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Research Paper

Micellar oxidative transformation of ciprofloxacin: a kinetic investigation

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Environmental context. Pollution of the aquatic environment by drugs results not only during their manufacture, but also from the excretion of drug residues and the discharge of expired drugs by households and hospitals. The transformation of ciprofloxacin, one of the leading antibiotic drugs, in the presence of surfactants has been investigated. The results provide a better understanding of how ciprofloxacin degrades in aquatic environments by considering the effect of omnipresent surfactants.

Abstract. The kinetics of the oxidative transformation, i.e. oxidative degradation, of ciprofloxacin (CIP) by chloramine-T (CAT) in cationic and anionic micelle media during the water chlorination process was studied spectrophotometrically at 275 nm and 298 K. The influence of added salts ($1–10 \times 10^{-4}$ mol dm^{-3}) and solvent polarity of the medium on the reaction was studied. The orders with respect to substrate CIP and oxidant CAT were found to be first order in each. The variation of acid concentrations showed opposite effects in cationic and anionic micellar aggregates. Liquid chromatography–electrospray ionisation mass spectrometry was used to identify degradation products of CIP, which confirmed the full dealkylation of the piperazine ring in CIP as the major product. The piperazine moiety of CIP is the principal active site for the CAT during oxidation. Activation parameters for the CIP degradation in cationic and anionic micelles were evaluated by studying the reaction at different temperatures, which lent further support to the proposed degradation mechanism for CIP. The rate constants were evaluated to confirm the micellar effect from incorporating sodium dodecyl sulfate and cetyltrimethylammonium bromide in the reaction mixture and the intrinsic reactivity constants were determined in the aqueous as well as in the micellar pseudo-phases as 4.85 and 0.0083.

Additional keywords: chloramine-T, degradation, micellar effects.

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Introduction

One of the primary tasks of environmental chemistry has been detection, determination and fate studies of pharmaceuticals and organic compounds in different compartments of the environment, particularly in water ecosystems where analytical chemists have played an important role in developing procedures for determination or degradation of a wide spectrum of chemical species including toxicants and species of biological interest in complex samples.[1–6] The persistence of different drugs in the aqueous environment results from their manufacturing by pharmaceutical industries to consumption by humans and excretion of drug residues, and discharge of large quantities of expired drugs by households as well as hospitals.[3,7,8] Therefore, the use of large amounts of antibiotics, hormones, analgesic, sedative drugs, and different disinfectants preparations as well as difficulty in their complete inactivation in water treatment has been a serious problem.[3,9] The use of water polluted with pharmaceutical residues and their metabolites disturbs balance in the body and enhances dangerous resistance to drugs, creating serious problems for human health.[10] Some review articles have been published dealing with environmental and analytical problems related to pharmaceutical residues.[3,11,12]

Micellar catalysis is an invention in the field of chemical kinetics. Thus, surfactants and their properties have received considerable attention in the last few decades.[13,14] Apart from their other specific properties, the ability of surfactants to affect the rates of chemical reactions has become of interest as they play a role of catalyst in various physical processes as well as in

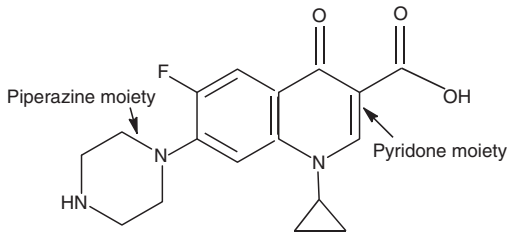


Fig. 1. Structure of CIP showing pyridine and piperazine moieties.

organic, biochemical and physiological reactions. During the oxidation of a substrate, the surfactant plays an important role in the reaction pathway in acidic as well as basic media[14–17] because micelles are effective catalysts for a wide range of organic reactions.[15–17] An overview of several extensive monitoring programs on the determination of various classes of surfactants in raw and treated waste water revealed that 95–98 % surfactant load removal can be achieved during conventional water treatment processes, leaving the rest either in their active forms or in metabolite forms that are more toxic than the parent compounds.[18–26] Release of sewage effluent into natural water reservoirs and sludge clearance onto soil cause contamination because surfactants as well as pharmaceuticals are the major contaminants reaching the water compartment of the environment. Thus, to reduce the concentration of surfactants, pharmaceuticals and their metabolites in waste-water effluents, some researchers have reported advanced oxidation processes (AOPs), especially for the removal of pharmaceutical from waste water.[27–34] However, to date, there are not many reports on the effect of surfactants on the oxidative transformations of pharmaceuticals, except where we have reported the influence of cationic[34] and anionic surfactants[35] on the oxidative transformation of norfloxacin.

With increased surfactant concentrations in aquatic systems, the chemical and physical properties of the solution change abruptly over a range up to the critical micelle concentration (CMC). After the achievement of CMC, micelles or aggregates tend to form in the solution, where the rates of various reactions are affected by the micelles formed from surfactants.[4,17] Thus, the kinetics of a bimolecular reaction between a neutral substrate and a charged reagent are usually strongly modified in aqueous solutions by the presence of micellar aggregates of ionic surfactants.[20–22,36–40] Therefore, the phenomenon of 'micellar catalysis' has been investigated by many researchers for several systems.[21,22,34–40]

The drug ciprofloxacin (cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(piperazinyl)-quinolone-3-carboxylic acid) (CIP) is one of the leading fluoroquinolones used in hospitals, where they make their way into the different environmental compartments because there is no regulation of concentration limits of such compounds. The structure of CIP, which has piperazine and pyridone moieties, is shown in Fig. 1. Few researchers have reported the oxidation of CIP by different oxidants.[41–46] However, a review of the literature revealed that none of the investigations considered the influence of surfactants on the degradation of CIP that has reached the aquatic environment, whereas the presence and simultaneous accumulation of surfactants have widely been reported.[33,34] Therefore, the present study was undertaken to elucidate the effect of surfactants on the oxidative transformation of the pharmaceutical CIP in an aqueous environment. Thus, in continuation of our studies,[34,35] the current report is on the study of kinetic aspects of the oxidative transformation of CIP by the commonly used disinfectant chloramine-T i.e. *N*-chloro-*p*-toluenesulfonamide (CAT) under the influence of cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulfate (SDS) micelle media.

Experimental

Materials

Analytical grade reagents were used without further purification. All the solutions were prepared using triple-distilled water. The CIP (Sigma–Aldrich) stock solution was prepared by dissolving a known amount of its hydrochloride salt and was stored in amber-coloured bottles to prevent any photochemical reactions. To recrystallise CTAB (Merck), it was dissolved in minimum quantity of lukewarm methanol (MeOH) at ~40 °C. Diethyl ether (Et_2O) was then added with constant stirring until a permanent white precipitate was obtained. The content was cooled to room temperature and placed in the refrigerator for further cooling. The crystalline white solid obtained was filtered in a Buchner funnel. Finally, the crystals were washed with excess cold ether and air-dried for further use. SDS (Sigma) was used as received, without further purification.

Kinetic measurement

All reactant solutions were placed in a thermostatic water bath for 30 min in order to attain a temperature of 298.0 ± 0.2 K. The kinetics of the reaction were studied by taking the requisite amounts of CIP, surfactant, acid (H_2SO_4 with CTAB, and $HClO_4$ with SDS) and CAT in a black-coated reaction vessel that was kept in the thermostatic water bath at 298 ± 0.2 K. The reaction initiation time was taken as the time when half of the required volume of thermally equilibrated CAT was added to the reaction system. The kinetics of the reaction were followed spectrophotometrically at 275 nm by measuring the absorbance (A), at constant intervals of time, on a Varian Cary 50 Bio UV-vis spectrophotometer (Systronics, India), using a 10-mm quartz cuvette, and under pseudo-first order conditions where [CIP] << [CAT]. The slope of log k_{obs} *v.* log(concentration) (where k_{obs} is the observed rate constant), while keeping all other concentrations and conditions constant, gave the reaction order with respect to the particular reagent. The experiments were carried out in duplicate and the rate constants were found to be reproducible and well within 4 % error.

The spectral changes occurring during a typical kinetic run at each minute for the oxidation of CIP by CAT in CTAB and SDS micelle media were recorded in the region of 220 to 360 nm and are shown in Fig. 2a, b, respectively. There is a continuous decrease of absorbance at 275 nm, which clearly indicates the disappearance of CIP with the progress of the reaction.

Determination of CMC

The determination of CMC values is important in understanding the self-organising activities of the surfactants. In the presence of the reactants at the required temperature, the CMCs of the surfactants, CTAB and SDS were evaluated conductometrically by measuring the conductivity with a Systronics 304 conductometer (Alpha Scientific Works, Bhilai (CG), India) at 298.0 ± 0.2 K.

Stoichiometry and product analysis

The stoichiometry of the reaction, with a large excess of CIP at 298 K, was determined by estimating unreacted CIP, which

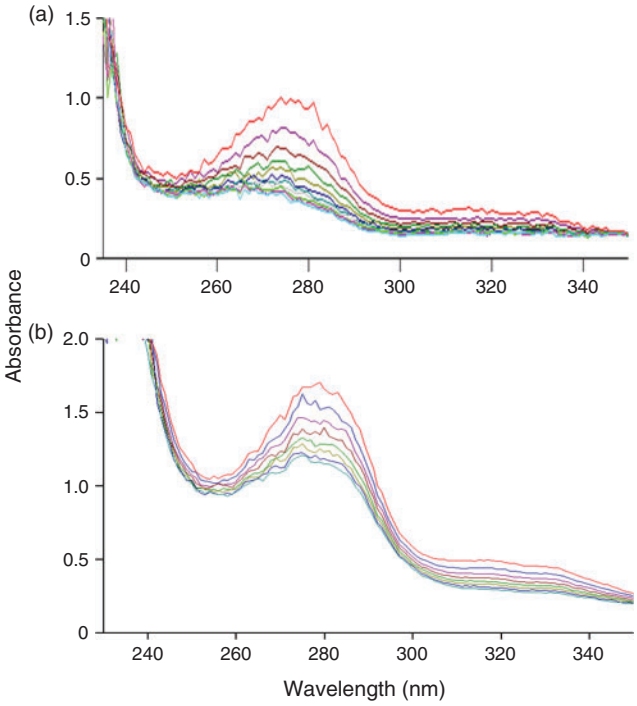


Fig. 2. Spectral changes at 1-min intervals under the influence of (a) cetyltrimethylammonium bromide (CTAB), and (b) sodium dodecyl sulfate (SDS) on the oxidative transformation of ciprofloxacin (CIP) (2.0×10^{-5} mol dm^{-3}) by CAT (chloramine-T) (2.0×10^{-4} mol dm^{-3}) in acidic medium.

revealed that the oxidation of each mole of CIP requires two moles of CAT. For the identification of the oxidation products of CIP, excess CAT over CIP was reacted in H_2SO_4 media. *p*-Toluenesulfonamide (PTS), the reduced product of the oxidant CAT, was visualised by thin-layer chromatography (TLC).[47] The main oxidation product of CIP has complete dealkylation of the piperazine ring, leading to formation of the $–NH_2$ product. The products isolated were confirmed by gas chromatography–mass spectrometry (GC-MS) analysis. The products were extracted with diethyl ether, with slow evaporation of the ether layer for concentration before analysing with GC-MS (Jeol-JMS, Mate-MS system, Nagoya, Japan). The illustration of liquid chromatography–electrospray ionisation mass spectrometry (LC-ESI-MS-MS) spectrum (Fig. 3) of the oxidation products of CIP showed the presence of products with molecular ions at *m*/*z* 364 (5 %), 351 (10 %), 295 (15 %), 263 (55 %) and 193 (40 %). The molecular ion of CIP is *m*/*z* 330; *m*/*z* 351 corresponds to the *N*-oxide product whereas *m*/*z* 364 corresponds to the $[M + 35]^+$ product ($C_{17}H_{18}FN_3O_5$) with respect to CIP.[48] The product with a fully dealkylated piperazine ring was identified as the major product, corresponding to *m*/*z* 263 (the $–NH_2$ product), and had the highest intensity. This has also been identified previously as photodegradation product[47,49] and an oxidation product[48,50] of CIP. The peak at *m*/*z* 295 may correspond to the chlorinated product of the fully dealkylated product (i.e. *m*/*z* 263). The oxidation product of CIP was also characterised by Fourier-transform infrared (FT-IR) spectral studies (KBr) showing absorbances at 1560m ($–NH_2$), 1621s (C=O), 3059s (=NH), 3500s (–OH) cm^{-1}, where s is strong and m is medium. On the basis of stoichiometric and product analysis, the formulated stoichiometric equation for the reaction between CIP and CAT is given in Scheme 1.

Results and discussion

Reaction–time curve

The slope of the plot of log *A* *v.* time (min) gave the pseudo-first order rate constants (Fig. S1) where kinetic plots were linear for more than four half-lives when *A* is taken up to 80 % completion of the reaction. The reaction time plots of CIP oxidation at various CAT concentrations in the presence of cationic (CTAB) and anionic (SDS) surfactants were found to be linear (Fig. S2). The linearity of the plots clearly indicates that the oxidation kinetics proceed at a consistent rate. For several reaction runs with [CIP] < [CAT], the unreacted CIP was determined spectrophotometrically by measuring the decrease in the absorbance of CIP at 275 nm. The rate constants of the reactions in each kinetic run were determined from the slope of the tangent in plots of log *A* against time.

Influence of [CIP]

The order with respect to [CIP] was determined by studying the kinetics of the reaction at different [CIP] in the presence of 0.6–2.5×10^{-5} mol dm^{-3} CTAB and 0.05–3.5×10^{-5} mol dm^{-3} SDS while keeping other reagent concentrations fixed. The rate constants were dependent on initial [CIP], confirming first order with respect to CIP. Fig. 4 shows the plot of the rate of the reaction against [CIP], based on which the rate dependence can be given by the following equation: $-d[CIP]/dt$ (reaction rate) $= k_{obs}[CIP]$, where *t* is time.

Influence of oxidant [CAT]

The effect of [CAT] on the reaction rate was studied by varying its concentration over different ranges. The order of reaction with respect to CAT was confirmed by varying its concentration from 1 to 10×10^{-4} mol dm^{-3} when studied in the presence of CTAB or 2–12×10^{-4} mol dm^{-3} in the presence of SDS, keeping other reaction variables constant. It was observed that the decrease in absorbance (reaction rate) after 2 min was quite slow, which indicated the retardation effect of the products formed, i.e. the rate of oxidation is influenced by the products formed during the reaction. As shown in Fig. 5, the plot of log (reaction rate) *v.* log [CAT] in cationic (CTAB) as well as anionic (SDS) micelles increases with increasing [CAT] at lower concentrations, i.e. it shows first-order dependence on CAT but tends towards zero order at higher concentrations. It is well documented that CAT undergoes a two-electron change in its reactions, forming PTS and sodium chloride.[50]

Effect of acid concentration

To observe the effect of [acid] on the rate constant, in the case of the CTAB-catalysed reaction, $[H_2SO_4]$ was varied in the range $1–10 \times 10^{-4}$ mol dm^{-3}. The reaction rate was found to decrease with increase in $[H_2SO_4]$. In the case of the SDS-catalysed reaction, $[HClO_4]$ was also varied from 1 to 10×10^{-4} mol dm^{-3} but the rate constant was found to increase at initial concentrations while achieving a constant value at higher concentrations. The effect of $[HClO_4]$ shows that the oxidation of CIP proceeds through the adsorption of H^+ and reactants (CIP and CAT) on the surface of SDS (Fig. S3).

Influence of additives

To judge the effect of additives on the oxidative transformation of CIP, different kinetic runs in the presence of varying concentrations of [acetic acid], [PTS], [HCOONa], [KCl], [KNO_3]

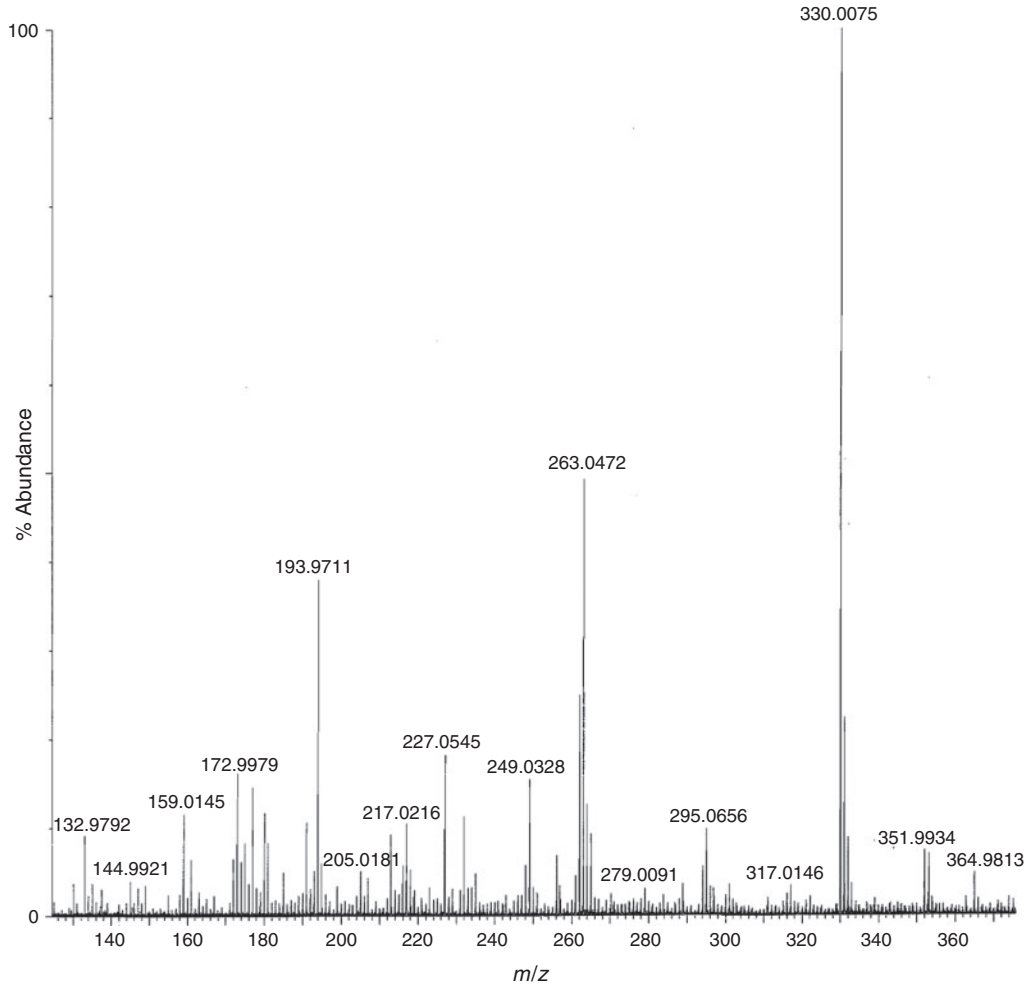
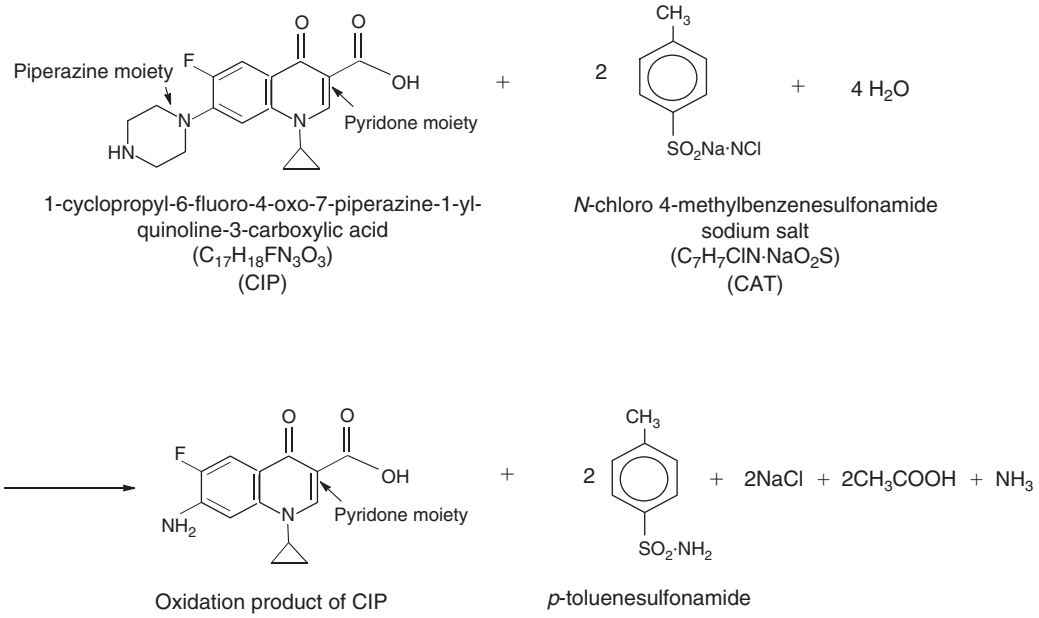


Fig. 3. Liquid chromatography–electrospray ionisation mass spectrometry (LC-ESI-MS-MS) spectra of the oxidation products of ciprofloxacin.



Scheme 1. Stoichiometric equation for the reaction between CIP and CAT.

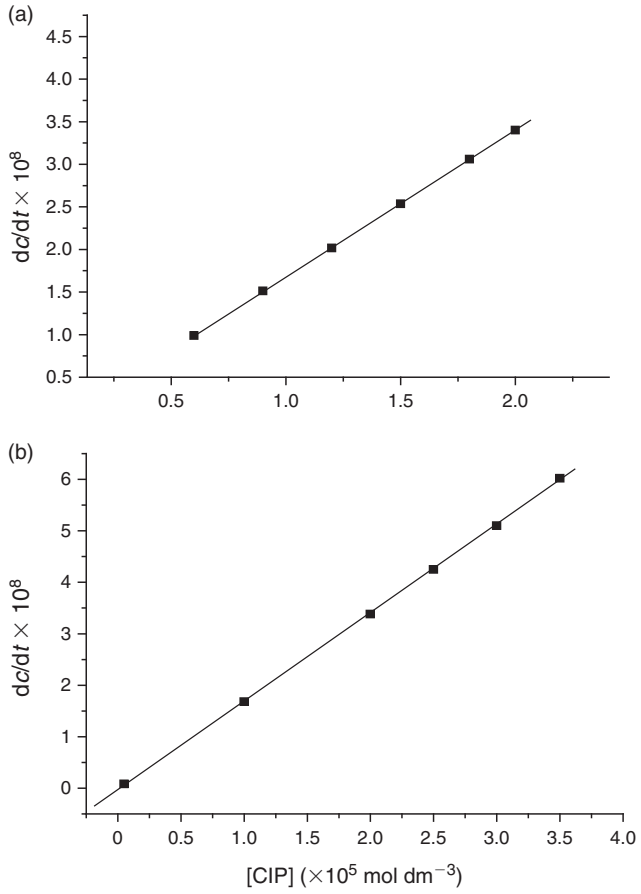


Fig. 4. The effect of the variation of substrate concentration, i.e. [CIP], (ciprofloxacin) on the rate of the reaction (d*c*/d*t*) in the presence of (a) cetyltrimethylammonium bromide (CTAB) (reaction conditions: $[H_2SO_4] = 2.0 \times 10^{-4}$ mol dm^{-3}, [CAT] = 2.0×10^{-4} mol dm^{-3}, [CTAB] = 10.0×10^{-4} mol dm^{-3} at $T = 298.0 \pm 0.2$ K) and (b) sodium dodecyl sulfate (SDS) (reaction conditions: $[HClO_4] = 4.0 \times 10^{-4}$ mol dm^{-3}, [CAT] = 2.0×10^{-4} mol dm^{-3}, [SDS] = 10.0×10^{-3} mol dm^{-3} at $T = 298.0 \pm 0.2$ K) (CAT, chloramine-T). *c*, concentration.

and $[K_2SO_4]$ were performed in cationic micellar media with CTAB. The results (k_{obs}) presented in Table 1 clearly show that the rate of reaction had no influence from [acetic acid] variation and had negligible effect from the variation of salts, $[HSO_4Na]$, [KCl] and $[KNO_3]$. However, the rate constant (k_{obs}), i.e. reaction rate, increases with increasing $[K_2SO_4]$ as shown in Table 1. The enhancement of the micellar catalysis rate by added electrolytes is caused by their changing shape or reducing the charge density on the micelles. Electrolytes decrease the CMC and increase the aggregation number of ionic micelles,[51] which may be owing to the increased screening by counter-ions and thereby decrease in the effective charge density of the micelle. The observed rate constant steadily decreased with increasing concentrations of PTS, which is the reduced product of the oxidant CAT, and the same is shown in Table 1 (Fig. S4).

The influence of the concentrations of various additives on the oxidative transformation of CIP by CAT in presence of anionic-micelle SDS was also studied by varying their concentrations and the results are presented in Table 2. As in case of CTAB, all the additives do not have any pronounced effect except PTS (Table 2). In an anionic micelle (SDS), increasing [PTS] from 1 to 10×10^{-4} mol dm^{-3} in the reaction mixture also caused a decrease in the reaction rate. The plot of k_{obs} *v.* [PTS] shows a fractional slope (−0.331), indicating PTS involvement in a fast pre-equilibrium to the rate-determining step (Fig. S5). The effect of the ionic strength of the medium was studied using KNO_3 and no noteworthy effect was observed on the reaction rate (Table 2). Also, there was no pronounced effect on the reaction rate, i.e. k_{obs}, due to the decrease in dielectric constant of the medium that was achieved by increasing addition of acetic acid to the reaction mixture (Table 2).

Effects of surfactants

The conductometer was calibrated with 0.01 M KCl solutions. The breakpoint of the near-straight line in the plots of equivalent (specific) conductivity *v.* [surfactant] gave the CMC values (Fig. 6) that are indicative of micelle formation (Fig. S6 and Table S1).

The typical profile of the pseudo-first order rate constants, k_{obs}, as a function of the concentration of the surfactants (CTAB and SDS) for the oxidation of CIP at 298 K in aqueous acidic solutions has been studied. The experimental rate profiles obtained are characteristics of micellar-catalysed reactions in aqueous solutions in the presence of both the surfactants CTAB and SDS. The addition of CTAB and SDS to the reaction media caused an increase in the rate of oxidation up to a point where there was total incorporation of the substrate (CIP) in the micellar phase. Subsequent addition of the surfactant caused a decrease in the reaction rate, probably due to the dilution of the reactive counter-ions in the Stern layer of a higher number of micelles. There is a well-defined maximum in the rate profile at 4.5×10^{-4} mol dm^{-3} for CTAB and at 4.0×10^{-3} mol dm^{-3} for SDS. Both the surfactants (cationic CTAB and anionic SDS) increase the reaction rate despite being opposite in nature. It may well be confirmed by the study of the effect of increasing acid (H_2SO_4 and $HClO_4$) concentrations (inset in Fig. S7).

Influence of temperature and activation parameters

To calculate activation parameters, the effect of temperature on the reactions between CIP and CAT in the absence and presence of CTAB and SDS was studied in the 298–313 K range. The enthalpy of activation ($\Delta H^{\ddagger}$) and entropy of activation ($\Delta S^{\ddagger}$) were calculated using the linear form of the Eyring equation (Eqn 1) where a plot of $\ln(k_{obs}/T)$ *v.* $1/T$ produced a straight line (T is absolute temperature)[52] while Gibbs free energy of activation ($\Delta G^{\ddagger}$) was calculated using Eqn 2. Energy of activation (ΔE_a) was calculated using the Arrhenius equation, where the slope of the straight-line plot of log k_{obs} *v.* log k gave the value of the activation energy, E_a. The calculated activation parameters for the oxidative transformation of the drug CIP in the presence and absence of the CTAB and SDS micelles are shown in Table 3.

$$\ln\frac{k_{obs}}{T} = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R} \quad (1)$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \quad (2)$$

Nearly the same values of $\Delta G^{\ddagger}$ in pure aqueous medium and in the presence of surfactants (CTAB and SDS) indicate that a similar mechanism is followed in both media. The large decrease in $\Delta S^{\ddagger}$ in case of CTAB is suggestive of the formation of a more ordered activated complex in surfactant media.[53–56] However, the positive values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ indicate that the

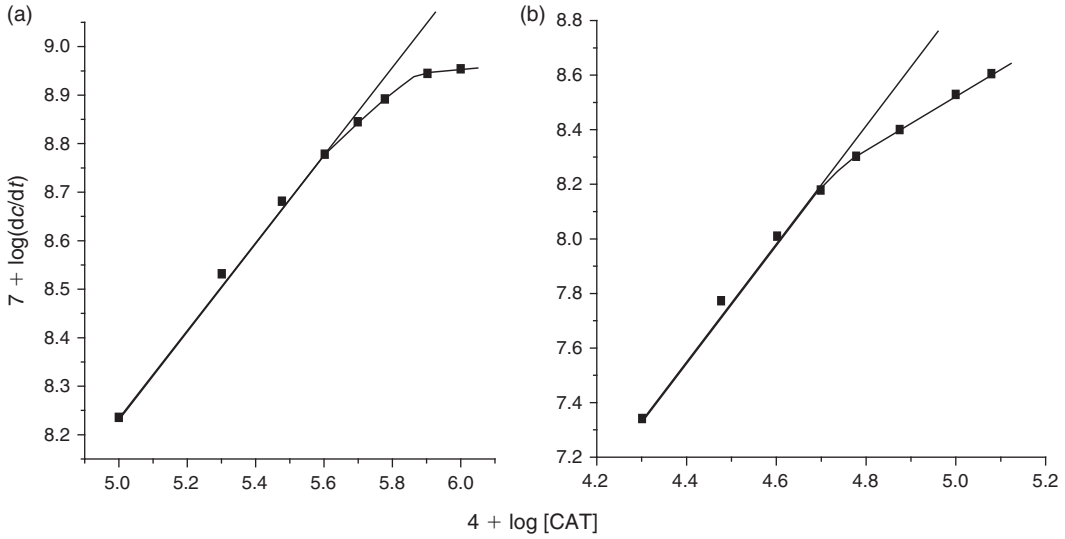


Fig. 5. Effect of [CAT] (chloramine-T) on reaction rate (dc/dt) in the presence of (a) cetyltrimethylammonium bromide (CTAB) (under reaction conditions: [CIP] = 2.0×10^{-5} mol dm^{-3}, [H_2SO_4] = 2.0×10^{-4} mol dm^{-3}, [CTAB] = 10.0×10^{-4} mol dm^{-3}) and (b) sodium dodecyl sulfate (SDS) (under the reaction conditions: [CIP] = 2.0×10^{-5} mol dm^{-3}, [$HClO_4$] = 4.0×10^{-4} mol dm^{-3}, [CAT] = 2.0×10^{-4} mol dm^{-3}, [SDS] = 10.0×10^{-3} mol dm^{-3}) at T = 298.0 ± 0.2 K (CIP, ciprofloxacin). c, concentration.

Table 1. Effects of additives on reaction rate, i.e. k_{obs}, in the presence of cetyltrimethylammonium bromide (CTAB)
Reaction conditions: T = 298.0 ± 0.2 K, [CAT] = 2.0×10^{-4} mol dm^{-3}, [CIP] = 2.0×10^{-5} mol dm^{-3}, [H_2SO_4] = 2.0×10^{-4} mol dm^{-3} and [CTAB] = 10×10^{-4} mol dm^{-3}

[Acetic acid] (%)	k_{obs} ($\times 10^3$ s^{-1})	[HSO_4Na] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})	[PTS] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})
5.0	0.10	1.0	1.68	1.0	1.62
				2.0	1.45
10.0	0.10	3.0	1.65	3.0	1.21
				4.0	0.89
20.0	0.10	6.0	1.66	5.0	0.69
				6.0	0.47
30.0	0.10	10.0	1.62	10.0	0.25
[KNO_3] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})	[KCl] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})	[K_2SO_4] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})
1.0	1.66	1.0	1.61	1.0	1.69
2.0	1.67	2.0	1.55	2.0	1.70
3.0	1.64	3.0	1.49	3.0	1.88
4.0	1.66	4.0	1.31	4.0	2.18
5.0	1.66	5.0	1.37	6.0	2.62
6.0	1.65	6.0	1.38	8.0	3.19
8.0	1.64	8.0	1.38	10	3.71
10.0	1.63	10.0	1.32		

transition state formed is highly solvated.[53,54] A large negative value of $\Delta S^{\ddagger}$ (Table 3) clearly indicates the associative mechanisms in the presence of surfactants where an inner-sphere mechanism for binding of reactants in the transition state takes place.[55–57]

Reactive species of CAT

The possibility of existence of free radicals in the reaction mixture and their interference was investigated by adding acrylonitrile to the reaction mixture and leaving it in an inert atmosphere for 24 h. No precipitate was observed on diluting the reaction mixture with methanol, confirming that free radicals were not involved in the reaction.[58]

CAT acts as a mild oxidant in both acidic and alkaline media and undergoes a two-electron change in its reactions, forming the reduced products PTS (p-$CH_3C_6H_4SO_2NH_2$, represented as $TsNH_2$) and sodium chloride.[52] Therefore, depending on the pH of the reaction medium, CAT provides different forms of reactive species.[59–61] Various probable chlorinating, i.e. oxidising, species (TsNHCl, $TsNCl_2$ (dichloramine-T), HOCl and $TsNH_2Cl^+$ or $(H_2OCl)^+$) of CAT exist in acidic media.[62] To confirm the identity of the CAT reactive species, a close look at the influence of acid and [PTS] on the rate of reaction was essential. $TsNCl_2$ is the reactive species in the oxidation of CIP because the reaction is not second order with respect to [CAT] and $TsNH_2$ does not have a negative effect. Experimental

Table 2. Effects of additives on reaction rate in the presence of sodium dodecyl sulfate (SDS)
Reaction conditions: $T = 298.0 \pm 0.2$ K, [CAT] $= 3.0 \times 10^{-4}$ mol dm^{-3}, [CIP] $= 3.0 \times 10^{-5}$ mol dm^{-3}, [$HClO_4$] $= 4.0 \times 10^{-4}$ mol dm^{-3} and [SDS] $= 10 \times 10^{-3}$ mol dm^{-3}

[Acetic acid] (%)	k_{obs} ($\times 10^3$ s^{-1})	[HSO_4Na] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})	[PTS] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})
5.0	1.97	1.0	1.97	1.0	1.95
10.0	1.95	2.0	1.89	2.0	1.54
20.0	1.97	4.0	1.58	4.0	1.09
30.0	1.92	6.0	1.46	6.0	0.83
		8.0	1.39	8.0	0.56
		10.0	1.36	10.0	0.45
[KNO_3] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})	[KCl] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})	[K_2SO_4] ($\times 10^4$ mol dm^{-3})	k_{obs} ($\times 10^3$ s^{-1})
1.0	1.96	1.0	1.99	1.0	1.95
2.0	1.99	2.0	1.99	2.0	1.96
3.0	2.01	3.0	2.04	4.0	1.97
4.0	2.04	4.0	2.07	6.0	1.96
5.0	2.07	5.0	2.09	8.0	1.97
6.0	2.11	6.0	2.12	10.0	1.96
8.0	2.11	10.0			
10.0	2.11				

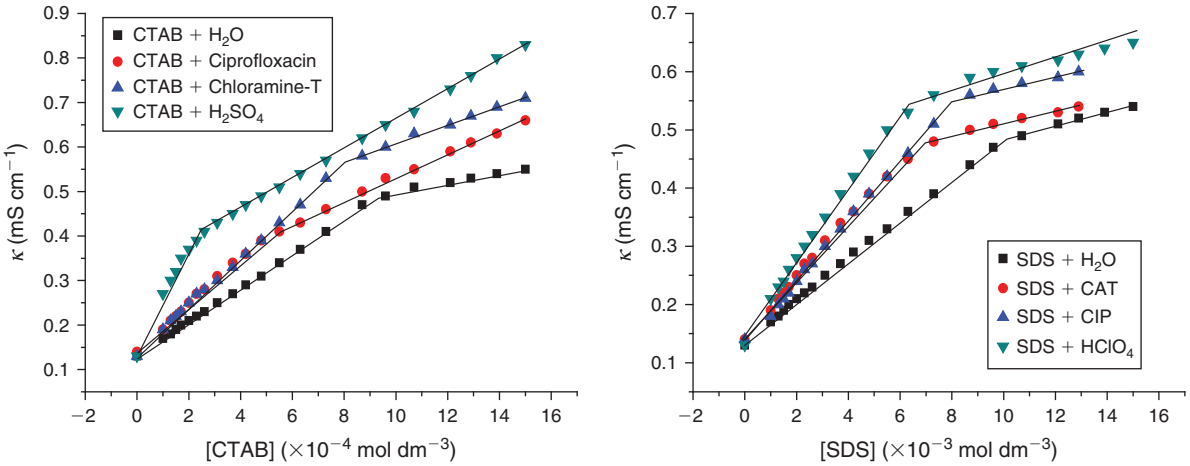


Fig. 6. Plots of specific conductivity versus surfactant concentrations for determination of critical micelle concentration (CMC) values under the experimental conditions given in Tables 1 and 2 for CTAB and SDS respectively.

observation has shown first order dependence on [CAT]. As there is no effect of acid, i.e. [H^+], on the reaction rate, so $TsNH_2Cl^+$ cannot be taken to be the reactive species. Thus, HOCl may be taken as the reactive species in the oxidative transformation of CIP.[59–61]

Rate law and proposed mechanism

The studies on the influence of the reaction variables, other experimental observations and the proposed reaction in Scheme 1 reported above lead us to propose the rate laws for the oxidative transformation of CIP in the absence and presence of the surfactants CTAB and SDS separately.

Oxidative transformation of CIP in absence of surfactant

The mechanism of the oxidative transformation of CIP by CAT in absence of surfactants is given in Eqns 3–5 where Ts stands for *p*-$CH_3C_6H_4SO_2$, K_1 and K_2 are equilibrium constants and k_w represents the rate constant in the aqueous pseudo-phase.

$$TsNHCl + H_2O \overset{K_1}{\rightleftharpoons} TsNH_2 + HOCl \quad (3)$$

$$HOCl + CIP \overset{K_2}{\rightleftharpoons} X^- + H^+ \quad (4)$$

$$X^- \xrightarrow{k_w} \text{Product} \quad (5)$$

On the basis of Eqns 3–5, it can be proposed that the electron flow during oxidation of CIP by CAT is in accordance with electrophilic attack by the oxidant resulting in the formation of an intermediate X^-, which slowly gets converted into product. Considering the conversion of X^- into product, the rate of the reaction is given by Eqn 6.

$$\text{Rate of reaction} = -\frac{d[CIP]}{dt} = k_w[X^-] \quad (6)$$

During the course of the oxidative transformation, the total concentration of CIP, i.e. $[CIP]_T$, is given by Eqn 9, which is derived with the help of Eqns 7 and 8.

Table 3. Comparative account of activation parameters for the oxidative transformation of the drug ciprofloxacin (CIP) in the presence and absence of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) micelles
Reaction conditions: [CIP] = 2.0×10^{-5} mol dm^{-3}, [CAT] = 2.0×10^{-4} mol dm^{-3}, [CTAB] = 10.0×10^{-4} mol dm^{-3}, [SDS] = 10.0×10^{-3} mol dm^{-3} and $T = 298.0 \pm 0.2$ K

Surfactant used	ΔE_a (kJ mol^{-1})		$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1})		$\Delta H^{\ddagger}$ (kJ mol^{-1})		$\Delta G^{\ddagger}$ (kJ mol^{-1})	
	Aqueous medium	Surfactant medium	Aqueous medium	Surfactant medium	Aqueous medium	Surfactant medium	Aqueous medium	Surfactant medium
Without surfactant[A]	34.96	–	−60.21	–	32.42	–	17.98	–
In presence of [H_2SO_4] = 2.0×10^{-4} mol dm^{-3}								
CTAB	22.88	12.63	−116.98	−130.14	20.43	10.09	34.90	38.79
In presence of [$HClO_4$] = 10.0×10^{-3} mol dm^{-3}								
SDS	40.38	28.89	−64.77	−93.32	37.87	26.38	19.34	27.84

[A]Reaction mixture contained CIP + CAT (chloramine-T) + acid.

$$[\mathrm{CIP}]_T = [\mathrm{CIP}] + [\mathrm{X}^-] \tag{7}$$

$$[\mathrm{CIP}]_T = [\mathrm{CIP}] + \frac{K_1K_2[\mathrm{TsNHCl}][\mathrm{CIP}]}{[\mathrm{TsNH_2}][\mathrm{H}^+]} \tag{8}$$

$$[\mathrm{CIP}]_T = [\mathrm{CIP}]\left(1 + \frac{K_1K_2[\mathrm{TsNHCl}]}{[\mathrm{TsNH_2}][\mathrm{H}^+]}\right) \tag{9}$$

Mathematical manipulation of Eqns 6 and 9 gives Eqn 10, which explained the observed kinetic order with respect to the reactants very well.

$$\text{Rate of reaction} = \frac{k_wK_1K_2[\mathrm{TsNHCl}][\mathrm{CIP}]_T}{[\mathrm{H}^+][\mathrm{TsNH_2}] + K_1K_2[\mathrm{TsNHCl}]} \tag{10}$$

From Eqn 10, it can be concluded that the observed rate of reaction depends on the concentration of the substrate CIP and reactive species of oxidant. However, the rate of reaction is inversely influenced by increasing acid concentration, [H^+].

Oxidative transformation of CIP in presence of CTAB

The mechanism of the oxidative transformation of CIP by CAT in the presence of CTAB is given by Eqns 11–14 where K_D, K_3 and K_4 are equilibrium constants. Y^- is an intermediate species formed during the oxidation of CIP by CAT in the presence of the surfactant CTAB, which slowly gives the final product. D_n shows the number n of detergent molecules (D) that aggregate with the substrate (S = CIP) to form the critical micelle (D_nS) associated with the substrate CIP that reacts to yield the product.

$$D_n + \mathrm{CIP} \overset{K_D}{\rightleftharpoons} D_nS \tag{11}$$

$$\mathrm{CAT} + \mathrm{H}^+ \overset{K_3}{\rightleftharpoons} \mathrm{CATH}^+ \tag{12}$$

$$\mathrm{CHATH}^+ + D_nS + H_2O \overset{K_4}{\rightleftharpoons} Y^- + \mathrm{PTS} + 2\mathrm{H}^+ \tag{13}$$

$$Y^- \xrightarrow[\text{slow}]{k_m} \text{Product} \tag{14}$$

The rate constant in the micellar pseudo-phase is represented by k_m and thus the rate of reaction in the presence of CTAB is given by Eqn 15 whereas total concentration of CIP is given by Eqn 16.

$$\text{Rate of reaction} = -\frac{d[\mathrm{CIP}]}{dt} = k_m[Y^-] \tag{15}$$

$$[\mathrm{CIP}]_T = [\mathrm{CIP}] + [D_nS] + [Y^-] \tag{16}$$

Using the equilibria Eqns 11–13 and Eqns 14–16, the following equation, Eqn 17, is obtained.

$$\text{Rate of reaction} = \frac{k_mK_DK_3K_4[D_n][\mathrm{CAT}][\mathrm{CIP}]_T}{[\mathrm{H}^+][\mathrm{PTS}] + K_D[D_n][\mathrm{H}^+][\mathrm{PTS}] + K_DK_3K_4[D_n][\mathrm{CAT}]} \tag{17}$$

The rate law deduced, i.e. Eqn 17, is in good agreement with experimental observations for the degradation of CIP in presence of surfactant CTAB.

Oxidative transformation of CIP in presence of SDS

The mechanism of the oxidative transformation of CIP in the presence of SDS using CAT as the oxidant is shown in Eqns 18–21, where the rate of reaction is given by Eqn 22 and the total concentration of CIP in Eqn 23. D_n is number of surfactant (SDS) molecules and D_nS is the micelle associated with the substrate S, which is CIP.

$$D_n + \mathrm{CIP} \overset{K_D'}{\rightleftharpoons} D_nS \tag{18}$$

$$\mathrm{CAT} + \mathrm{H}^+ \overset{K_5}{\rightleftharpoons} \mathrm{CATH}^- \tag{19}$$

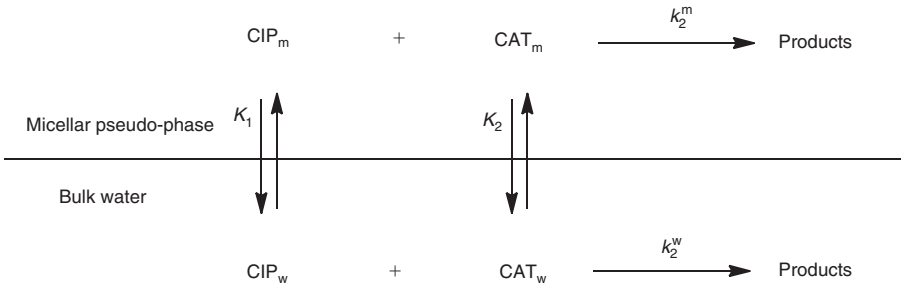
$$\mathrm{CATH}^+ + D_nS \overset{K_6}{\rightleftharpoons} Y + \mathrm{PTS} \tag{20}$$

$$Y \xrightarrow[\text{slow}]{k_m} \text{Product} \tag{21}$$

$$\text{Rate of reaction} = -\frac{d[\mathrm{CIP}]}{dt} = k_m[Y] \tag{22}$$

$$[\mathrm{CIP}]_T = [\mathrm{CIP}] + [D_nS] + [Y] \tag{23}$$

Here K_D', K_5 and K_6 are equilibrium constants and Y is the intermediate species, which slowly dissociates, leading to the formation of the product. On the basis of equilibria Eqns 18–20 and Eqns 21–23, a rate of reaction (Eqn 24) has been obtained that explains the experimental observations for the degradation of CIP in the presence of the surfactant SDS.



Scheme 2. Reaction in aqueous and micellar pseudo phases with different reactivity.

$$\text{Rate of reaction} = \frac{k_m K_D' K_3 K_4 [D_n][CAT][CIP]_T[H^+]}{[H^+][PTS] + K_D'[D_n][H^+][PTS] + K_D' K_3 K_4 [D_n][CAT]} \quad (24)$$

Model application to micelle-catalysed oxidative transformation of CIP by CAT

To understand the catalytic activity of the micelles (CTAB and SDS) in the oxidation of CIP by CAT in acidic medium, a series of kinetic runs were performed in presence of varying [CTAB] and [SDS] separately in the range of 0–12 × 10^{-4} mol dm^{-3} while keeping all other reaction variables constant. The observed pseudo-first-order rate constants plotted against surfactant concentrations clearly show that with increased [CTAB] and [SDS], the rate increases, attains a maximum and decreases steadily. The [CTAB] and [SDS] at which the k_{obs} value becomes maximum are taken as the CMC of the surfactants (Fig. S7). Oversimplified two-dimensional schematic representation of the concentration effect of micelles showing incorporation of reactants into the Stern layer of anionic and cationic micelle moieties are shown in the supplementary material (Fig. S8). The catalysed oxidative transformation of CIP by CAT in the presence of micelles can be well explained by the pseudo-phase kinetic model[62] (for CTAB) and Piszkiewicz's model[63] (for SDS).

Pseudo-phase kinetic model for CTAB-catalysed oxidative transformation of CIP by CAT

The catalytic performance observed during oxidative transformation of CIP by CTAB (Fig. S9) is well explained using the pseudo-phase model of micelles,[62] which is in consensus with reported bimolecular reactions.[62,64] For [CTAB] less than its CMC, the rate constant stays almost constant because it is the reaction only in water where concentrations of the two reactants remain constant. For CTAB concentrations in which the monomers start aggregating, the catalysis effect is observed as a consequence of local reactive concentrations in the Stern layer. Thus, k_{obs} increases as the surfactant concentration increases until it reaches a maximum value, i.e. the CMC. After the CMC, the rate constant decreases owing to dilution of the reactants in the micellar pseudo-phase. When [CTAB] increases, the number and size of the micelles also increases. This behaviour suggests the use of the micellar pseudo-phase model, considering that the loci of reaction are both, i.e. in the aqueous pseudo-phase as well as in the micellar pseudo-phase. The different reactivities in the two pseudo-phases, i.e. aqueous pseudo-phase and micellar pseudo-phase, are defined using the second-order rate constants k_2^w and k_2^m respectively, as shown in Scheme 2.

The micelle concentration was calculated using the phase separation concept and assuming that the unassociated surfactant concentration remains constant above the CMC of the surfactant CTAB. Thus, the surfactant concentration, i.e. [D_n], is defined as the micellised surfactant concentration, as shown in Eqn 25. Thus, CMC was determined in each case (aqueous and micellar) experimentally because it depends on [CIP]. The surfactant concentration, from which we observe a kinetic effect on the reaction, was taken as the CMC in Eqn 25. According to reaction Scheme 2, the CIP is distributed between the two pseudo-phases, in a balanced process. In other words, the CIP will be considered as substrate, which is associated with the micellar pseudo-phase with a constant K_1 coincident with the CAT association constant K_2. These constants were calculated using different experimental techniques involving Eqns 26–30.[64,65]

$$[D_n] = [CTAB] - CMC \quad (25)$$

$$K_1 = \frac{[CIP]_m}{[CIP]_w[D_n]} \quad (26)$$

$$K_2 = \frac{[CAT]_m}{[CAT]_w[D_n]} \quad (27)$$

The total CIP and CAT concentration is the sum of concentrations in each pseudo-phase as shown in Eqns 28 and 29. Thus, based on Scheme 2 and according to the considerations above, the observed rate constant may be given by Eqn 30 where V is the partial molar volume of the interfacial region in the micellar pseudo-phase, determined by Bunton as 0.14 dm^3 mol^{-1}.[62,66]

$$[CIP]_{total} = [CIP]_w + [CIP]_m \quad (28)$$

$$[CAT]_{total} = [CAT]_w + [CAT]_m \quad (29)$$

$$k_{obs} = \frac{k_2^w + \frac{k_2^m}{V} K_1 K_2 [D_n]}{1 + K_1[D_n] + K_2[D_n]} [CIP]_{Total} \quad (30)$$

The rate constant in the aqueous phase, k_2^w, has been calculated kinetically.[64] To determine k_2^w and k_{obs} for the oxidation of CIP by CAT in a cationic micelle moiety, the reaction was studied in the absence of CTAB (which gave k_2^w) and then in the presence of CTAB (which gave k_{obs}). The association constants K_1 and K_2 have been determined with the Raghvan and Srinivasan model.[67] The rate constant in the micellar pseudo-phase, k_2^m, was calculated by putting the experimental data into Eqn 30. Table 4 shows the results obtained for oxidative degradation of

Table 4. Parameters of surfactant and different constants calculated from model

Parameter	Value
n (index of cooperativity)	6.8×10^{-4}
K_D	6.86
K_1	4.85
K_2	0.0083
k_2^w	$0.43 \times 10^{-4}\ s^{-1}$

CIP. In the present investigation, we observe that there is a good relationship between the experimental and theoretical values, which predicts the micellar pseudo-phase model (Fig. S9).

Piszkiewicz's model for SDS-catalysed oxidative transformation of CIP by CAT

According to Piszkiewicz's model,[63] the SDS-catalysed oxidative transformation of CIP by CAT may be explained by considering the concentration effect of the reactants on, or around, the micellar surface. The higher rate found in SDS could be attributed to the adsorption of CIP on the micellar surface, which increases the local molarities of the complex in the Stern layer. The SDS concentrates both CIP and CAT onto the surface of micelles and brings the reactants into close proximity, which increases the reaction rate. Both the reactants, CIP and CAT, are fairly soluble in water; therefore, K_D (the binding constant) is evaluated by the kinetic method.[63] In the presence of SDS, the binding constant was calculated by Piszkiewicz's approach.[63] The values of n (8.195×10^{-4}) and K_D ($-\log K_D = -8.574$) were determined from the gradient and intercept respectively of the straight line plot of $\log [(k_{obs} - k_w)/(k_m - k_{obs})]$ *v.* $\log D$ with the help of Eqn 31 where n is the index of cooperativity (Fig. S10). Applying Piszkiewicz's model, we obtained values of the binding constant, n, which refer to the positive cooperativity of substrates with a micelle.

$$\log \frac{k_{obs} - k_w}{k_m - k_{obs}} = n \log [D] - \log K_D \qquad (31)$$

Conclusion

For the first time, the influence of cationic and anionic surfactants on oxidative transformation of CIP using the mild oxidant CAT have been investigated along with observations in aqueous solution. Three main conclusions are drawn from the experimental results. First, pH plays a significant role in both the micelle media i.e. CTAB and SDS. Second, cationic as well as anionic micelles influenced the rate of CIP transformation by CAT in a similar way to that observed by the change in [acid] in the reaction system. Third, applicability of the pseudo-phase model to the kinetic data justifies the transformation influenced by the cationic micelles well whereas the anionic micelle-influenced transformation kinetic data fitted well in Piszkiewiz's model. The present investigation may widen the applicability of CAT as a mild oxidant in various redox reactions.

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