CTAB Reverse Micelles as Catalysts for the Oxidation of Ascorbic Acid by K₃[Fe(CN)₆]

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Abstract

The oxidation of ascorbic acid by K₃[Fe(CN)₆] was studied in reverse micellar systems composed of CTAB (Cetyltrimethylammonium bromide), and it was found the observed first order (k₁(aq) = 5.2×10⁻⁵ s⁻¹, k₁(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 (k₂(aq) = 0.9×10⁻⁵ mole⁻¹.dm³.sec⁻¹, k₂(rev) = 1.75×10⁻³ mole⁻¹.dm³.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 = {[H₂O]/[surfactant]} parameter. The effect of surfactant concentration on rate was explained on the basis of Berezin pseudo phase model.


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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 = {[H₂O]/[surfactant]} parameter. Examples of physical properties which differ 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
water in the reverse micelles are different in
CTAB/CHCl3/Hexane, the rates of reactions are
also expected to be different than that of con-
ventional aqueous medium.
In studies of reactions in reverse micelles in-
volving water-soluble reactants, the reactants
are confined to the water pool. The volume of
the water pool is around 0.01 mL while the to-
tal overall volume is 10 mL. Since the reactants
are present in the water pool at a microscopic
level, the concentration of reactants with re-
spect to water pool is around 100 times more
than that compared to whole volume. This
leads to a huge concentration effect. Conse-
quently, a concentration scale is defined in or-
der 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 concen-
trations in water pool is considered instead of
overall volume as follows formula \([\text{[Reactant]}_{\text{eff}} = \frac{\text{[Reactant]}_{\text{overall}}}{f} \]
where, \(f = \text{volume of water pool / (volume of water pool + volume of sol-
vent)}\) [6,7].

Since reverse micelles involve a water /or-
ganic medium interface, they closely resemble
the microenvironment of the living cells and
can be considered as model system for biologi-
cal studies / experiments at molecular levels.
They can also solubilise all kinds of substrate
molecules, hydrophilic, hydrophobic, and am-
phiphilies. Ascorbic acid is a very important
antioxidant in biological systems and undergos
oxidation with reactive oxygen species and
transition metals [8–10]. The redox chemistry
of ascorbic acid is important in human nutri-
tion [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 ac-
bility [11,12]. The kinetics of Oxidation of
ascorbic acid by hexacyanoferrate(III) in aque-
ous 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 acid by K3[Fe(CN)6] in re-
verse micellar medium and the results are re-
ported 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 re-
verse micelles, were also different in the pres-
ence of reverse micelles as reported elsewhere.

2. Materials and Methods
2.1 Preparation of CTAB Reverse Micelles

CTAB (Cetyltrimethylammonium bromide
reverse micellar solution (0.1 M) was prepared
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 K3[Fe(CN)6] was added from
a stock solution of 0.25 M. The reaction
was initiated by adding 0.02 mL of ascorbic ac-
id from a stock solution of 2 M. W was varied
by changing the volume of water in the range
(0 to 1.094) to get W value (3.33 to 16.6). The
kinetic study of oxidation of ascorbic acid by
K3[Fe(CN)6] was carried out under pseudo-first order conditions, i.e.,
[HA]\(\rightarrow\)\([K_3[Fe(CN)6]\). The reaction were moni-
tored by measuring the decrease in the absorb-
ance of [K3[Fe(CN)6] at 420 nm using a Shi-
madzu-1800 spectrophotometer. Out of two re-
actants K3[Fe(CN)6] and H2A, H2A has no ab-
sorbance in range 400-700 nm. The absence of
H2A was confirmed by chlorauric test [18].

3. Results and Discussion

The reaction between K3[Fe(CN)6] and H2A
in CTAB/Chloroform/Hexane/Water mixtures
follows first order kinetics with respect to
K3[Fe(CN)6] as observed by the linear plots be-
tween log of absorbance \(\text{[due to } K_3[Fe(CN)6]\) vs.
time, under the conditions, \([\text{[HA]}_0] >> K_3[Fe(CN)6].\). In the present of K3[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 di-
rectly proportional to \([H_2A]\) indicating first or-
der kinetics with respect to H2A (Table 1)
(Figure 1). Since reverse micelles contains
large concentration of bromide ion to compare

<table>
<thead>
<tr>
<th>([H_2A]_0 \times 10^{-2})</th>
<th>(k_1 \times 10^5)</th>
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<td>0.2</td>
<td>1.074</td>
</tr>
<tr>
<td>0.6</td>
<td>2.303</td>
</tr>
<tr>
<td>1.0</td>
<td>3.454</td>
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<td>1.4</td>
<td>4.989</td>
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<td>1.8</td>
<td>6.141</td>
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Table 1. Effect of varying \([H_2A]\) on the observed
rate constants \(k_1\): K3[Fe(CN)6] = 5.0 \times 10^{-1} M;
[CTAB] = 0.1 M; T = 302 K.

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 $1/\text{[Br}^−\text{]}$ 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 ($k_i$) 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 ($k_2 = k_i/\text{[H}_2\text{A}]_0$) 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:

$$k_2 = \frac{\gamma_{\text{HA}}\gamma_{\text{[Fe(CN)₆]}}}{{y}}$$

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

<table>
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<tr>
<th>Added [Br$^−$] (mol.dm$^{−3}$)</th>
<th>[Br$^−$]$_0$ (mol.dm$^{−3}$)</th>
<th>$k'_{\text{aq.m}}\times10^5$ (sec$^{−1}$)</th>
<th>$k'_{\text{r.m}}\times10^4$ (sec$^{−1}$)</th>
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<tr>
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<td>3.46</td>
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<tr>
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<td>8.8</td>
<td>2.30</td>
<td>1.76</td>
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<tr>
<td>0.6</td>
<td>20.3</td>
<td>0.92</td>
<td>4.5</td>
<td>3.22</td>
<td>1.59</td>
</tr>
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</table>

<p>| Table 2. Effect of variation of [Br$^−$] ([Fe(CN)$_6$]$^{3+} = 5.0\times10^{−4}$ mol.dm$^{−3}$; $W = 16.6$; CTAB = 0.1 M). |
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<p>| Table 3. Observed first order ($k'$) and second order rate constants ($k_2$) for the oxidation of ascorbic acid by $\text{K}_3\text{[Fe(CN)₆]}$. ($\text{[H}_2\text{A]} = 1.8\times10^{−2}$ M; $K_3\text{[Fe(CN)₆]} = 5.0\times10^{−3}$ M; $T = 302.0$ K). |
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tion state and \( k_2^0 \) is the rate constant at zero ionic strength and the activity co efficient \( \gamma_i \) of an ion is given by:

\[
-\log \gamma_i = \frac{AZ_i^2 \mu^{1/2}}{1 + \mu^{1/2}} - \sum_j B_{ij} C_j
\]  
(2)

where, \( C_j \) = the summation of extending overall ions concentration, \( B_{ij} \) = the summation of extending specific interaction parameters.

Using equations (1) and (2), it can be shown that

\[
\log k_2 = \log k_2^0 - \frac{A\mu^{1/2}}{1 + \mu^{1/2}} - b[Br^-]
\]  
(3)

where, \( \Sigma B_i(C) = b[Br^-] \) ‘b’ contain the relevant specific interactions between positively charged micellar surface (M) and [Fe(CN)₆]⁻³, [H₂A] (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].

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,

\[
k_2 = \frac{k_m P_{[Fe(CN)₆]^-} P_{H₂A} CV + k_w (1 - CV)}{[1 + K_{[Fe(CN)₆]}] + C[1 + K_{H₂A} C]}
\]  
(4)

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

\[
k_2 = \frac{k_m P_{[Fe(CN)₆]} + K_{H₂A} C + k_w (1 - CV)}{1 + K_{[Fe(CN)₆]} C[1 + K_{H₂A} C]}
\]  
(5)

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

\[
k_2 = k_m P_{[Fe(CN)₆]} K_{H₂A} C + k_w
\]  
(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 \( 1 >> K_{H₂A} C, K_m[Fe(CN)₆] \). The slope corresponds to \( k_m K_{H₂A} \), \( K_m[Fe(CN)₆] \) 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.
ion ($k_2 = 9.1 \times 10^{-5} \text{mol}^{-1} \text{dm}^3 \text{sec}^{-1}$). 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 $K_3[\text{Fe(CN)}_6]$ 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.

Acknowledgments

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