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Research Article

CTAB Reverse Micelles as Catalysts for the Oxidation of Ascorbic Acid by $K_3[Fe(CN)_6]$

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Abstract

The oxidation of ascorbic acid by $K_3[Fe(CN)_6]$ was studied in reverse micellar systems composed of CTAB (Cetyltrimethylammonium bromide), and it was found the observed first order ($k_{1(aq)}$ = 5.2×10^{-5} s^{-1}, $k_{1(rev)}$ = 61.4×10^{-4} s^{-1}) rate constant in reverse micellar medium is around forty times higher compared to aqueous medium under identical conditions. The rate enhancement ($k_{2(aq)}$ = 0.9×10^{-5} mole^{-1}.dm^3.sec^{-1}, $k_{2(rev)}$ = 1.75×10^{-3} mole^{-1}.dm^3.sec^{-1}) is attributed to the large concentration effect and lower dielectric constant in the reverse micelles. The rate of the reaction increases with increase in W = {[H_2O]/[surfactant]} which is explained in terms of ionic strength of the water pool. The effect of surfactant concentration on rate was explained on the basis of Berezin pseudo phase model.

Keywords: Ascorbic acid; [$K_3Fe(CN)_6$]; CTAB (Cetyltrimethylammonium bromide); dielectric constant; reverse micelles.

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1. Introduction

The water droplets solubilized in the reverse micelles forms a water pools and shows different physical properties from those of bulk water. The properties of the solubilised water are dependent on a W = {[H_2O]/[surfactant]} parameter. Examples of physical properties which different from ordinary bulk water are low activity, high nucleophilicity, low dielectric constant and high ionic strength, *etc*. The dielectric constant in the case of cationic surfactant like CTAB (Cetyltrimethylammonium bromide) reverse micelles is nearer to that of methanol at low W values [1]. In the case of anionic surfactant like AOT (Aerosol Orange T) polarity of reverse micelle is between methanol and water [1–3]. The increase in W value leads to increase in micro polarity (or dielectric constant) and reaches that of bulk water [4,5]. In the case of ionic surfactant, W value regulates the concentration of the polar head groups of the surfactants and its counter ion concentrations. Ionic strength in a reverse micelle is the effective concentration of counter ion of the surfactant at a particular W. A variation of W between 4.0 and 16.0 involves changes in ionic strength between 20 to 4 M which also effects rate of reaction. Since all the above mentioned properties of the

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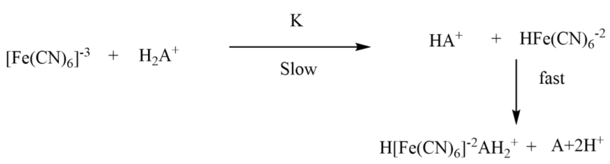
water in the reverse micelles are different in CTAB/$CHCl_3$/Hexane, the rates of reactions are also expected to be different than that of conventional aqueous medium.

In studies of reactions in reverse micelles involving water-soluble reactants, the reactants are confined to the water pool. The volume of the water pool is around 0.01 mL while the total overall volume is 10 mL. Since the reactants are present in the water pool at a microscopic level, the concentration of reactants with respect to water pool is around 100 times more than that compared to whole volume. This leads to a huge concentration effect. Consequently, a concentration scale is defined in order to interpret data in terms of comparisons of reactivity in reverse micelles and bulk solvent media. In the kinetic investigation of reactions take place only in water pool, effective concentrations in water pool is considered instead of overall volume as follows formula {$[Reactant]_{\mathrm{eff}} = [Reactant]_{\mathrm{overall}}/f$}, where, f = volume of water pool / (volume of water pool + volume of solvent) [6,7].

Since reverse micelles involve a water /organic medium interface, they closely resemble the microenvironment of the living cells and can be considered as model system for biological studies / experiments at molecular levels. They can also solubilise all kinds of substrate molecules, hydrophilic, hydrophobic, and amphiphilies. Ascorbic acid is a very important antioxidant in biological systems and undergoes oxidation with reactive oxygen species and transition metals [8–10]. The redox chemistry of ascorbic acid is important in human nutrition [11]. The auto oxidation of ascorbic acid by oxygen in the presence of transition metals (Cu(II)/Fe(III)) leads to loss of ascorbic acid activity [11,12]. The kinetics of Oxidation of ascorbic acid by hexacyanoferrate(III) in aqueous perchloric acid medium have been reported earlier [13] Since reverse micelles are a good medium to mimic biological conditions, we have taken up a kinetic study of the oxidation of ascorbic of ascorbic acid by $K_3[Fe(CN)_6]$ in reverse micellar medium and the results are reported in this paper. We have earlier found that the rates of aquation of tris-2, 2'-bipyridyl iron(II) [14], base hydrolysis of tris-1,10'-phenanthroline iron(II) [15], oxidation of iodide by V(V) [16], and reduction of toluidine blue by ascorbic acid [17] in the presence of CTAB reverse micelles, were also different in the presence of reverse micelles as reported elsewhere.



Scheme 1. Oxidation of ascorbic acid by $K_3[Fe(CN)_6]$

2. Materials and Methods

2.1 Preparation of CTAB Reverse Micelles

CTAB (Cetyltrimethylammonium bromide reverse micellar solution (0.1 M) was prepared by dissolving 3.64 g of CTAB in a mixture of chloroform and hexane (3:2 ratios) for a 100 mL solution. 10 mL of 0.1 M CTAB was taken and then 0.02 mL of $K_3[Fe(CN)_6]$ was added from a stock solution of 0.25 M. The reaction was initiated by adding 0.02 mL of ascorbic acid from a stock solution of 2 M. W was varied by changing the volume of water in the range (0 to 0.1094) to get W value (3.33 to 16.6). The kinetic study of oxidation of oxidation of ascorbic acid by $K_3[Fe(CN)_6]$ was carried out under pseudo-first order conditions, *i.e.*, $[H_2A^+] >> [K_3[Fe(CN)_6]$. The reaction were monitored by measuring the decrease in the absorbance of $[K_3[Fe(CN)_6]$ at 420 nm using a Shimadzu-1800 spectrophotometer. Out of two reactants $K_3[Fe(CN)_6]$ and H_2A, H_2A has no absorbance in range 400-700 nm. The absence of H_2A was confirmed by chloroauric test [18].

3. Results and Discussion

The reaction between $K_3[Fe(CN)_6]$ and H_2A^+ in CTAB/Chloroform/Hexane/Water mixtures follows first order kinetics with respect to $K_3[Fe(CN)_6]$ as observed by the linear plots between log of absorbance {due to $K_3[Fe(CN)_6]$} *vs.* time, under the conditions, {$[HA^-]_o >> K_3[Fe(CN)_6]_o$}. In the present of $K_3[Fe(CN)_6]$, it exists in the protonated form {$H^+K_3\ [Fe(CN)_6]$} and ascorbic acid exists in the unionised. The mechanism was given under Scheme 1.

The pseudo first order rate constant is directly proportional to $[H_2A^+]$ indicating first order kinetics with respect to H_2A (Table 1) (Figure 1). Since reverse micelles contains large concentration of bromide ion to compare

Table 1. Effect of varying $[H_2A]$ on the observed rate constants (k'); $K_3[Fe(CN)_6]$ = 5.0×10^{-4} M; [CTAB] = 0.1 M; T = 302 K) .

$[H_2A]_o\times10^2$	$k_1\times10^5$	
	W = 4.44	W = 8.88
0.2	1.074	1.98
0.6	2.303	2.59
1.0	3.454	3.852
1.4	4.989	5.12
1.8	6.141	6.52

rate of reaction in aqueous media and reverse micellar medium, kinetics runs were performed in aqueous medium in presence of bromide ion. It was found that as concentration of bromide ion increases the rate constant decreases and a plot of the pseudo first order constant k_1 versus $1/[Br^-]$ was found to be linear as shown in (Table 2).

3.1 Effect of Variation of *W* and CTAB Concentrations

The first order rate constant (k_1) has been determined over a wide range of W (3.33-16.6) at constant [CTAB] and also at different Concentrations of CTAB (Table 3). At constant [CTAB], second order rate constant (k_2 = $k_1/[H_2A]_{eff}$) increases with W. This is because with increase in W, the ionic strength decreases, and lower ionic strength favours cation-anion reaction. The attenuation of special properties of water pools (like low dielectric constant) takes place at around W = 4.44 and the k_2 values are governed only by change in ionic strength [16–20]. The effect of change of W on the rate of reaction has been quantitatively correlated with change in ionic strength, as follows:

$$k_2 = k_2^0 \frac{\gamma_{HA^+}\gamma_{[Fe(CN)_6]^{-3}}}{\gamma_{\#}} \quad (1)$$

where, $\gamma_{[Fe(CN)6]^{-3}}$, $\gamma_{\neq}$ and γ_c are the activity coefficients of $[Fe(CN)_6^{-3}]$, $[HA]^+$ and the transi-

Table 2. Effect of variation of $[Br^-]$ ($[Fe(CN)_6]_o^{3+} = 5.0\times10^{-4}$ mol.dm^{-3}; W = 16.6; CTAB = 0.1 M).

Added $[Br^-]$ (mol.dm^{-3})	$[Br^-]_e$ (mol.dm^{-3})	$k'_{(aq.m)}\times10^5$ (sec^{-1})	$k_{2(aq.m)}\times10^4$ (sec^{-1})	$k'_{(r.m)}\times10^3$ (sec^{-1})	$k_{2(r.m)}\times10^4$ (dm^3.mol^{-1}.sec^{-1})
0.1	3.33	3.85	38.5	1.38	4.15
0.16	5.33	1.95	12.18	1.84	3.46
0.39	13.0	1.15	8.8	2.30	1.76
0.6	20.3	0.92	4.5	3.22	1.59

Table 3. Observed first order (k') and second order rate constants (k_2) for the oxidation of ascorbic acid by $K_3[Fe(CN)_6]$. ($[H_2A] = 1.8\times10^{-2}$ M; $K_3[Fe(CN)_6] = 5.0\times10^{-4}$ M; T = 302.0 K).

W	[CTAB]	$k_1\times10^4$ (sec^{-1})	$k_2\times10^3$ (mol^{-1} dm^3 sec^{-1})
3.33	0.05	61.4	0.91
4.44		49.8	0.98
6.66		38.3	1.15
8.88		26.8	1.47
12.2		18.8	1.63
16.6		10.2	1.83
3.33	0.1	21.4	6.3
4.44		15.0	6.7
6.66		12.4	7.4
8.88		12.0	13.2
12.2		11.0	14.3
16.6		10.0	15.0
3.33	0.2	17.2	10.3
4.44		10.5	10.4
6.66		8.99	10.8
8.88		8.60	22.4
12.2		8.33	25.0
16.6		6.63	26.0
3.33	0.3	9.00	16.9
4.44		7.80	18.2
6.66		6.01	19.8
8.88		4.152	29.0
12.2		3.28	31.0
16.6		2.69	35.6

tion state and k_2^0 is the rate constant at zero ionic strength and the activity co efficient γ_i of an ion is given by:

$$-\log \gamma_i = \frac{AZ_i^2\,\mu^{1/2}}{1+\mu^{1/2}} - \sum_j B_{i,j}\,C_j \qquad (2)$$

where, C_j = the summation of extending overall ions concentration, $B_{i,j}$ = the summation of extending specific interaction parameters.
Using equations (1) and (2), it can be shown that

$$\log k_2 = \log k_2^{o} - \frac{A\mu^{1/2}}{1+\mu^{1/2}} - b\left[\mathrm{Br}^-\right] \qquad (3)$$

where, $\Sigma_j B_{ij} C_j = b[\mathrm{Br}^-]$ 'b' contain the relevant specific interactions between positively charged micellar surface (M) and $[Fe(CN)_6]^{-3}$, $[H_2A]$ (C) and Br^-, between the singly charged transition state (#) and Br^-, Na^+ and Br^-. According to equation 3, a plot of k_2 versus Br^- has to be straight line. Such a plot was obtained at three different concentrations of CTAB (Figure 2) [21–23].

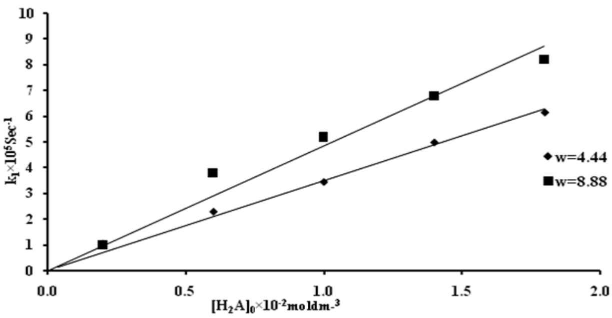


Figure 1. Effect of $[H_2A]$ at different W (from 4.44 to 8.88) on the oxidation of ascorbic acid by $K_3[Fe(CN)_6]$.

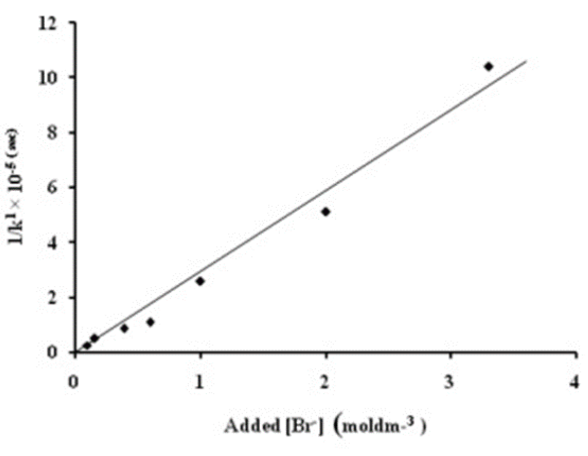


Figure 2. Effect of Variation of [Br] vs $1/k_1$ at W = 12.2 and W = 3.33.

3.2 Effect of CTAB

With increase in CTAB concentration, at constant W, the second order rate constant increases. This study has been carried out in a detailed manner at two W values one is the low W range (3.33) and other in the high W range (16.6) [23–26]. According to Berezin pseudo phase model, the second order rate constant k_2 is given by,

$$k_2 = \frac{k_m P_{\left[\mathrm{Fe(CN)_6}\right]^-} P_{H_2A^+} CV + k_w\left(1-CV\right)}{\left(1+K_{\left[\mathrm{Fe(CN)_6}\right]^-}+C\right)\left(1+K_{H_2A^+}C\right)} \qquad (4)$$

where, $K_{\{Fe(CN)6]}^{-3} = P_{H2A^+}V$, P_{H2A^+} is the partition co-efficient, and V is the molar volume.

$$k_2 = \frac{k_m P_{\left[\mathrm{Fe(CN)_6}\right]^-} + K_{H_2A^+}C + k_w\left(1-CV\right)}{\left(1+K_{\left[\mathrm{Fe(CN)_6}\right]^-}C\right)\left(1+K_{H_2A^+}C\right)} \qquad (5)$$

Since both the reactants are hydrophilic and weakly bound at the micellar surfaces,

$$k_2 = k_m P_{\left[\mathrm{Fe(CN)_6}\right]^-} K_{H_2A^+} C + k_w \qquad (6)$$

In the equation (5), CV can be neglected in comparison to 1 in the denominator. k_m is the rate constant of the reaction at the interface and k_w corresponding to the entrapped water. In the present case a plot of k_2 versus C was found to be linear with a positive intercept (Figure 3) giving evidence to the assumption that 1 >> $K_{H2A^+}C$, $K_3[Fe(CN)_6]$. The slope corresponds to $k_m K_{H2A^+}$, $K_{[Fe(CN)6]}^{-3}$ and intercept gives the rate constant k_w for the reaction in the entrapped water. The value of k_w (2.95×10^{-3} min^{-1} from Figure 3) is thirty three times greater than the rate constant of the reaction in aqueous medium in the absence of bromide

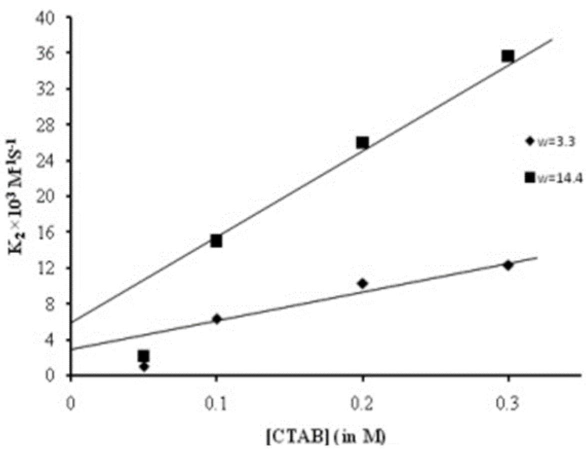


Figure 3. Effect of [CTAB] at different W on the oxidation of ascorbic acid by $K_3[Fe(CN)_6]$.

ion (k_2 = 9.1×10^{-5} mol^{-1}.dm^3.sec^{-1}). In presence of bromide ion [Br$^-$] (Figure 4), the rate is around forty two times greater in comparison to aqueous medium. This large increase of rate in the reverse micelles illustrates the special properties of entrapped water, *i.e.*, micro polarity at low *W*s.

4. Conclusion

The pseudo first order rate constant of oxidation of ascorbic by $K_3[Fe(CN)_6]$ is forty two times faster in the CTAB/$CHCl_3$/hexane reverse micellar medium compared to conventional aqueous medium. The significant increase is attributed to the concentration effect produced in the reverse micelles and lower micro polarity of the reverse micelles which facilitates the reaction between oppositely charged ions.

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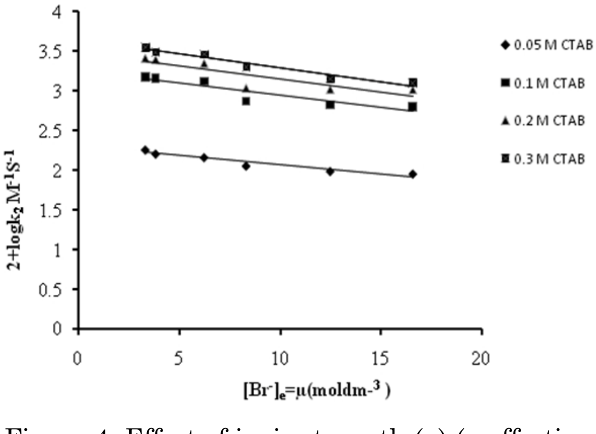

Figure 4. Effect of ionic strength (μ) (= effective bromide ion concentration [Br$^-$]$_e$) the oxidation of ascorbic acid by K_3 [Fe(CN)$_6$].

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