



Effect of AOT/Heptane Reverse Micelles on Oxidation of Ferriin by Metaperiodate: Kinetic and Mechanistic Aspects

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Abstract: A kinetic study of the oxidation of Ferriin, $[\text{Fe}(\text{phen})_3]^{2+}$ by metaperiodate (IO_4^-) has been carried out in AOT/heptane reverse micelles by changing $W = ([\text{H}_2\text{O}]/[\text{AOT}])$ and AOT concentration. The reaction order is first order with respect to Ferriin, while zero order with respect to IO_4^- . The reaction rate is faster in aqueous medium compared to AOT reverse micelles by eight times. The oxidation rate increases with an increase in the value of W (at fixed surfactant concentration, $[\text{AOT}]$) and decreases with AOT concentration. The effect of W on rate is elucidated based on the low dielectric constant of the water pool. Berezin's pseudo-phase model has been applied to explain the effect of AOT on rate.

Keywords: Ferriin, periodate, AOT, Reverse micelles, and water pool.

Submitted: December 31, 2022. **Accepted:** September 19, 2023.

Cite this: Leela Kumari B, Shyamala P, Klina VN. Effect of AOT/Heptane Reverse Micelles on Oxidation of Ferriin by Metaperiodate: Kinetic and Mechanistic Aspects. JOTCSA. 2023;10(4):1099-106.

DOI: <https://doi.org/10.18596/jotcsa.1226805>

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1. INTRODUCTION

Reverse micelles are stable surfactant aggregates formed spontaneously in organic solvents. Their hydrophilic head groups combine to create structures with polar cores, while their hydrophobic tails extend outward into the surrounding organic solvent, unlike normal micelles. One important feature of reverse micelles is their ability to solubilize water within them, resulting in optically transparent and thermodynamically stable structures. This water-containing region within the reverse micelle is referred to as the "water pool" and is characterized by its radius (r , in nanometers), which is linearly related to an externally controlled parameter known as W ($W = [\text{H}_2\text{O}]/[\text{Surfactant}]$) (1-4).

The water solubilized within reverse micelles hydrates the hydrophilic head groups of the surfactants. This water is tightly bound and exhibits lower mobility compared to bulk water. It is important to note that only the initial portions of water added to the reverse micelle are tightly bound, and as solvation progresses, free water becomes available. The behavior exhibited by these initial

water portions is characterized by certain anomalies, including a diminished dielectric constant, decreased activity, limited mobility, modified pH, and heightened nucleophilicity compared to conventional aqueous solutions. As the water content within the reverse micelle increases, the physical properties of the water pool gradually approach those of ordinary aqueous solutions (5-9). Three structural changes occur within reverse micelles when varying the water and surfactant concentrations can be categorized (10). They are:

1. When water and surfactant concentrations are adjusted simultaneously while keeping W constant, the reverse micelle concentration changes, but its size remains unchanged.
2. An increase in the amount of water results in an enlargement of the micelle size.
3. Increasing water and surfactant concentrations simultaneously increases micelle concentration while maintaining a fixed micelle size. Conversely, an increase in surfactant concentration causes a reduction in micelle size.

Reverse micelles have many advantages compared to aqueous media. For example, they offer a unique capacity to accommodate a wide range of substrate molecules, regardless of their hydrophilic, hydrophobic, or amphiphilic nature. The compartmentalization of reactants in reverse micelles is a key aspect of their utility in various chemical and biochemical applications. The localization of reactants gives rise to catalytic effects on the rates of the reactions, thereby controlling the kinetics and mechanism of reactions (11-14).

We have reported a few reactions taking place in the presence of CTAB/CHCl₃/Hexane reverse micelles, explored the unique properties of CTAB reverse micelles, and applied Berezin's pseudo-phase model to explain the results (15-19). To explore the unique properties of AOT/Heptane reverse micelles, oxidation of ferrioxalate by metaperiodate has been chosen.

2. EXPERIMENTAL SECTION

2.1. Materials

Double distilled water was used for the preparation of solutions. All the chemicals used were of Analytical grade. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (Fluka) was used without further purification. Heptane was distilled before use. A solution of AOT with a concentration of 0.3 mol/dm³ was prepared by dissolving 66.68 g of AOT in heptane. Additionally, solutions with concentrations of 0.2 mol/dm³ and 0.1 mol/dm³ were prepared similarly by dissolving the appropriate amount of AOT in heptane. The stock solutions of ferrioxalate (0.02 mol/dm³) were produced by dissolving the necessary amount of FeSO₄·7H₂O and 1,10-phenanthroline in water. Sodium metaperiodate (Merck, India) solution was prepared by dissolving the necessary quantities in water.

2.2. Determination of binding constants of [Fe(phen)₃]²⁺

The binding constants of [Fe(phen)₃]²⁺ in AOT reverse micelles have been determined at different concentrations of AOT. For each concentration, the absorbance of [Fe(phen)₃]²⁺ has been noted at λ=510 nm (Fig. 1). The absorbances recorded are

A_M, the absorbance of the complex in the presence of reverse micellar medium; A⁰_w, is the absorbance of the complex in the presence of water and C, the concentration of surfactant (20). The binding constant has been determined by following Benesi-Hildebrand equation,

$$\frac{1}{(A_M - A_W^0)} = \frac{1}{(A_M^0 - A_W^0)} + \frac{1}{(A_M^0 - A_W^0)K_S C}$$

A graph between 1 / (A_M - A⁰_w) vs 1/C gives straight line, binding constant values determined from slope and intercept given in Table 1.

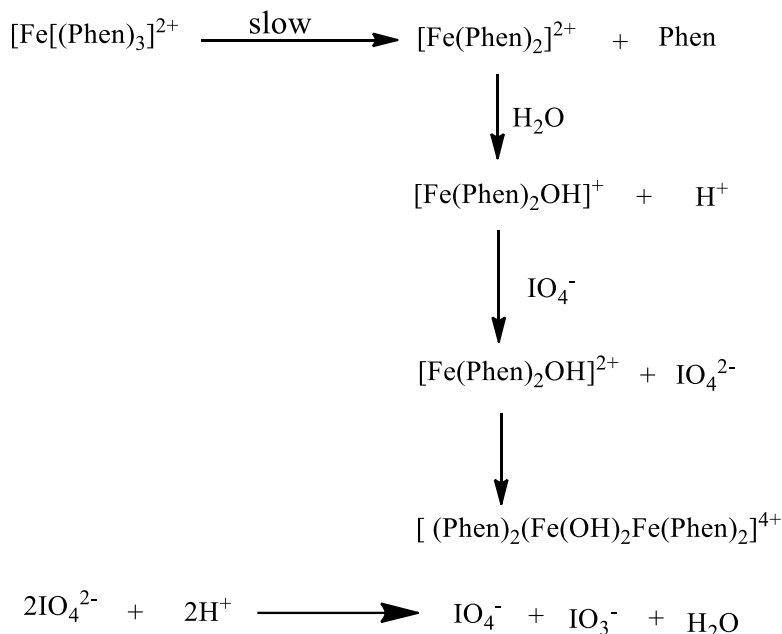
2.3. Experimental method:

[Fe(phen)₃]²⁺ (0.02 mol/dm³, 0.02 mL) was taken into 0.1 mol/dm³, 10 mL of AOT solution using a micropipette followed by IO₄⁻ solution (0.2 mol/dm³, 0.04 mL/dm³) the reaction mixtures were thoroughly shaken to obtain a clear solution. W was varied in the range of 3.33 to 12.2 in the subsequent experiments, and the concentration of IO₄⁻ was varied from (4-40) × 10⁻⁴ mol/dm³.

The decrease in absorbance of [Fe(phen)₃]²⁺ at a wavelength of 510 nm was measured as a function of time. [IO₄⁻] >> [[Fe(phen)₃]²⁺]. Good linear plots were obtained for log(absorbance) vs. time, showing first-order kinetics with respect to [Fe(phen)₃]²⁺. Triplicate runs were performed, and averages were taken. A UV-Vis double-beam spectrophotometer was used.

3. RESULTS AND DISCUSSION

The kinetics of the reaction have been carried out in the presence of AOT reverse micelles under pseudo-first-order conditions, taking [IO₄⁻] >> [Fe(phen)₃]²⁺. [Fe(phen)₃]²⁺ is therefore isolated. Good linear plots between log (A_t) versus time (Figure 2) were obtained, indicating first-order kinetics with respect to [Fe(phen)₃]²⁺. The pseudo-first-order rate constant, k₁, has no dependence on [IO₄⁻], confirming zero-order kinetics with respect to IO₄⁻ (Table 2). Based on these results, the mechanism has been given in Scheme 1.



Scheme 1: The reaction between metaperiodate and ferroin.

The reaction is around eight times slower in AOT reverse micellar medium compared to aqueous medium under the same conditions. The present reaction is a cation-anion reaction. Since the reverse micelles have a low dielectric constant, which does not favor a cation-anion reaction, the reaction is slower in the AOT reverse micellar medium. Similar results based on the dielectric constant effect on reaction rates have been reported by Ayoko G et al. (12).

Effect of molar ratio (*W*) on rate

The pseudo-first-rate constant, k_1 , increases slightly with an increase in molar ratio ($W = [\text{H}_2\text{O}]/[\text{AOT}]$) (Table 3). The slight rate increase is because of two factors.

1. The first is the dielectric constant of the medium: It is well known that the rate of the reaction is dependent on the dielectric constant of the medium (21)

$$\ln k = \ln k_0 - \frac{Z_A Z_B e^2}{(4\pi\epsilon_0 \epsilon d_{AB} kT)}$$

Since the present reaction is an anion-cation reaction, according to the above equation, as *W* increases, the dielectric constant increases, and therefore the reaction rate increases with *W*.

2. IO_4^- is a hydrophilic species, and because of the lack of electrostatic attraction with AOT, it exists totally in the water pool. $[\text{Fe}(\text{phen})_3]^{2+}$ is partitioned between the water pool and AOT surface (Figure 3). As *W* increases $[\text{Fe}(\text{phen})_3]^{2+}$ goes more into the water pool while IO_4^- is already available in the water pool, so there is an increase in rate with change in *W*.

Effect of concentration of AOT

At constant *W*, with an increase in AOT concentration, k_1 decreases. This is because the positively charged $[\text{Fe}(\text{phen})_3]^{2+}$ is increasingly

bound by the negatively charged micellar surface, whereas IO_4^- is left behind only at the core of the water pool. This results in a decrease in rate with an increase in concentration of AOT. Berezin's pseudo-phase model has been applied to explain this behavior, and accordingly, the expression related to a reaction involving one strongly bound reactant and another strongly repelled reactant has been applied (22). The observed rate constant k_1 is thus given by:

$$k_1 = \frac{k_m P_{\text{IO}_4^-} K_{[\text{Fe}(\text{Phen})_3]^{2+}} C + k_w (1 - CV)}{(1 + K_{\text{IO}_4^-} C)(1 + K_{[\text{Fe}(\text{Phen})_3]^{2+}} C)}$$

Where, k_m is the rate constant at the micellar phase, k_w is the rate constant of reaction in the water pool, *C* is $[\text{AOT}]$, and *V* is the molar volume of AOT ($P_{\text{IO}_4^-}$) is the partition coefficient of the periodate. $K_{[\text{Fe}(\text{phen})_3]^{2+}}$ and $K_{\text{IO}_4^-}$ are the binding constants of $[\text{Fe}(\text{phen})_3]^{2+}$ and IO_4^- and $K_{[\text{Fe}(\text{phen})_3]^{2+}} = P_{[\text{Fe}(\text{phen})_3]^{2+}} V$ and $K_{\text{IO}_4^-} = P_{\text{IO}_4^-} V$. IO_4^- is repelled by the micellar surface and is water-soluble, and therefore $K_{\text{IO}_4^-}$ can be neglected in the above equation. Since $k_w > k_m$, the above equation changes to

$$\begin{aligned}
 &+ k_1 = \frac{k_w}{(1 + K_{[\text{Fe}(\text{Phen})_3]^{2+}} C)} \\
 &\frac{1}{k_1} = \frac{1}{k_w} + \frac{K_{[\text{Fe}(\text{Phen})_3]^{2+}} C}{k_w}
 \end{aligned}$$

According to the above equation, $1/k_1$ versus *C* was found to be linear, showing the applicability of Berezin's pseudo-phase model to reverse micelles (Fig. 4). The binding constant of $[\text{Fe}(\text{phen})_3]^{2+}$ was calculated from slope and intercept of the above plot (Table 1). It was found that the binding constants thus obtained agree with the binding constant obtained from spectral data (experimental section). This shows the validity of Berezin's model to the present reaction.

Table 1: Binding constants of $[\text{Fe}(\text{phen})_3]^{2+}$

W	Spectral data	Kinetic data
4.44	17.80	18.81
6.66	16.60	10.46
12.2	10.02	8.65

Table 2. Influence of periodate on reaction rate
 $[\text{Fe}(\text{phen})_3]^{2+} = 4.0 \times 10^{-5} \text{ mol/dm}^3$; $T = 304 \text{ K}$

$[\text{IO}_4^-]_0 \times 10^4$ (mol/dm ³)	W = 5.55			W = 12.2	
	$[\text{IO}_4^-]_e$ (mol/dm ³)	$k_1 \times 10^4$ (sec ⁻¹)		$[\text{IO}_4^-]_e$ (mol/dm ³)	$k_1 \times 10^4$ (sec ⁻¹)
4.0	0.04	1.30		0.018	1.90
12.0	0.12	1.30		0.054	2.00
16.0	0.16	1.60		0.072	1.79
20.0	0.20	1.64		0.090	1.81

Table 3: Influence of W and [AOT] on observed first-order rate constant (k_1)
 $[\text{Fe}(\text{phen})_3]^{2+} = 4.0 \times 10^{-5} \text{ mol/dm}^3$; $[\text{IO}_4^-] = 8.0 \times 10^{-4} \text{ mol/dm}^3$; $T = 304 \text{ K}$

[AOT] (mol/dm ³)	W	$k_1 \times 10^4$ (sec ⁻¹)
0.1	3.33	1.1
	4.44	1.50
	5.55	1.53
	6.66	1.70
	7.77	1.80
	8.88	1.97
	12.2	1.99
0.2	3.33	0.94
	4.44	1.35
	5.55	1.53
	6.66	1.54
	7.77	1.60
	8.88	1.61
	12.2	1.72
0.3	3.33	0.75
	4.44	0.78
	5.55	0.90
	6.66	1.00
	7.77	1.27
	8.88	1.35
	12.2	1.47

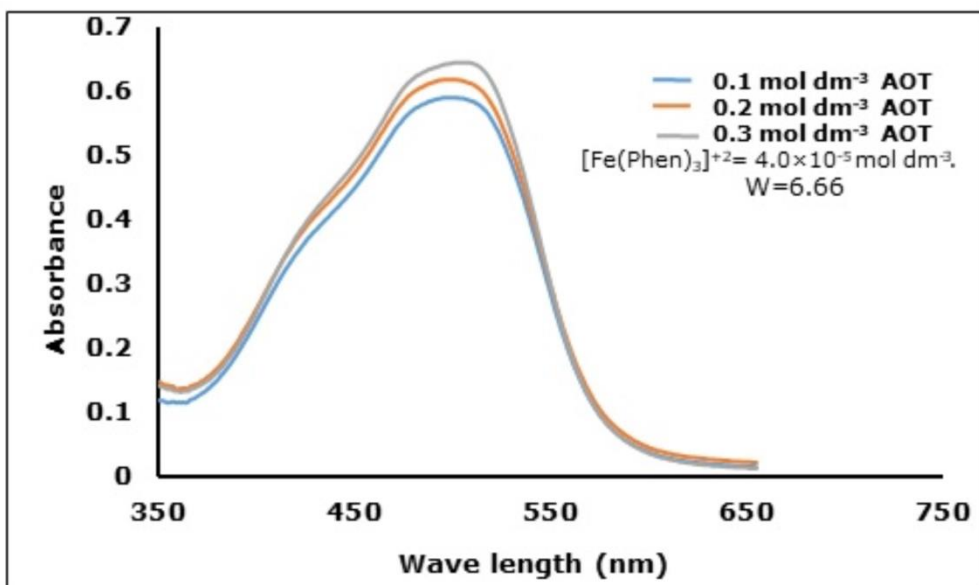


Figure 1: Spectra of Absorbance of $[\text{Fe}(\text{phen})_3]^{2+}$ versus wavelength (nm) at different [AOT].

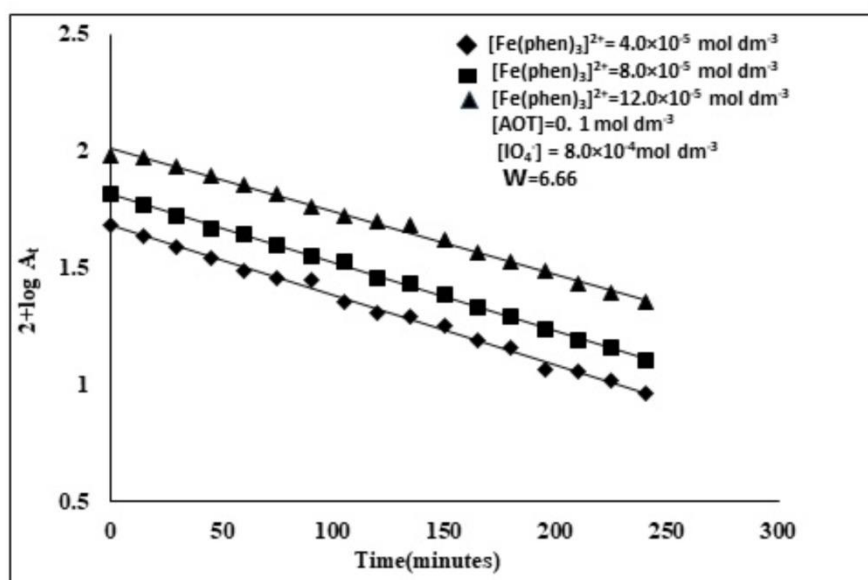


Figure 2: A Plot of $2 + \log (\text{Absorbance})$ versus Time (min) at different concentrations of $[\text{Fe}(\text{phen})_3]^{2+}$

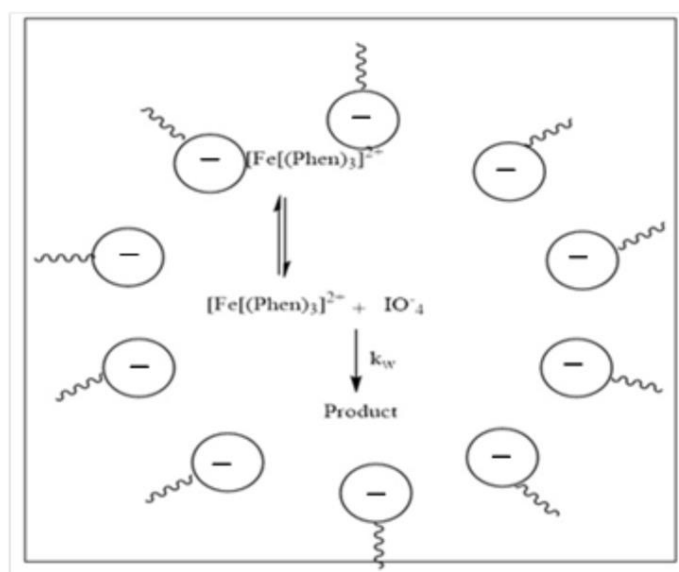


Figure 3: Graphical representation of the distribution of reactants in AOT/Heptane reverse micelles.

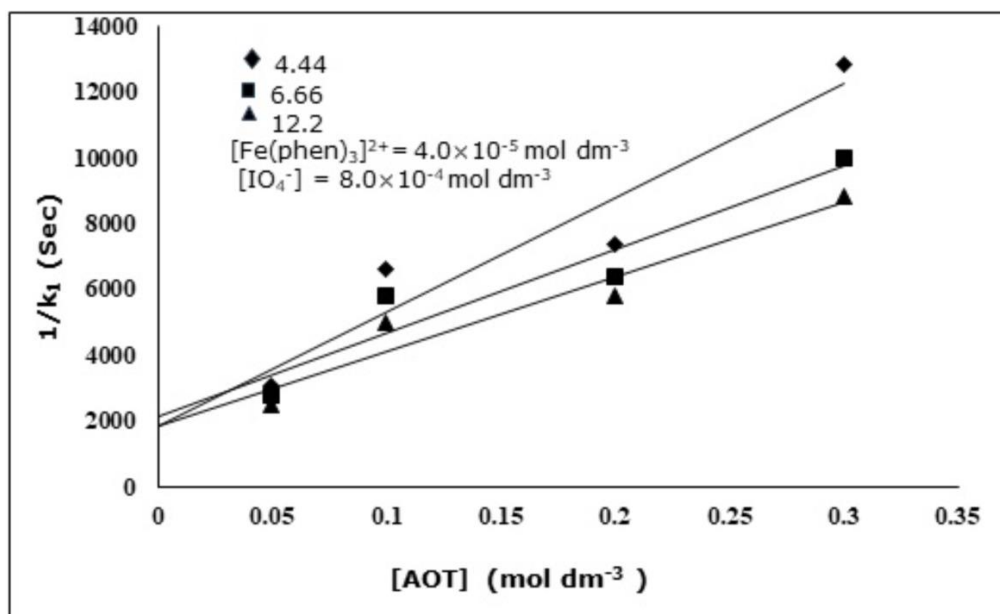


Figure 4: A Plot of $1/k_1$ versus [AOT].

4. CONCLUSION

- The reaction's order is zero concerning IO_4^- while the first is concerning $[\text{Fe}(\text{phen})_3]^{2+}$.
- The reaction is inhibited eight times in the presence of AOT reverse micelles.
- As W increases, the rate of the reaction increases slightly due to an increase in the availability of $[\text{Fe}(\text{phen})_3]^{2+}$ in the water pool, and also, with an increase of W , the dielectric constant increases, which favors the reaction between two oppositely charged reactants.
- The rate constant, k_1 , decreases with an increase in AOT concentration. This is because the positively charged $[\text{Fe}(\text{phen})_3]^{2+}$ is increasingly bound by the negatively charged micellar surface and less available for reaction.

5. CONFLICT OF INTEREST

We have no conflicts of interest to disclose.

6. ACKNOWLEDGMENTS

P. Shyamala thanks the Ministry of Earth Sciences (MOES), National Centre for Coastal Research (NCCR), and the Government of India for financial support under major project No MOES/ICMAM - PD/Supply. Order/81/2017.

B. Leela Kumari is thankful to the Management of Chaitanya Women's Degree & P.G College of Gajuwaka, Visakhapatnam, for their encouragement.

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