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Research Article

KINETICS AND MECHANISM OF PERMANGANATE OXIDATION OF ENROFLOXACIN IN AQUEOUS ALKALINE MEDIUM

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ABSTRACT

The reaction kinetics of oxidation of enrofloxacin by potassium permanganate has been investigated in aqueous alkaline medium using spectrophotometric technique at 30 ± 1°C at constant ionic strength of 0.10 mol L^{-1}. The reaction exhibits 2:1 stoichiometry (2 $KMnO_4$:1 Enrofloxacin). The order with respect to oxidant and substrate is found to be unity in each, whereas fractional order with respect to alkali concentration. The oxidation products were identified by using FTIR, LCMS spectral studies. The effects of added products, ionic strength and dielectric constant have been studied on the rate of reaction. Based on the experimental results a suitable mechanism is proposed. There is no evidence of intermediate complex formation, thus, the outer-sphere mechanism is proposed as the mechanism for this reaction.

Keywords: Permanganate ion, Enrofloxacin, Kinetics, Oxidation, Mechanism.

INTRODUCTION

Potassium permanganate used widely as oxidizing agent and plays a dynamic role in the kinetics of number of organic and biological active compounds.[1-5] Oxidation reactions by Potassium permanganate are of great academic and technological importance because of its variable oxidation states. Permanganate is a powerful multi-electron oxidant which can exist in numerous oxidation states, among which +7 is its highest oxidation state, which occurs in the Oxo compounds like MnO_4^-, Mn_2O_7, MnO_3F. Out of which MnO_4^- is the most commonly used oxidant species to carry out kinetic studies in acidic, neutral and alkaline media. Oxidations by permanganate ion find widespread applications in organic syntheses[1, 6-11] especially as the introduction of phase transfer catalysis[8, 9, 11] which permits the use of solvents like methylene chloride and benzene. An important sources of mechanistic information on these reactions are kinetic studies, as certified by result stating to unsaturated acids in both aqueous[1, 6-12] and non-aqueous media.[12] Previous studies reveals that the permanganate ion oxidizes a number of organic compounds in aqueous alkaline medium, which are very slowly, attacked in acidic or neutral medium.[2, 3, 13-15] The oxidation mechanism depends on the nature of the substrate and pH of the reaction mixture.[16] In strongly alkaline medium, permanganate ion gives the manganate ion, MnO_4^{2-} as the stable reduction product.[17–19] No mechanistic information is available to differentiate between a direct one-electron reduction to Mn(VI) and a mechanism in which a hypomanganate ion formed in a two-electron reduction followed by its rapid re-oxidation.[20, 21] The multistep redox reactions are major source of information as when the manganese intermediates have sufficiently long life time, it's quite easy to identify them and the possible reaction mechanism were presumed by the oxidation states of the intermediates.

Fluoroquinolones are broad-spectrum antibacterial agents used to treat the bacterial infections in human beings. Pharmaceuticals, of which antibacterial groups are important, have been identified as growing environmental pollutants.[22] Fluoroquinolones are partially metabolised in human body due to which a major fraction of it pass into the domestic sewage. This signifies the main route for entry of such pharmaceutical compounds into natural aquatic environment. So the transformations of fluoroquinolone in suitable water treatment process definitely play a major role.[23] Enrofloxacin (ENR) with molecular formula $C_{19}H_{22}FN_3O_3$, {1-Cyclopropyl-7-(4-ethyl-1-piperazinyl)-6-fluoro-1,4-dihydro-4-oxo- 3- quinolone carboxylic acid} (Figure 1), is a broad-spectrum antibacterial agent from the class of fluoroquinolones, is the antibiotic most frequently used for the treatment of domestic animals. The structure of ENR is similar to the fluoroquinolone ciprofloxacin, with an additional ethyl substituent in the N4 atom on the piperazine ring, which contains the tertiary aromatic group and tertiary aliphatic amine groups. A previous investigation has shown that minor substitutions on the piperazine ring might affect the degradation products.[24] ENR might illustrate a different degradation pathway with Mn(VII).The literature survey reveals that there are few study reports on the oxidation of enrofloxacin in either alkaline or acidic medium.[24-30] Due to pharmaceutical importance and lack of literature on the kinetic and mechanistic study of oxidation of this drug, prompted us to kinetic study of oxidation the enrofloxacin by permanganate in aqueous alkaline medium.

MATERIALS AND METHODS

Materials

All chemicals used were of analytical grade and doubly distilled water was used throughout this study. An aqueous solution of enrofloxacin (Cipla Limited) was prepared by dissolving known amount of drug in double distilled water. Permanganate solution was obtained by dissolving potassium permanganate (BDH Analar) in water and standardized by titrating against oxalic acid.[31] Freshly prepared & standardized permanganate solutions were always used in kinetics experiments. The Mn (VI) solution was made by boiling the aqueous solution of $KMnO_4$ [100 °C]

in 8.0 mol dm-3 KOH solution. The green-coloured solution of K2MnO4 is formed. NaOH (BDH) and $NaNO_3$ (MERCK) were used to provide required alkalinity and ionic strength respectively.

Methods

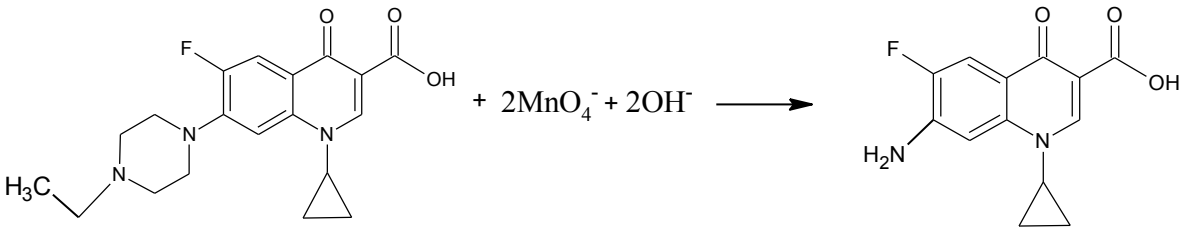
For kinetic measurements, a Peltier accessory (temperature-Controlled) attached to a U.V. 3000^+ UV-Visible spectrophotometer (LABINDIA) was used. For product analysis, an LC-ESI-MS, (Q-TOF Micromass, WATERS Company, UK), an alpha-T FTIR spectrophotometer (Bruker, Germany), and for pH measurement MSW-552 pH meter were used.

Kinetic measurements

All the chemical reactants were placed in a thermostatic bath at 30.0 ± 0.1°C for at least 30 min to attain thermal equilibrium. The kinetic measurements were followed under pseudo- first-order condition where concentration of ENR is at least ten times greater than concentration of $KMnO_4$ at a constant ionic strength 0.10 $molL^{-1}$. The reaction was initiated by mixing permanganate solution to ENR with the required volume of NaOH and $NaNO_3$. The course of the reaction was followed by monitoring decrease in the absorbance of $KMnO_4$ at 525 nm as a function of time in a 1 cm path length quartz cell of UV-Visible spectrophotometer. The application of Beer's law of $KMnO_4$ at λ_{max} 525 nm had been verified giving $\varepsilon = 2260 \pm 60$ L mol^{-1} cm^{-1} (Literature, ε = 2389 L mol^{-1} cm^{-1}).[32] The first order rate constants, k_{obs} were evaluated by plots of log absorbance versus time. The plots were linear to more than 75% completion of the reaction and rate constants were reproducible within ± 6%.

Stoichiometry and product analysis

A reaction mixture containing ten-fold molar excess of Mn(VII) over enrofloxacin in the presence of constant amounts of alkali and ionic strength was allowed to stand for 24 h at 30 ± 1°C. The experiments at alkaline pH showed that two moles of permanganate consume one mole of enrofloxacin. Thus the overall reaction stoichiometry may be written as:



ENR + $2MnO_4^{2-}$ + NH_3 + Other produts

The reaction products were identified as manganese(VI) and 7-amino-1-cyclopropyl-6-fluoro-4-oxo-quinolone-3-carboxylic acid. The main reaction product of ENR was isolated with the help of TLC (Thin-Layer Chromatography) and characterized by LC-MS and FT-IR. LC-MS analysis of the reaction mixture indicated the presence of product with molecular ion peak of m/z 263 (Figure 2). The m/z 263 corresponds to full dealkylation of the piperazine ring and classified as (M – 69) product because of its structural similarity to the (M – 69) product of ciprofloxacin.[33] However, the product does not have the same mass loss of 69 from the parent molecule. This product was also identified previously as oxidation product of enrofloxacin.[29, 30] It was also confirmed by its IR spectrum which showed the band at 3327.10 cm^{-1} indicating the presence of the $–NH_2$ group in the major oxidation product (Figure 3).[34] All other peaks observed in the IR spectrum correspond to the parent compound. The other product ammonia was detected by Nesseler's reagent test.[35]

RESULTS

Effect of Concentration of Manganese(VII)

The oxidant permanganate [MnO_4^-] concentration varied from $1.0 \times 10^{-4} – 7.0 \times 10^{-4}$ mol L^{-1} at 30°C and all other concentrations and conditions were constant. The linear plot of log absorbance versus time (Figure 4) shows that the order with respect to [$KMnO_4$] was unity. This fact was also confirmed by the fairly constant values of k_{obs} for varying [MnO_4^-].

Effect of Concentration of Enrofloxacin

The effect of concentration variation of enrofloxacin on the rate of reaction was studied in the range $2.0 \times 10^{-3} – 10.0 \times 10^{-3}$ mol L^{-1} at constant concentration of permanganate, alkali and ionic strength at 25°C, 30°C and 35°C respectively. The rate of reaction increases with increasing concentration of enrofloxacin (Table 1). The order with respect to ENR concentration was found to be unity which was confirmed by the plot of k_{obs} versus enrofloxacin concentration (Figure 5) which gives a straight line passing through the origin.

Effect of Concentration of Alkali

The effect of hydroxyl ion concentration on the reaction was studied in the concentration range $2.0 \times 10^{-2} – 10.0 \times 10^{-2}$ mol L^{-1} at fixed concentration of permanganate, enrofloxacin and ionic strength at three temperature 25°C, 30°C and 35°C respectively. Pseudo first-order rate constant (k_{obs}) was found to be increased with increase in [OH^-] (Table 1). A plot of log k_{obs} versus log [OH^-] was linear with less than unit order (0.68).

Effect of Ionic Strength and Dielectric Constant

At constant concentration of reactants and other conditions constant, the ionic strength was varied by varying concentration of sodium nitrate from 0.01 – 0.10 mol L^{-1}. Ionic strength had negligible effect on the rate of reaction. The effect of the dielectric constant (D) was studied by varying the t-butanol–water content (v/v) in the reaction mixture with all other conditions being maintained constant. The rate of reaction increases with increasing t-butanol volume. The plot of log k_{obs} versus 1/D was linear with positive slope (Figure 6).

Effect of Initially Added Products

The manganate ion concentration was varied from 4.0×10^{-5} – 4.0×10^{-4} mol L^{-1} at constant concentrations of permanganate, enrofloxacin, alkali, and ionic strength. It was found that initially added manganate ion had no effect on the rate of reaction.

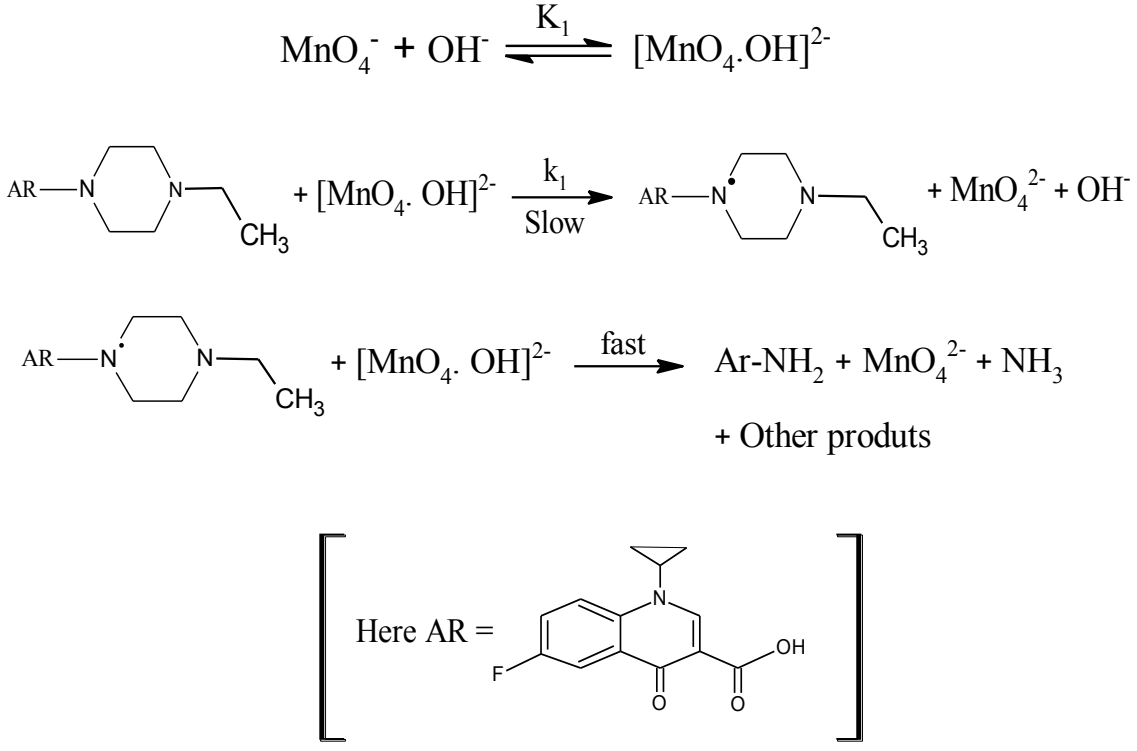
Test for Free Radicals

Free radical involvement in oxidation of enrofloxacin by alkaline permanganate was studied by adding acrylonitrile in the reaction mixture for 5 h in an inert atmosphere followed by methyl alcohol dilution which involves precipitate formation indicating that reaction path is restricted by radical mechanism.

DISCUSSION

Permanganate ion is a strong oxidant in an aqueous alkaline media. Since it shows various oxidation states, the stoichiometric results and the pH of reaction medium play a significant role. Under the present experimental conditions at pH > 12, the reduction product of Mn(VII) is stable and further reduction of Mn(VI) might be stopped.[17,18] However, prolong standing, green Mn(VI) is reduced to Mn(IV) under experimental conditions. The permanganate shows various oxidation states, such as Mn(VII), Mn(V), and Mn(VI) in the alkaline medium. The colour of the reaction mixture changes from violet Mn(VII) to dark green through blue Mn(IV) were observed. It is plausible that blue colour originated from the violet of permanganate and the green from manganate, excluding the accumulation of hypomanganate. It is clear from figure 7 that the concentration of MnO_4^- decreases at wavelength 526 nm, while increases at 610 and 460 nm are due to Mn(VI).

The reaction between Mn(VII) and enrofloxacin in alkaline medium has Stoichiometry 2:1, having first order dependence with permanganate and enrofloxacin and less than unit order with OH^- concentration. The results shows that OH^- ions first combined with permanganate to form a basic permanganate reactive species $[MnO_4 \cdot OH]^{2-}$.[33, 36] Then $[MnO_4 \cdot OH]^{2-}$ reacts with the one mole of enrofloxacin in the rate determining step to give a free radical derived from enrofloxacin and Mn(VI). In further fast step, free radical reacts with another molecule of $[MnO_4 \cdot OH]^{2-}$ to produce the product 7-amino fluoroquinolone, Mn(VI), NH_3 and other products (Scheme 1). The effect of ionic strength and dielectric constant on the rate explains qualitatively the involvement of a neutral molecule in the reaction.



Scheme 1: Proposed mechanism for the oxidation of enrofloxacin by alkaline permanganate

From the scheme 1, the following rate law can be derived as follows:

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = k_1[MnO_4.OH]^{2-}\,[ENR] \quad (1)$$

$$= k_1 K_1 [MnO_4^-]_f [ENR]_f [OH^-]_f \quad (2)$$

The total concentration of permanganate is given by:

$$[MnO_4^-]_t = [MnO_4^-]_f + [MnO_4.OH]^{2-}_f$$

$$= [MnO_4^-]_f + K_1[OH^-]_f[MnO_4^-]_f$$

$$= [MnO_4^-]_f\,(1 + K_1[OH^-]_f)$$

$$\text{So, } [MnO_4^-]_f = \frac{[MnO_4^-]_t}{(1 + K_1[OH^-]_f)} \quad (3)$$

Here "t" and "f" stands for total and free concentration.

$$[OH^-]_f = \frac{[OH^-]_t}{(1 + K_1[MnO_4^-]_f)} \quad (4)$$

Putting equation (3) and (4) in equation (2) and omitting "t" and "f" subscripts

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = \frac{k_1K_1[MnO_4^-]\,[ENR]\,[OH^-]}{(1 + K_1[OH^-])\,(1 + K_1[MnO_4^-])} \quad (5)$$

$$= \frac{k_1K_1[MnO_4^-]\,[ENR]\,[OH^-]}{1 + K_1[OH^-] + K_1[MnO_4^-] + K_1^2[OH^-][MnO_4^-]} \quad (6)$$

$K_1[MnO_4^-]$ And $K_1^2[OH^-][MnO_4^-] \ll 1$ or neglected due to low concentration of $[MnO_4^-]$ used in the experiment so equation (6) change into equation (7)

$$\text{Rate} = \frac{-d[MnO_4^-]}{dt} = \frac{k_1K_1[MnO_4^-]\,[ENR]\,[OH^-]}{1 + K_1[OH^-]} \quad (7)$$

$$\frac{\text{Rate}}{[MnO_4^-]} = k_{obs} = \frac{k_1K_1[ENR]\,[OH^-]}{1 + K_1[OH^-]} \quad (8)$$

$$k' = \frac{k_{obs}}{[ENR]} = \frac{k_1K_1\,[OH^-]}{1 + K_1[OH^-]} \quad (9)$$

Equation (9) can be rearranged as

$$\frac{1}{k'} = \frac{[ENR]}{k_{obs}} = \frac{1}{k_1K_1\,[OH^-]} + \frac{1}{k_1} \quad (10)$$

According to Equation (10) the plot of $1/k'$ versus $1/[OH^-]$ is linear with positive intercept and slope (Figure 8) at three different temperature 25°C, 30°C and 35°C. The rate constant k_1, of the slow step and the equilibrium constant K_1 of scheme 1 was obtained from the intercept and slope of the plots $1/k'$ versus $1/[OH^-]$. The energy of activation was determined by the plot of log k_1 versus 1/T (Table 2) from which activation parameters was calculated. The value of K_1 (9.38 L mol^{-1}) is in good agreement with that derived in earlier work[33] (literature value is 9.3 L mol^{-1} at 30°C). Van't Hoff's plot of log K_1 versus 1/T give the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG (Table 2).

The ionic strength had no effect on rate of reaction which is in the correct way of involvement of neutral species. The effect of solvent on the rate of reaction has been described in detail in the literature.[37] For the interaction between a negative ion and dipole or two dipoles, a plot of log k_{obs} versus $1/D$ gives a straight line with negative slope while for interaction between a positive ion and dipole a positive slope results. In the present study, rate of the reaction increases with decrease in the dielectric constant of the medium, which cannot be explained by Amis theory[37] because the existence of a positive ion is improbable in the alkaline medium. Since permanganate is a one electron oxidant in alkaline medium, the reaction between substrate and oxidant would give rise to a radical intermediate. However, an increase in the rate of reaction with decreasing dielectric constant may be due to the increased formation of active reactant species at low dielectric constant.

The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ are both favourable for electron transfer process.[38] The value of $\Delta S^{\#}$ within the range of radical reaction has been ascribed[39] to the nature of electron pairing and un-pairing process. Absence of the evidence of intermediate complex formation suggests that the reaction most probably occurs through outer-sphere mechanism.[40]

CONCLUSION

The Kinetic study of oxidation of enrofloxacin by permanganate in alkaline medium has been studied. It is interesting to note that the oxidant species $[MnO_4^-]$ requires pH > 12, below which the system becomes disturbed and the reaction proceeds further to give a reduced oxidation product as manganese(IV), which slowly develops a yellow turbidity. Hence, the role of pH in the reaction medium is important. The oxidant, manganese(VII), exists in alkali media as alkali-permanganate species $[MnO_4{\cdot}OH]^{2-}$, which takes part in the chemical reaction. The main reaction product was characterized by LC-MS and FT-IR techniques. Chemical oxidation using Mn(VII) has been widely used for treatment of pollutants in drinking water and waste water applications. The proposed mechanism is consistent with product, mechanism and kinetic studies.

Table 1: Effects of Variation of [MnO_4^-], [ENR] and [OH^-] on the Oxidation of Enrofloxacin by Permanganate in Aqueous Alkaline Medium at 30°C and I = 0.10 mol L^{-1}

$10^4 \times [MnO_4^-]$ (mol L^{-1})	$10^3 \times$ [ENR] (mol L^{-1})	$10^2 \times [OH^-]$ (mol L^{-1})	$10^3 \times k_{obs}$ (s^{-1})
1.0	5.0	5.0	6.12
2.0	5.0	5.0	6.10
3.0	5.0	5.0	6.16
4.0	5.0	5.0	6.14
5.0	5.0	5.0	6.10
6.0	5.0	5.0	6.18
7.0	5.0	5.0	6.09
5.0	2.0	5.0	2.48
5.0	3.0	5.0	3.71
5.0	4.0	5.0	4.92
5.0	5.0	5.0	6.10
5.0	7.5	5.0	8.96
5.0	10.0	5.0	11.99
5.0	5.0	2.0	3.12
5.0	5.0	3.0	4.16
5.0	5.0	4.0	5.18
5.0	5.0	5.0	6.10
5.0	5.0	7.5	7.64
5.0	5.0	10.0	8.37

Table 2: Activation and Thermodynamic Parameters for the Oxidation of Enrofloxacin by Alkaline Permanganate from Scheme 1

Temperature (Kelvin)	k_1 (L mol^{-1} s^{-1})
298	3.09
303	4.30
308	5.84
Activation parameters	Value
E_a (kJ mol^{-1})	34.08
$\Delta H^{\#}$ (kJ mol^{-1})	31.57
$\Delta S^{\#} \pm$ (J K^{-1} mol^{-1})	–133.03
$\Delta G^{\#} \pm$ (kJ mol^{-1})	70.19
Temperature (Kelvin)	K_1 (L mol^{-1})
298	11.22
303	9.38
308	6.73
Thermodynamic quantities	Value
ΔH (kJ mol^{-1})	–28.72
$\Delta S \pm$ (J K^{-1} mol^{-1})	–92.8
$\Delta G \pm$ (kJ mol^{-1})	–1.72

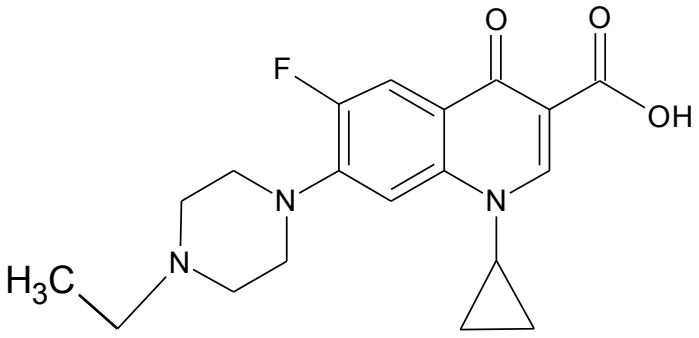


Figure 1: Structure of Enrofloxacin (ENR)

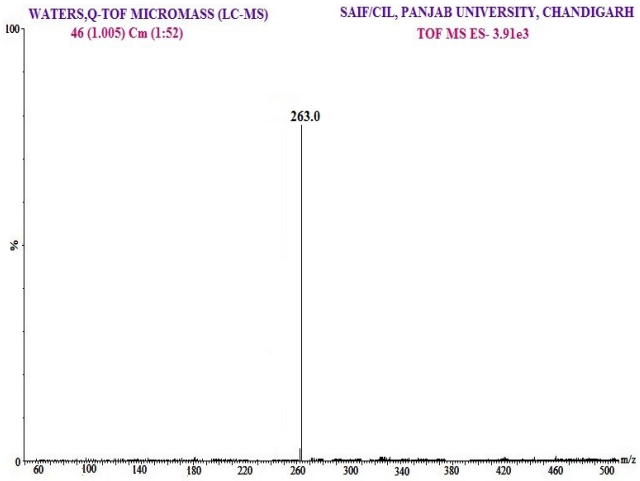


Figure 2: LC-ESI-MS spectra of oxidation product of enrofloxacin

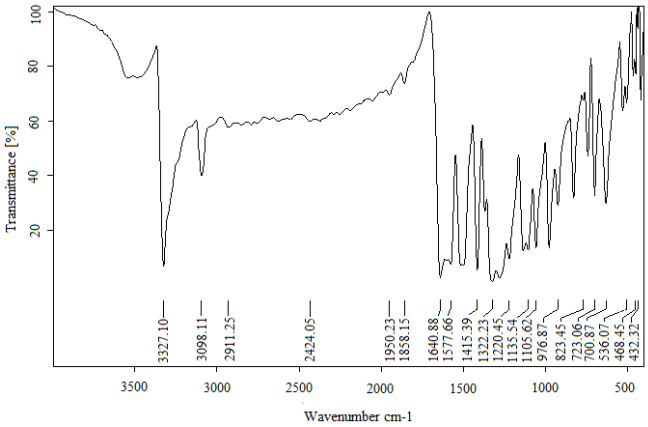


Figure 3: FTIR spectra of the oxidative product of enrofloxacin by permanganate in aqueous alkaline medium

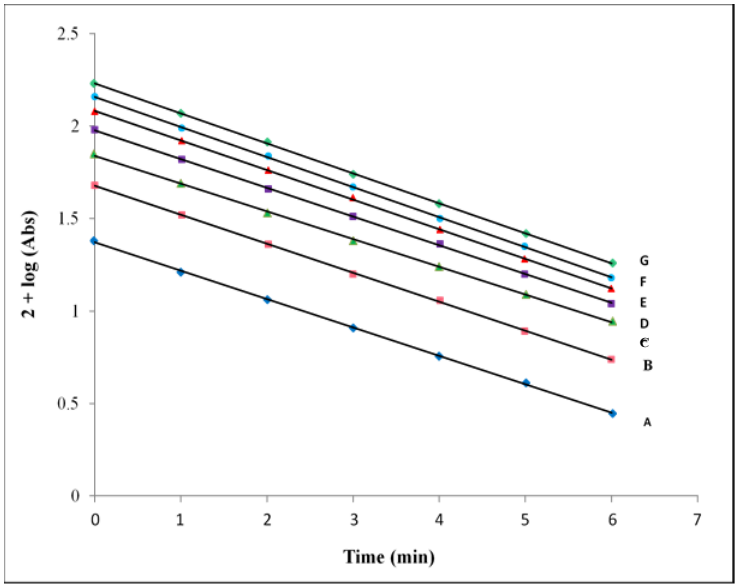


Figure 4: First order plots of the variation of permanganate concentration at 30°C: [ENR] = 5.0 × 10^{-3} mol L^{-1}, [OH^-] = 5.0 × 10^{-2} mol L^{-1} and I = 10.0 × 10^{-2} mol L^{-1}. [MnO_4^-] × 10^{-4} mol L^{-1} = (A) 1.0, (B) 2.0, (C) 3.0, (D) 4.0, (E) 5.0, (F) 6.0, (G) 7.0

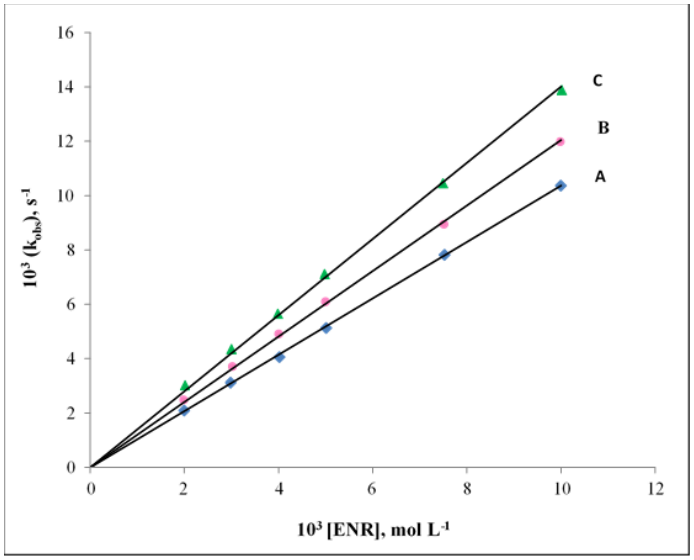


Figure 5: Plot of [ENR] versus k_{obs} at (A) 25°C, (B) 30°C, (C) 35°C: [KMnO4] = 5.0 × 10^{-4} mol L^{-1}, [OH^-] = 5.0 × 10^{-2} mol L^{-1} and I = 10.0 × 10^{-2} mol L^{-1}

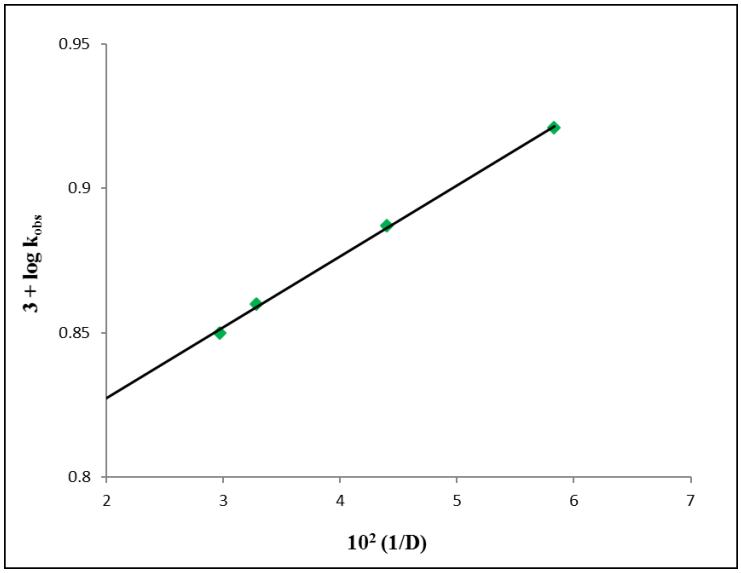


Figure 6: Effect of dielectric constant on the oxidation of enrofloxacin by alkaline permanganate at 30°C

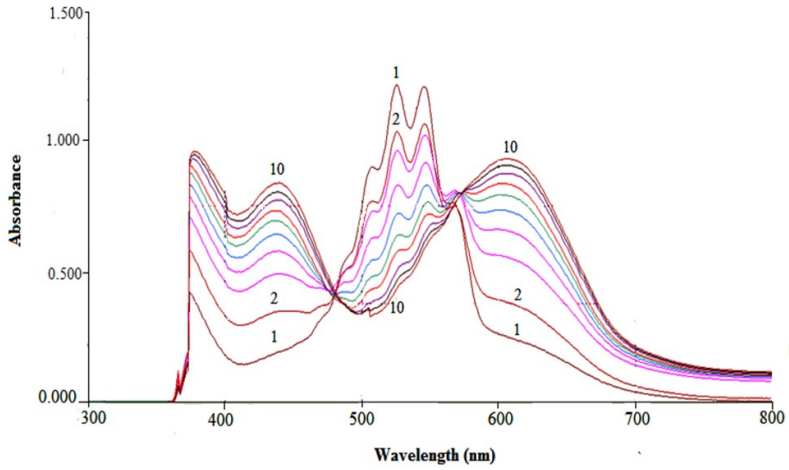


Figure 7: Spectral changes during the oxidation of enrofloxacin (ENR) by permanganate in alkaline medium at 30°C: [$KMnO_4$] = 5.0 × 10^{-4} mol L^{-1}, [ENR] = 5.0 × 10^{-3} mol L^{-1}, [OH^-] = 5.0 × 10^{-2} mol L^{-1} and I = 10.0 × 10^{-2} mol L^{-1}

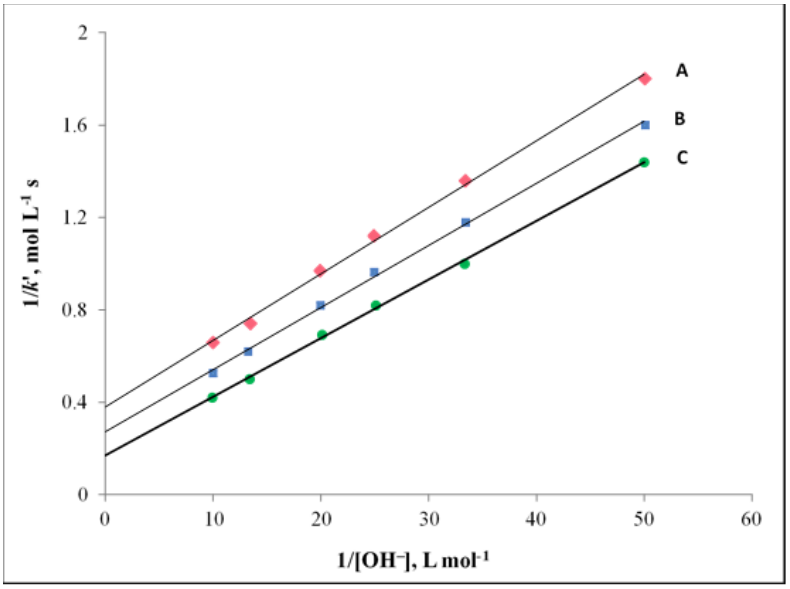


Figure 8: Plots of 1/k' versus 1/[OH^-] at different temperatures (A) 25°C, (B) 30°C, (C) 35°C: [$KMnO_4$] = 5.0 × 10^{-4} mol L^{-1}, [ENR] = 5.0 × 10^{-3} mol L^{-1} and I = 10.0 × 10^{-2} mol L^{-1}

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