and -2, the charges of the respective ions. B' is interaction parameter. In the present case, the specific interactions are between the positively charged micellar surface, CTA^+ and $S_2O_8{}^{2-}$ & $[Fe(phen)_3]^{2+}$ and Br^-, represented by the specific interaction terms $B_{CTA}{}^{+}{}_{,\ S2O82-}$ and $B_{[Fe(Phen)3]}{}^{2+}{}_{Br-,}$ respectively.

The effect of ionic strength on the rate of reaction can be examined using Guggenheim equation [23]. In the case of ionic surfactants, the value of *W* controls the concentration of polar heads of surfactants (CTA^+) and its counter ions (Br^-) in the aqueous water pool [24].

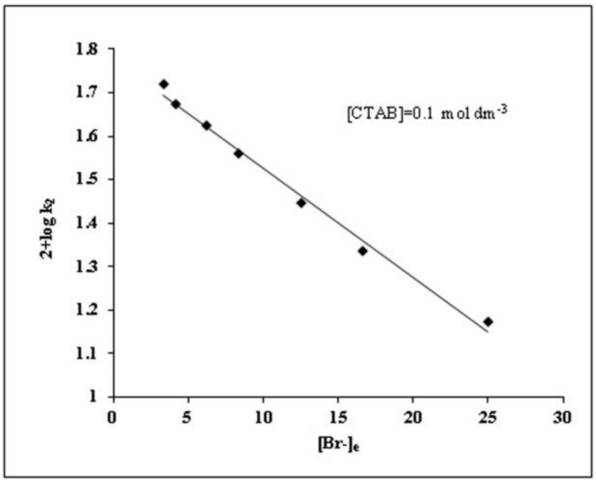

Fig. 3. Plots of log k_2 *vs* $[Br^-]_e$ at different values of *W*; $[Fe(phen)_3]^{2+}$ = 4.0×10^{-5} mol dm^{-3}; $[S_2O_8{}^{2-}]$ = 4.0×10^{-4} mol dm^{-3}; [CTAB] = 0.1 mol dm^{-3}, T= 304 ± 0.1 K.

At high ionic strength the variation of the second term in Eqn. (2) with μ $\{=[Br^-]_e\}$ can be neglected in comparison with the third term. If this is true, plots of log k_2 *vs*. μ $\{=[Br^-]_e\}$ should be linear. Interestingly, the plot of log k_2 *versus* μ $\{=[Br^-]_e\}$ was found to be linear for all concentrations of CTAB (Fig. 3) and the interaction parameter B' was obtained from the slope of the plot. The value of B' was found to be -0.0252, -0.0256, and -0.0254 for 0.1, 0.2 and 0.3 mol dm^{-3} CTAB, respectively.

Effect of variation of [CTAB] on rate

The effect of variation of the concentration of CTAB on the rate of reaction was studied and Table 2 shows that the variation of the concentration of CTAB (0.1-0.3 mol dm^{-3}) at all *W* values does not have any significant effect on the rate. Since the increase in CTAB concentration at constant *W* increases the interfacial area, this shows that the reaction is taking place mainly in the water pool and not on the micellar surface, so there is no significant change in rate with the change in CTAB concentration. If reaction occured at the interface of the reverse micelle, the rate constant would change with variation of CTAB concentration.

Table 2. Effect of *W* and [CTAB] on rate constant (k$_2$). [Fe(phen)$_3$]$_o^{2+}$ = 4×10^{-5} mol dm^{-3}; [S$_2$O$_8^{2-}$]$_o$ = 4×10^{-4} mol dm^{-3}; T = 304 K

CTAB (mol dm^{-3})	*W*	μ{=[Br$^-$]$_e$	k$_1$×10^3(s^{-1})	k$_2$×10^3 (mol $^{-1}$dm^3 s $^{-1}$)
0.1	2.22	25.0	1.49	14.9
	3.33	16.6	1.45	21.6
	4.44	12.5	1.40	28.0
	6.66	8.33	1.20	36.3
	8.88	6.25	1.05	42.0
	13.3	4.16	0.756	47.2
	16.6	3.33	0.682	52.4
0.2	2.22	25.0	0.735	14.7
	3.33	16.6	0.725	21.9
	4.44	12.5	0.706	28.2
	6.66	8.33	0.616	38.5
	8.88	6.25	0.529	42.3
	13.3	4.16	0.436	47.9
	16.6	3.33	0.343	51.9
0.3	2.22	25.0	0.481	14.5
	3.33	16.6	0.482	21.9
	4.44	12.5	0.461	27.7
	6.66	8.33	0.403	36.6
	8.88	6.25	0.351	42.1
	13.3	4.16	0.258	46.9
	16.6	3.33	0.227	51.5

CONCLUSIONS

1. The reaction between [Fe(phen)$_3$]$^{2+}$ and S$_2$O$_8^{2-}$ obeys first-order kinetics with respect to each of the reactants in the CTAB reverse micellar medium.

2. The reaction was found to be accelerated fifty times in the presence of CTAB reverse micelles. The significant increase of rate in the CTAB reverse micellar medium is due to the low dielectric constant of the bound water, which favours ion-pair formation of the complex with persulphate ion and facilitates the reaction between opposite charges.

3. The increase in second-order rate constant (k$_2$) of the reaction with *W* was assessed in terms of ionic strength using Guggenheim equation.

4. The second-order rate constant (k$_2$) of the reaction is almost the same at all concentrations of CTAB, indicating that the reaction completely takes place in the water pool.

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