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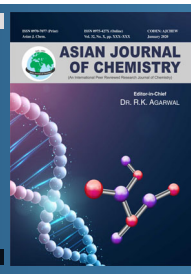

Kinetics of Micellar Effect of Non-Ionic Surfactant on Oxidative Degradation of Ciprofloxacin

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Oxidative degradation kinetics of leading fluoroquinolone family drug ciprofloxacin (CIP) by chloramine-T (CAT) in TX-100 micelle media was studied spectrophotometrically at 275 nm and 298 K. In pseudo-first-order conditions the rate constant (k_{obs}) decreased regularly with increasing [TX-100]. To understand the self-organizing activities of TX-100, CMC values in varying reaction conditions had been evaluated. The role of non-ionic surfactant in the oxidative degradation process of ciprofloxacin by chlorinating agent chloramine-T is explained in terms of mathematical model explained by Menger-Portnoy. The reaction showed first to zero order dependence on [CAT] and fractional order on [CIP]. Increasing [H^+] decreased the rate of reaction. The effect of ionic strength and solvent polarity of the medium in reaction conditions were studied. The effects of added salts [HSO_4Na], [KCl], [KNO_3] and [K_2SO_4] had also been studied. The stoichiometry of the reaction determined was 1:2 and the oxidation products were identified by LC-EI-MS. The analysis of degradation product of ciprofloxacin evidently reveals that the piperazine moiety is active site for oxidation in the reaction. Activation parameters were studied to propose appropriate mechanism for the reaction.

Keywords: Ciprofloxacin, Chloramine-T, Triton X-100, Oxidative degradation, Micelle.

INTRODUCTION

Surfactants have significant physical adsorption properties that may involve entropic effect, charge-charge interactions, associations of hydrophobic groups, solvency and hydrogen bonding effects. Therefore surfactants have been used as solubilizers [1] and surface modifiers frequently during past 2-3 decades. Based on their applications in various fields non-ionics are the second largest class after the anionic surfactants [2]. Non-ionic surfactants exhibit strong affinity for hydroxylated surfaces and their adsorption on solid surfaces is affected by hydrophobic interactions. Apart from their compatibility with other surfactants these also show peculiar temperature behaviour. In comparison to respective ionic counterparts, non-ionic surfactants have much less sensitivity to pH and ionic strength of medium [3-6]. Widespread use of non-ionic surfactants [7-10] has drawn environmental concern for assessment of their bio-degradability and toxicity. In aquatic environment TX-100 (Triton X-100) has been found to show typical detergent properties thus may solubilize the lipid bilayer membrane by integration into the cell membrane. In micelle environment polyoxyethylene chains of TX-100 stay outside the core and move freely in solvent and stabilize interface [8]. In this way it may show toxic effects to some aquatic species [11]. TX-100 has a hydrophilic polyethylene oxide group (on average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group. It is related to the pluronic range of detergents. The pluronics are triblock copolymers of ethylene oxide and propylene oxide. The part formed from ethylene oxide is more hydrophilic than the part from propylene oxide. Triton X-100 is very viscous at room temperature and is thus easiest to use after being gently warmed [12].

Present study reports the kinetic investigation of effect of TX-100 on degradation of ciprofloxacin by chloramine-T in aqueous medium. We have reported the effects of cationic

(CTAB) and anionic (SDS) surfactants on the oxidative degradation of two frequently used fluoroquinolone family drugs (ciprofloxacin and norfloxacin) by common chlorinating agent chloramine-T [13-15]. Present investigation reveals the effect of non-ionic surfactant TX-100 on oxidation of ciprofloxacin.

Studies have been reported showing varying quantities of ciprofloxacin in aquatic environment as well as in effluents of WWTPs (wastewater treatment plants) [16,17]. Chlorine based disinfectants are most frequent disinfection agents used during wastewater treatment processes [18,19], chloramine-T is one among such disinfectant. Present study aims to find the kinetics and mechanism of oxidation reaction of ciprofloxacin by chloramine-T in the presence of TX-100.

EXPERIMENTAL

Solutions were prepared using analytical grade reagents without further purification. 1/100 stock solution of TX-100 (Merck) was prepared by dissolving its requisite quantity in triple distilled water. The stock solution of chloramine-T (LOBA Chemie) was stored in dark coloured bottle and its strength was checked iodometrically [20]. Ciprofloxacin (Sigma Aldrich) stock solution was prepared by dissolving known amount of its hydrochloric salt and was stored in amber coloured bottle to prevent any photochemical degradation.

Determination of CMC: To determine the self-organizing activities of TX-100, CMC values have been determined. In the presence of reactants at required temperature the CMC of TX-100 was measured conductometrically (Systronics conductometer 304 at 298.0 ± 0.2 K). The calibration of conductometer was done with 0.01 M KCl solution. The breakpoint of nearly straight line in the plots of equivalent conductivity *vs.* [TX-100] gave the CMC values which are indicative of micelle formation (Fig. 1, Table-1).

Kinetic measurements: All reactant solutions were placed in the thermostatic water bath for 30 min in order to attain a temperature of 298 ± 0.2 K. The kinetics of the reaction was studied taking the requisite amounts of ciprofloxacin, TX-100,

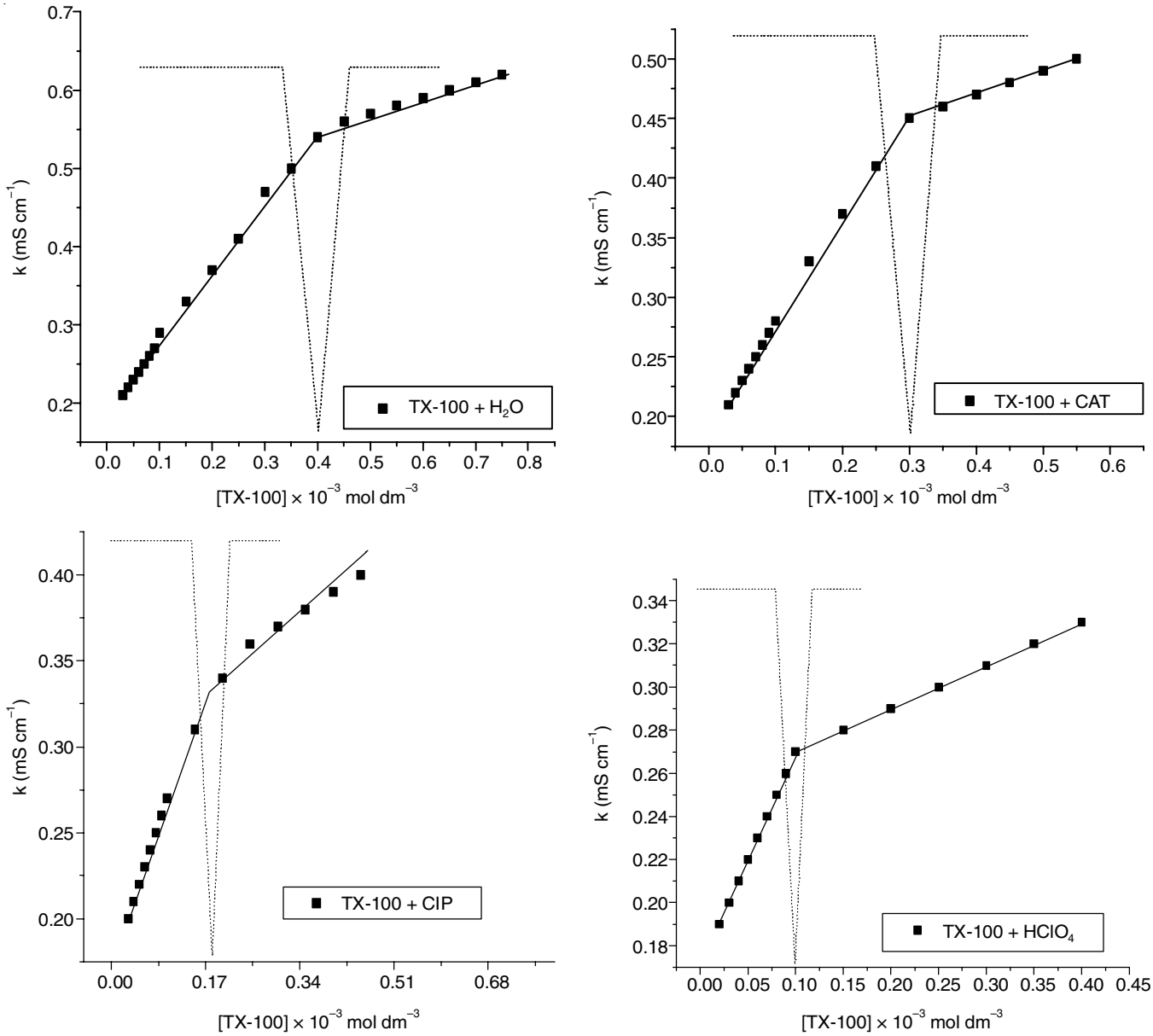


Fig. 1. Plots of equivalent conductivity *vs.* [surfactant] with different reactants

TABLE-1
CMC VALUES OF TX-100 IN DIFFERENT EXPERIMENTAL CONDITIONS

Solution	CMC ($\times 10^{-3}$) (mol dm^{-3})
Water + TX-100	0.4 (0.3-0.9)[a]
Water + TX-100 + Chloramine-T	0.30
Water + TX-100 + Ciprofloxacin	0.18
Water + TX-100 + H_2SO_4	0.10

T = 298 K; [CIP] = 3×10^{-5} mol dm^{-3}; [CAT] = 3×10^{-4} mol dm^{-3}; [$HClO_4$] = 2×10^{-4} mol dm^{-3}
[a]Literature value given in parentheses [Ref. 21]

$HClO_4$ and chloramine-T in a black coated reaction vessel that was kept in the thermostatic water bath at 298 ± 0.2 K. Reaction initiation time was taken when half of the required volume of thermally equilibrated chloramine-T was added to the reaction system. The kinetics of the reaction was followed spectrophotometrically at 275 nm by measuring the absorbance (A), at constant intervals of time, on a UV-visible spectrophotometer Varian Cary 50 Bio, using 10 mm quartz cuvette and under pseudo 1st order condition where [CIP] << [CAT]. The slope of the plot of log A *versus* time (min) gave the pseudo 1st order rate constants (k_{obs}) (Fig. 2). Kinetic plots were linear for more than four half-lives where A is taken up to 75 % completion of the reaction. The slope of log k_{obs} *versus* log (concentration), 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 where the rate constants were found to be reproducible and well within 4 % error.

The reaction was monitored with respect to ciprofloxacin at 275 nm wavelength. Disappearance of ciprofloxacin can be seen in the time scan of the reaction mixture. The spectral changes occurring during the typical kinetic runs at each minute for the oxidation of ciprofloxacin by chloramine-T in TX-100 micelle media were recorded in the region of 220 to 360 nm. There is a continuous decrease of absorbance at 275 nm which clearly indicates disappearance of ciprofloxacin with the progress of the reaction.

In all the kinetic measurements, the chloramine-T was used in excess (≥ 10-fold) relative to the ciprofloxacin, to ensure pseudo-first order condition. The observed rate constants were evaluated from the linear plots of log (absorbance) against time record upto 5 min only (which was giving fairly straight line) but the reaction was monitored upto ≈ 75 % completion of the reaction.

Stoichiometry and product analysis: The stoichiometric analysis of different sets of reaction mixtures containing chloramine-T, sulphuric acid and surfactant with excess quantity

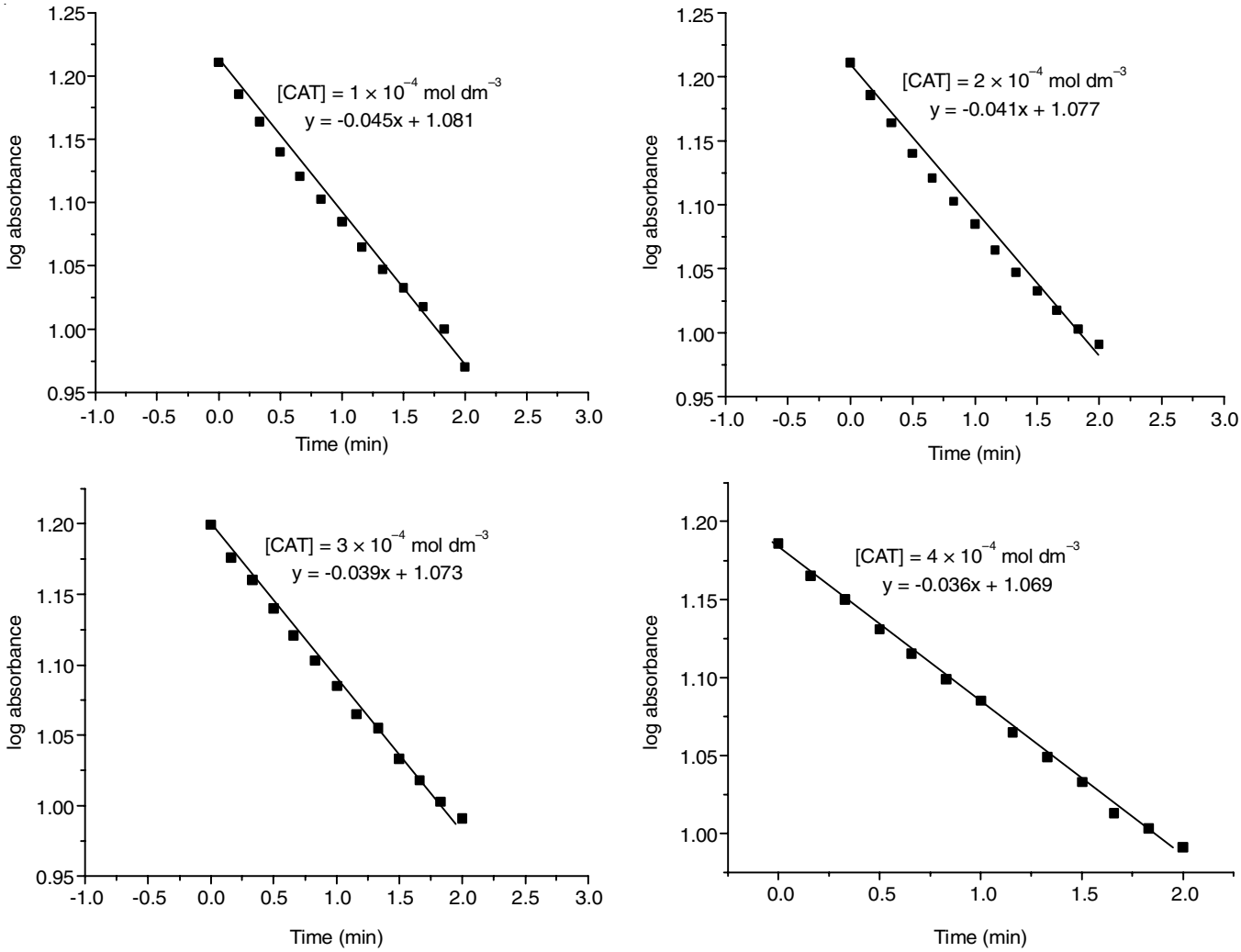


Fig. 2. Plots of log absorbance *vs.* time

of ciprofloxacin were kept at 298 K. Determination of unconsumed ciprofloxacin in each set gave the idea that one mole of ciprofloxacin was consumed for the oxidation of two mole of chloramine-T (Table-2). For the identification of oxidation products of ciprofloxacin, excess of chloramine-T over ciprofloxacin was allowed to react in the presence of sulphuric acid. The reduced product of oxidant chloramine-T *i.e.*, *p*-toluene sulphonamide (PTS) was initially characterized by TLC [22]. Finally the main oxidation product of ciprofloxacin that corresponds to full dealkylation of the piperazine ring (*i.e.*, the -NH_2 product) and other products were isolated and confirmed by GC-MS analysis (Fig. 3) in which the reaction mixture was extracted with diethyl ether. The ether layer was concentrated by slow evaporation before analyzing with GC-MS, JEOL-JMS (Mate-MS system, Japan). Analysis of ciprofloxacin reaction indicated the presence of main products with molecular ions of *m/z* 364 (yield 5 %), 351 (yield 10 %), 295 (yield 15 %), 263 (yield 55 %) and 193 (yield 40 %), respectively. The molecular ion of ciprofloxacin is *m/z* 330. The *m/z* 351 corresponds to N-oxide product. The *m/z* 364 corresponds to M+ 35 products with respect to ciprofloxacin. The full dealkylation of the piperazine ring produced the *m/z* 263 (*i.e.*, the -NH_2 product) with highest intensity. This product was also identified previously as oxidation product [23] and photo degradation product of ciprofloxacin [24]. The *m/z* 295 may correspond to the chlorinated product of fully dealkylation product (*i.e.*, *m/z* 263). The oxidation product of ciprofloxacin was also characterized by FT-IR spectral studies. IR (KBr, ν, cm^{-1}): 1560m (-NH_2), 1621s (C=O), 3059s (NH), 3500s (OH).

TABLE-2
STOICHIOMETRIC RESULTS OF OXIDATION OF CIPROFLOXACIN BY CHLORAMINE-T AT 298 K

Ciprofloxacin × 10^2 (mol dm^{-3})	[CAT] × 10^3 (mol dm^{-3})			No. of equivalence
	Initial	Final	Consumed	
2.00	20.00	16.00	4.06	1:2.03
4.00	40.00	31.87	8.16	1:2.04
6.00	60.00	47.79	12.30	1:2.05

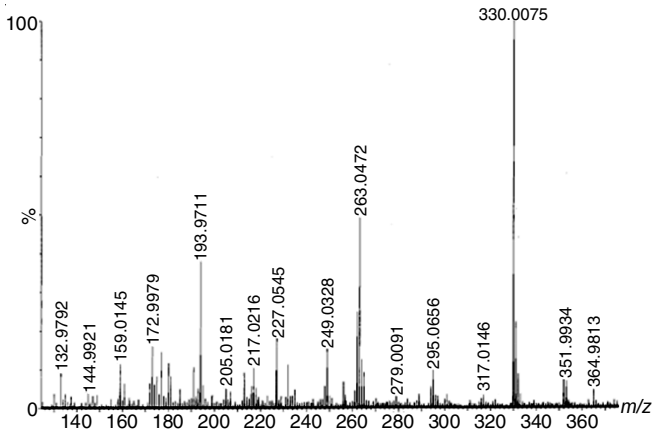


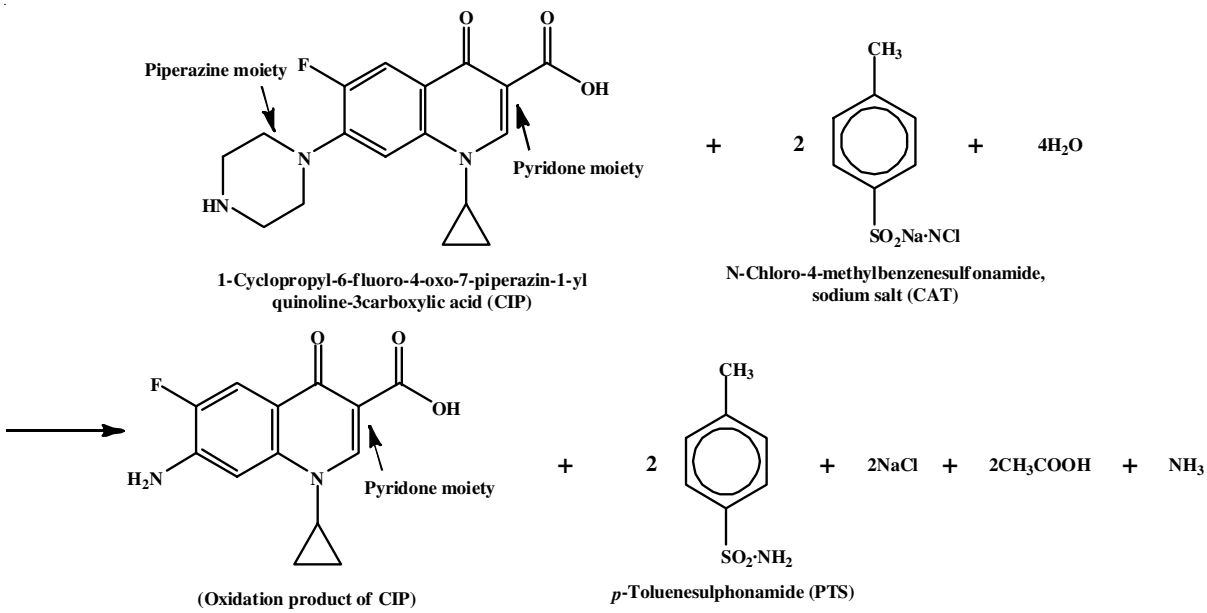
Fig. 3. LC-ESI-MS-MS spectra of oxidation products of ciprofloxacin

On the basis of stoichiometric and product analysis formulated stoichiometric equation is given in **Scheme-I**.

RESULTS AND DISCUSSION

To obtain the rate constants as functions of [CAT], [CIP] and [$HClO_4$], pseudo-first-order conditions were maintained in each kinetic run. First to zero-order-rate is observed with respect to [CAT], whereas fractional-order-rates are determined in both [CIP] and [$HClO_4$]. The additives have been found to put composite effects (catalytic and inhibition). Arrhenius and Eyring equations are found valid for the reaction over a range of temperatures and different activation parameters have been evaluated. A probable reaction mechanism, in agreement with the observed kinetic results, has been proposed and discussed. Influence of changes in the surfactant concentrations on the observed rate constant is also investigated and the reaction followed the same type of kinetic behaviour in micellar media. Pseudo-first-order rate constant (k_{obs}) is found to show a regular decrease with increasing [TX-100]. Role of non-ionic surfactant TX-100 is explained in terms of the mathematical mode.

Effect of variation of chloramine-T: To find out the order of the reaction with respect to [CAT], the rate constant was



Scheme-I

determined at different initial concentrations of chloramine-T ranging from 2.0 to 8.0×10^{-4} mol dm^{-3}. The concentrations of ciprofloxacin (3.0×10^{-3} mol dm^{-3}), $HClO_4$ (2.0×10^{-4} mol dm^{-3}) and temperature (298 K) were kept constant. Pseudo-first-order rate constant (k_{obs}), obtained at different [CAT] are shown in Table-3. The result shows that the rate constant decreases with increasing [CAT]. The decrease in rate constant may be due to the retardation influence of the reduced product PTS. The rate of reaction was found to show first to zero order dependence (Fig. 4) to [CAT].

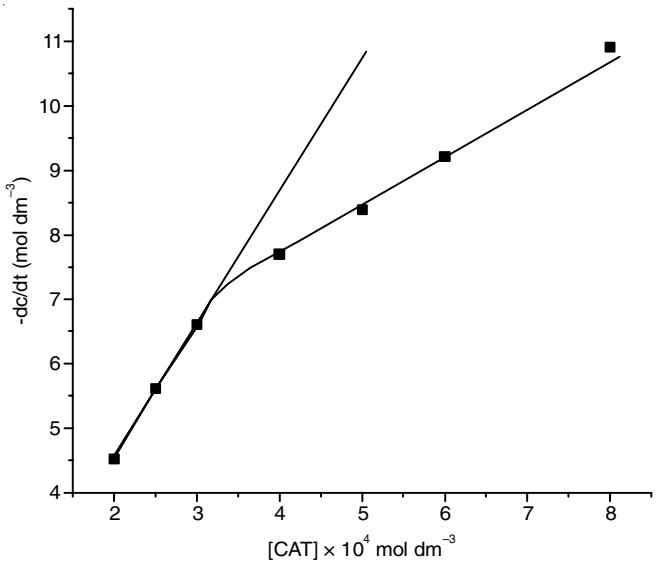


Fig. 4. Effect of oxidant chloramine-T on observed rate constant and rate of the reaction

Effect of variation of ciprofloxacin: The dependence of the rate constant on [CIP] was determined by carrying out the kinetic experiments at different concentrations of ciprofloxacin keeping the [CAT] = 3.0×10^{-4} mol dm^{-3}, [$HClO_4$] = 2.0×10^{-4} mol dm^{-3} and temperature = 298 K constant. The k_{obs} values are summarized in Table-4 (Fig. 5). The rate constant increased with [CAT]. The plot of rate constant *versus* [CIP] is nonlinear passing through the origin. The linear plot between log k_{obs} *versus* log [CIP] yield slope equal to 0.13, indicating fractional-order in [CIP]. The first order dependence of reaction on ciprofloxacin is further supported by the parallel plots of log absorbance *versus* time for the varying concentrations of ciprofloxacin (Fig. 6).

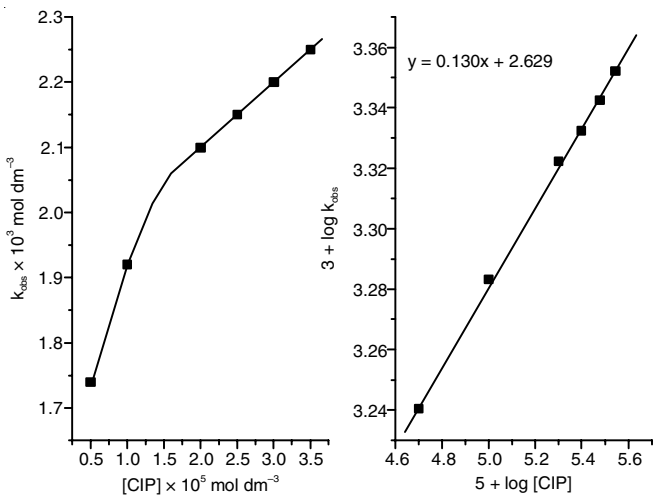


Fig. 5. Effect of ciprofloxacin on the observed rate constant

Effect of variation of acid: To study the effect of variation of [$HClO_4$] on the rate constant, the reaction was monitored in varying concentrations of $HClO_4$ (1×10^{-4} to 10×10^{-4} mol

TABLE-3
EFFECT OF OXIDANT ON RATE CONSTANT FOR THE TX-100 MEDIATED OXIDATION OF CIPROFLOXACIN BY CHLORAMINE-T

Time (min)	Absorbance at 275 nm wavelength with respect to variation of [CAT] (× 10^4 mol dm^{-3})						
	2.0	2.5	3.0	4.0	5.0	6.0	8.0
0.0	1.056	1.043	1.037	1.039	1.053	1.068	1.068
0.5	0.992	0.987	0.971	0.968	0.995	1.015	1.015
1.0	0.932	0.926	0.911	0.911	0.935	0.961	0.961
1.5	0.867	0.862	0.858	0.858	0.889	0.918	0.918
2.0	0.812	0.807	0.807	0.807	0.846	0.881	0.881
2.5	0.765	0.755	0.752	0.767	0.809	0.839	0.839
3.0	0.711	0.708	0.702	0.723	0.769	0.798	0.798
3.5	0.660	0.662	0.657	0.682	0.732	0.762	0.762
4.0	0.617	0.611	0.616	0.643	0.697	0.728	0.728
4.5	0.576	0.576	0.572	0.611	0.665	0.698	0.698
5.0	0.538	0.534	0.536	0.573	0.632	0.666	0.666
5.5	0.519	0.51	0.503	0.492	0.492	0.623	0.623
6.0	0.482	0.472	0.465	0.459	0.463	0.583	0.583
6.5	0.458	0.448	0.441	0.435	0.441	0.561	0.561
7.0	0.431	0.425	0.419	0.415	0.428	0.544	0.544
7.5	0.418	0.411	0.405	0.400	0.412	0.518	0.518
8.0	0.402	0.396	0.391	0.387	0.392	0.489	0.489
8.5	0.389	0.381	0.374	0.368	0.375	0.462	0.462
9.0	0.365	0.357	0.357	0.351	0.358	0.455	0.455
9.5	0.342	0.338	0.332	0.326	0.332	0.427	0.427
10.0	0.324	0.316	0.312	0.305	0.318	0.411	0.411
20.0	0.312	0.302	0.296	0.286	0.297	0.388	0.388
$k_{obs} \times 10^3$ s^{-1}	2.26	2.25	2.20	1.93	1.68	1.54	1.36
-dc/dt	2.53	3.14	3.69	4.31	4.69	5.16	6.11

T = 298 K; [CIP] = 3.0×10^{-5} mol dm^{-3}; [H^+] = 2.0×10^{-4} mol dm^{-3}; [TX-100] = 1.2×10^{-3} mol dm^{-3}

TABLE-4
EFFECT OF SUBSTRATE CIPROFLOXACIN ON TX-100 MEDIATED OXIDATION OF CIPROFLOXACIN BY CHLORAMINE-T

Time (min)	Absorbance at 275 nm wavelength with respect to variation of [CIP] ($\times 10^5$ mol dm^{-3})					
	0.5	1.0	2.0	2.5	3.0	3.5
0.0	0.999	1.026	1.035	1.057	1.067	1.098
0.5	0.949	0.968	0.971	0.971	0.999	1.028
1.0	0.901	0.911	0.911	0.911	0.939	0.959
1.5	0.851	0.861	0.858	0.858	0.867	0.897
2.0	0.807	0.813	0.807	0.807	0.812	0.835
2.5	0.767	0.767	0.752	0.752	0.765	0.783
3.0	0.723	0.723	0.702	0.702	0.711	0.728
3.5	0.689	0.682	0.657	0.657	0.668	0.683
4.0	0.659	0.643	0.622	0.622	0.631	0.642
4.5	0.624	0.611	0.581	0.581	0.587	0.599
5.0	0.591	0.573	0.545	0.545	0.551	0.556
5.5	0.492	0.492	0.503	0.514	0.519	0.457
6.0	0.455	0.459	0.461	0.476	0.482	0.415
6.5	0.431	0.435	0.437	0.451	0.458	0.371
7.0	0.409	0.415	0.415	0.428	0.431	0.356
7.5	0.396	0.4	0.392	0.416	0.418	0.332
8.0	0.387	0.381	0.378	0.391	0.402	0.315
8.5	0.365	0.364	0.362	0.378	0.389	0.288
9.0	0.351	0.347	0.348	0.351	0.365	0.259
9.5	0.325	0.321	0.321	0.333	0.342	0.234
10.0	0.305	0.305	0.302	0.311	0.324	0.211
20.0	0.279	0.278	0.284	0.289	0.312	0.186
$k_{obs} \times 10^3$ s^{-1}	1.74	1.92	2.10	2.15	2.20	2.25

T = 298 K; [CIP] = 3.0×10^{-5} mol dm^{-3}; [H$^+$] = 2.0×10^{-4} mol dm^{-3}; [TX-100] = 1.2×10^{-3} mol dm^{-3}

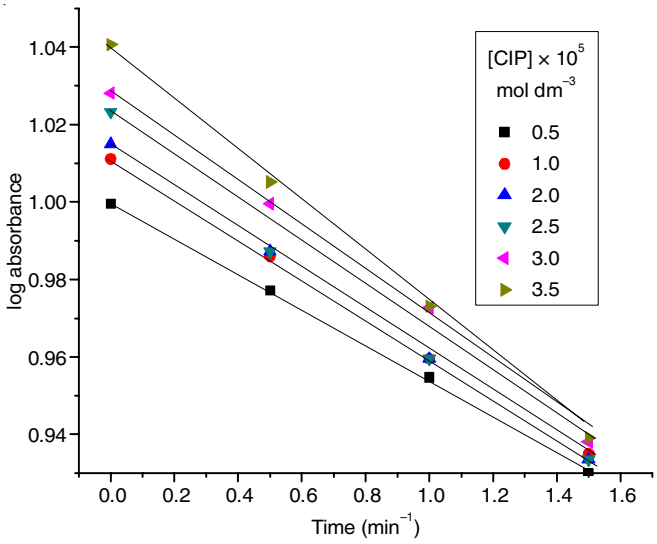


Fig. 6. First order plots of log absorbance *versus* time

dm^{-3}, keeping other experimental conditions constant. Regular decrease in rate constant is reported with the increasing [$HClO_4$] (Table-5, Fig. 7).

Effect of TX-100: The effect of TX-100 concentration on the reaction was studied at constant [CAT] (3.0×10^{-4} mol dm^{-3}), [CIP] (3.0×10^{-5} mol dm^{-3}), [$HClO_4$] (2.0×10^{-4} mol dm^{-3}) and temperature (298 K) (Table-6). The results show that as the [TX-100] increases, the rate constant show regular decrease and towards higher concentration tending to achieve a constant value. From Fig. 8, it can be concluded that the TX-100 put retardation effect on the oxidative transformation of drug ciprofloxacin by chloramine-T in acidic conditions.

TABLE-5
EFFECT OF VARIATION OF ACID ON THE RATE CONSTANT

Time (min)	Absorbance at 275 nm wavelength with respect to variation of [$HClO_4$] ($\times 10^4$ mol dm^{-3})					
	1.0	2.0	4.0	6.0	8.0	10
0.0	1.569	1.562	1.564	1.543	1.530	1.521
0.5	1.557	1.553	1.555	1.535	1.525	1.517
1.0	1.545	1.544	1.543	1.527	1.520	1.513
1.5	1.536	1.533	1.533	1.521	1.515	1.509
2.0	1.525	1.525	1.524	1.514	1.509	1.504
2.5	1.513	1.514	1.514	1.508	1.505	1.499
3.0	1.501	1.503	1.505	1.502	1.500	1.495
3.5	1.489	1.492	1.495	1.495	1.495	1.491
4.0	1.481	1.483	1.485	1.487	1.491	1.487
4.5	1.469	1.473	1.477	1.481	1.487	1.484
5.0	1.458	1.462	1.468	1.475	1.482	1.48
5.5	1.441	1.438	1.438	1.445	1.458	1.463
6.0	1.435	1.425	1.425	1.432	1.442	1.456
6.5	1.415	1.412	1.412	1.418	1.426	1.432
7.0	1.404	1.403	1.403	1.408	1.413	1.419
7.5	1.387	1.381	1.381	1.387	1.391	1.409
8.0	1.371	1.369	1.369	1.373	1.377	1.382
8.5	1.362	1.359	1.359	1.367	1.369	1.375
9.0	1.355	1.351	1.351	1.354	1.357	1.363
9.5	1.341	1.337	1.337	1.343	1.342	1.348
10.0	1.325	1.325	1.325	1.335	1.337	1.332
15.0	1.276	1.269	1.269	1.114	1.107	0.949
20.0	1.115	1.100	1.100	0.987	0.993	0.799
25.0	0.855	0.841	0.841	0.862	0.835	0.632
30.0	0.622	0.612	0.612	0.655	0.662	0.554
35.0	0.472	0.432	0.432	0.511	0.532	0.469
$k_{obs} \times 10^3$ s^{-1}	2.42	2.19	1.88	1.47	1.05	0.92

T = 298 K; [CIP] = 3.0×10^{-5} mol dm^{-3}; [CAT] = 3.0×10^{-4} mol dm^{-3}; [TX-100] = 1.2×10^{-3} mol dm^{-3}

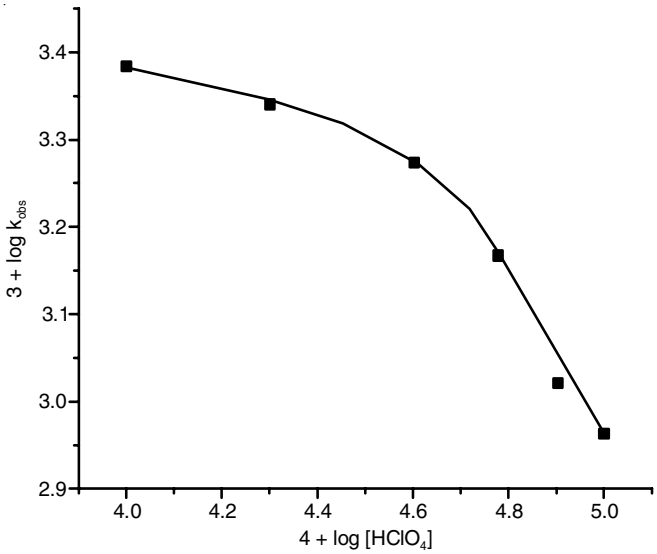


Fig. 7. Plots of log k_{obs} *versus* log [acid]

Effect of additives: The rate constant did not show measurable change with increasing dielectric constant of the medium. Addition of PTS in the reaction mixture showed that the rate of reaction decreased with increasing [PTS] (Table-7). A plot of observed rate constant *versus* [PTS] has been shown in Fig. 9a. Variations of ionic strength of the medium [K_2SO_4], [KNO_3] and [KCl] did not bring about any significant change in the values of observed rate constants under the constant experimental conditions (Table-8). The rate constant was found to

TABLE-6
EFFECT OF INCREASING CONCENTRATION OF TX-100 ON OXIDATION OF CIPROFLOXACIN BY CHLORAMINES-T

Time (min)	Absorbance at 275 nm wavelength with respect to variation of [TX-100] (× 10^3 mol dm^{-3})							Time (min)	Absorbance at 275 nm wavelength with respect to variation of [TX-100] (× 10^3 mol dm^{-3})						
	0.1	0.2	0.3	0.4	0.5	0.6	0.7		0.8	0.9	1.0	1.1	1.2	1.3	1.4
0.00	0.460	0.432	0.466	0.487	0.485	0.495	0.482	0.0	1.095	1.056	1.038	1.098	1.076	1.066	1.037
0.16	0.427	0.403	0.429	0.461	0.461	0.468	0.467	0.5	0.976	0.961	0.944	1.028	1.000	0.997	0.971
0.33	0.395	0.384	0.41	0.428	0.435	0.444	0.449	1.0	0.911	0.888	0.843	0.959	0.926	0.932	0.911
0.50	0.372	0.359	0.391	0.409	0.409	0.415	0.429	1.5	0.797	0.766	0.766	0.897	0.862	0.867	0.858
0.66	0.345	0.337	0.368	0.389	0.389	0.396	0.413	2.0	0.684	0.695	0.695	0.835	0.799	0.812	0.807
0.83	0.322	0.315	0.347	0.362	0.378	0.381	0.393	2.5	0.598	0.622	0.636	0.776	0.742	0.755	0.752
1.00	0.303	0.294	0.321	0.348	0.354	0.365	0.375	3.0	0.545	0.575	0.575	0.715	0.693	0.698	0.702
1.16	0.283	0.276	0.307	0.331	0.339	0.349	0.360	3.5	0.499	0.525	0.539	0.661	0.641	0.651	0.657
1.33	0.269	0.261	0.288	0.316	0.325	0.331	0.354	4.0	0.466	0.483	0.511	0.608	0.591	0.609	0.616
1.50	0.254	0.245	0.271	0.295	0.308	0.325	0.333	4.5	0.416	0.442	0.482	0.551	0.535	0.569	0.572
1.66	0.239	0.231	0.254	0.284	0.295	0.316	0.325	5.0	0.388	0.413	0.448	0.504	0.491	0.529	0.536
1.83	0.228	0.22	0.245	0.273	0.283	0.301	0.313	5.5	0.335	0.345	0.35	0.488	0.456	0.491	0.503
2.00	0.214	0.206	0.234	0.261	0.275	0.291	0.303	6.0	0.313	0.321	0.333	0.472	0.421	0.465	0.465
2.16	0.202	0.202	0.231	0.257	0.255	0.278	0.288	6.5	0.287	0.295	0.305	0.459	0.395	0.432	0.441
2.33	0.191	0.189	0.217	0.242	0.238	0.263	0.275	7.0	0.271	0.276	0.284	0.433	0.361	0.409	0.419
2.50	0.178	0.172	0.207	0.231	0.223	0.246	0.261	7.5	0.258	0.269	0.271	0.415	0.338	0.377	0.405
5.00	0.065	0.066	0.078	0.081	0.083	0.098	0.126	8.0	0.225	0.224	0.229	0.388	0.312	0.345	0.391
–	–	–	–	–	–	–	–	8.5	0.202	0.198	0.211	0.365	0.284	0.311	0.374
–	–	–	–	–	–	–	–	9.0	0.184	0.181	0.195	0.341	0.255	0.277	0.357
–	–	–	–	–	–	–	–	9.5	0.161	0.160	0.170	0.325	0.227	0.248	0.332
–	–	–	–	–	–	–	–	10.0	0.111	0.118	0.125	0.288	0.191	0.219	0.312
k_{obs} × 10^3 (s^{-1})	6.30	6.23	5.80	4.75	4.36	3.90	3.55	k_{obs} × 10^3 (s^{-1})	3.20	2.80	2.58	2.35	2.20	2.20	2.20

T = 298 K; [CIP] = 3.0×10^{-5} mol dm^{-3}; [H^+] = 2.0×10^{-4} mol dm^{-3}; [CAT] = 3.0×10^{-4} mol dm^{-3}

TABLE-7
EFFECTS OF [ACETIC ACID], [PTS] AND [HCOONa] ON REACTION RATE

Acetic acid × 10^4 (mol dm^{-3})	[PTS] × 10^4 (mol dm^{-3})	[HSO_4Na] × 10^4 (mol dm^{-3})	k_{obs} × 10^3 (s^{-1})
5	–	–	2.23
10	–	–	2.22
20	–	–	2.24
30	–	–	2.22
–	0	–	2.21
–	1	–	1.55
–	2	–	0.48
–	4	–	0.46
–	6	–	0.46
–	8	–	0.44
–	10	–	0.45
–	–	0	2.21
–	–	1	1.96
–	–	2	1.43
–	–	4	0.95
–	–	6	0.78
–	–	8	0.77
–	–	10	0.66

T = 298 K; [CIP] = 3.0×10^{-5} mol dm^{-3}; [CAT] = 3.0×10^{-4} mol dm^{-3}; [$HClO_4$] = 2.0×10^{-4} mol dm^{-3}; [TX-100] = 2.0×10^{-3} mol dm^{-3}

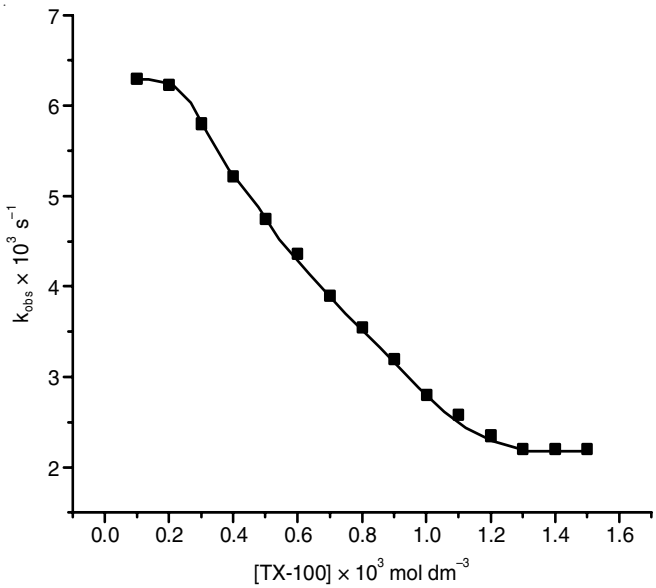


Fig. 8. Effect of TX-100 on the pseudo first order rate constants

decrease with the increasing [HSO_4Na] (Fig. 9b). This may be due to the fact that electrolytes decrease the CMC and increase the aggregation number of ionic micelle [25] may be due to the increased screening by counter ions and thereby decrease the effective charge density of the micelle.

Activation parameters for the uncatalyzed and TX-100 catalyzed oxidative transformation of ciprofloxacin by chloramine-T in acidic conditions.

A series of kinetic runs were carried out at different temperatures with fixed [CAT] = 2.0×10^{-4} mol dm^{-3}, [CIP] = 2.0×10^{-5} mol dm^{-3} and [$HClO_4$] = 2.0×10^{-4} mol dm^{-3} to find the different activation parameters. The value of rate constants at different temperatures is summarized in Table-9 along with the activation parameters. The activation energy (E_a) was calculated from the slope of Arrhenius plot (Fig. 10a). To determine whether the reaction mechanism is associative or dissociative, the entropy of activation is needed, which can be evaluated from an Eyring plot (Fig. 10b). A large negative value of $\Delta S^{\#}$ indicates an associative reaction and a large positive value of $\Delta S^{\#}$ indicates a dissociative reaction [26]. Using Eyring equation the calculated values of $\Delta H^{\#}$ is 31.21 kJ mol^{-1} and $\Delta S^{\#}$ is -71.22 JK^{-1} mol^{-1}. Thus, an inner sphere mechanism, with both reactants binding in the transition state, occurs.

TABLE-8
EFFECTS OF [KCl], [KNO_3] AND [K_2SO_4] ON REACTION RATE

[KCl] × 10^4 (mol dm^{-3})	[KNO_3] × 10^4 (mol dm^{-3})	[K_2SO_4] × 10^4 (mol dm^{-3})	k_{obs} × 10^3 (s^{-1})
1.0	–	–	2.22
2.0	–	–	2.21
3.0	–	–	2.22
4.0	–	–	2.22
5.0	–	–	2.22
6.0	–	–	2.21
8.0	–	–	2.21
10.0	–	–	2.21
–	1.0	–	2.19
–	2.0	–	2.19
–	3.0	–	2.30
–	4.0	–	2.11
–	5.0	–	2.29
–	6.0	–	2.56
–	8.0	–	2.65
–	10	–	2.33
–	–	1.0	2.20
–	–	3.0	2.19
–	–	6.0	2.15
–	–	10	2.19

T = 298 K; [CIP] = 3.0 × 10^{-5} mol dm^{-3}; [CAT] = 3.0 × 10^{-4} mol dm^{-3}; [$HClO_4$] = 2.0 × 10^{-4} mol dm^{-3}; [TX-100] = 1.2 × 10^{-3} mol dm^{-3}

TABLE-9
TEMPERATURE EFFECT AND ACTIVATION PARAMETERS FOR UNCATALYZED AND TX-100 CATALYZED REACTIONS OF OXIDATION OF CIPROFLOXACIN BY CHLORAMINE-T

Parameter	Without TX-100 k_{obs} × 10^3 (s^{-1})	With TX-100 k_{obs} × 10^3 (s^{-1})
293K	0.63	1.49
298 K	0.72	2.12
303K	1.03	2.73
308K	1.25	3.30
E_a (kJ mol^{-1})	33.89	37.22
Δ $H^{\#}$ (kJ mol^{-1})	36.39	39.73
Δ $S^{\#}$ (JK mol^{-1})	-62.88	-43.69
Δ $G^{\#}$ (kJ mol^{-1})	18.77	13.06

[CIP] = 2.0 × 10^{-5} mol dm^{-3}; [CAT] = 2.0 × 10^{-4} mol dm^{-3}; [H_2SO_4] = 2.0 × 10^{-4} mol dm^{-3}; [CTAB] = 3.5 × 10^{-3} mol dm^{-3}

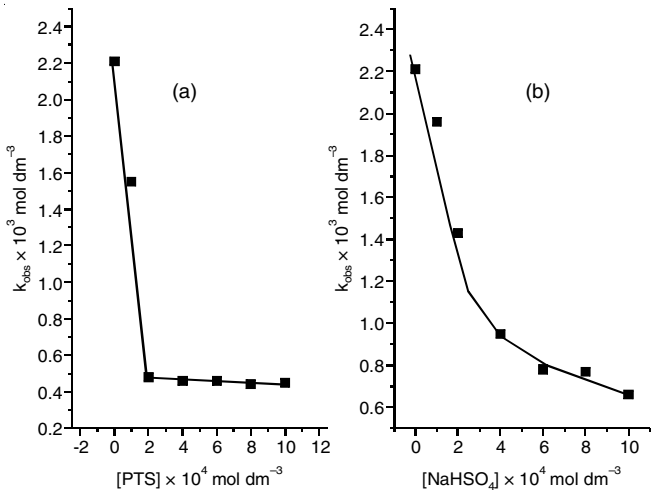


Fig. 9. Effect of reduced product of oxidant chloramine-T and added electrolyte

The effect of TX-100 concentration on the reaction was also studied at constant [CAT] = 2.0 × 10^{-4} mol dm^{-3}, [CIP] = 2.0 × 10^{-5} mol dm^{-3} and [$HClO_4$] = 2.0 × 10^{-4} mol dm^{-3} and temperature (35 °C), taking fixed [TX-100] = 1.2 × 10^{-3} mol dm^{-3}. To confirm whether mechanism of the oxidation of oxidative transformation of ciprofloxacin by chloramine-T in both aqueous as well as micellar media is similar, different experiments were performed as a function of [CIP], [CAT] and [$HClO_4$] in the presence of [TX-100] (1.2 × 10^{-3} mol dm^{-3}) at 298 K temperature (Table-9). The behaviour with respect to [CIP], [CAT] and [$HClO_4$] was similar to that in the aqueous medium, which shows that reaction mechanism in the presence of TX-100 remains the same as that in the homogeneous aqueous medium. The effect of temperature on the reaction rate in micellar media was also studied. The activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$), evaluated by using Arrhenius and Eyring equations, show that TX-100 micelles act as catalyst providing a new reaction path with lower E_a (aqueous > TX-100).

TX-100 catalyzed oxidative transformation of ciprofloxacin by chloramine-T.

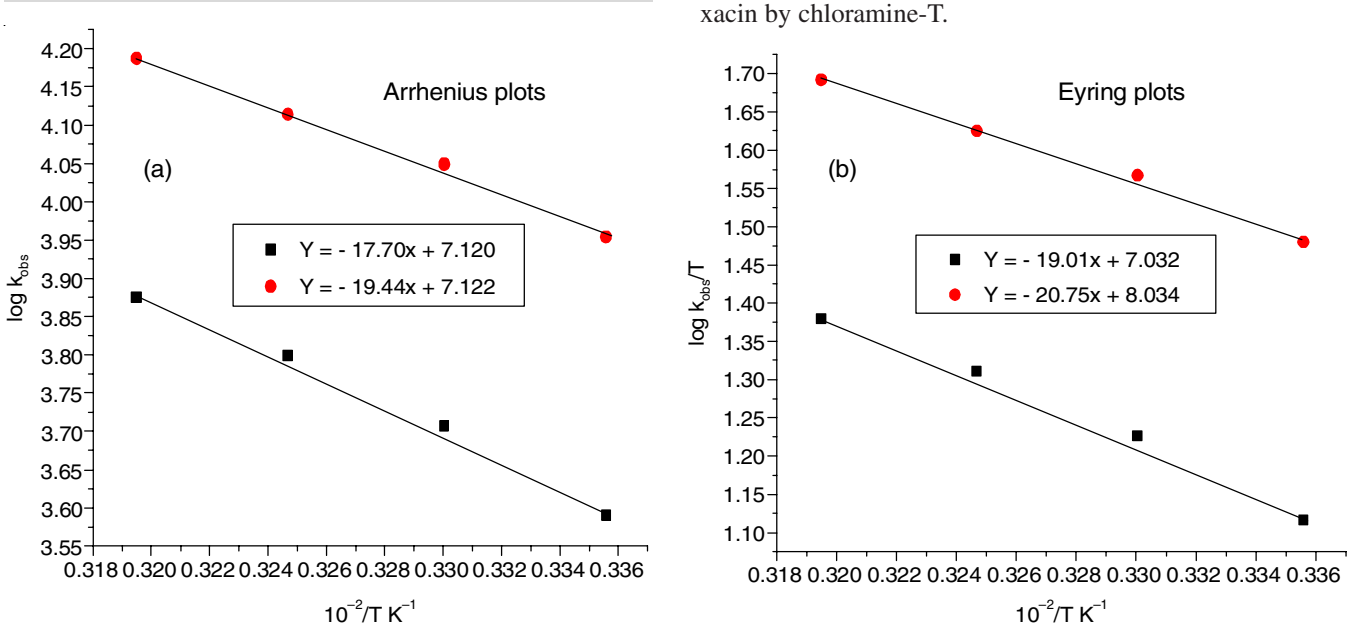
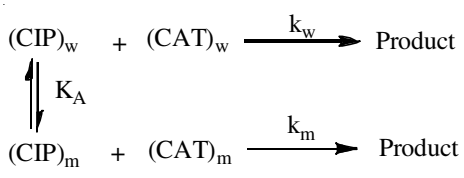


Fig. 10. Effect of temperature on the pseudo-first-order rate constant for TX-100 catalyzed oxidation of ciprofloxacin by chloramine-T in acidic medium

Menger-Portnoy model: The Menger-Portnoy model [27] considers the partitioning of only one reactant between the micellar and aqueous phase (**Scheme-II**).



Scheme-II

Based on **Scheme-II** following rate law can be proposed:

$$k_{obs} = \frac{k_m K_A C + k_w}{1 + K_A C} \quad (a)$$

where K_A is the binding constant in terms of micellized surfactant; k_m and k_w are the first-order rate constants in micellar and aqueous phase and include the concentration of other reactant ciprofloxacin in these pseudo-phases; C ($[D]_T$ - CMC) is the concentration of micelle. For $k_m > k_w$, the reaction rate increases with the increase of C and ultimately it reaches the limiting value k_m conversely, for $k_m < k_w$, an increase in C produces a decrease in rate constant and it tends to attain the limiting value k_m. Equation (a) can be rearranged into the reciprocal form as follows:

$$\frac{1}{k_{obs} - k_w} = \frac{1}{K_A C(k_m - k_w)} + \frac{1}{k_m - k_w} \quad (b)$$

A plot of $(k_w - k_m)^{-1}$ *versus* $[C]^{-1}$ should be linear. The applicability of Menger Potnoy's model allows determination of the binding constant K_A and rate constant k_m in micellar phase. Bunton and Cerichelli [28] have pointed out that the treatment of Equation (b) is very sensitive to the values of CMC that may be affected by the reaction media. They have suggested that in the case of rate retardation by the surfactant, assuming $k_m \approx 0$, modified equation (c) gives the better estimation of the binding constant K_A [29].

$$k_{obs} = \frac{k_w}{1 + K_A C} \quad (c)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_w} + \frac{K_A C}{k_w} \quad (d)$$

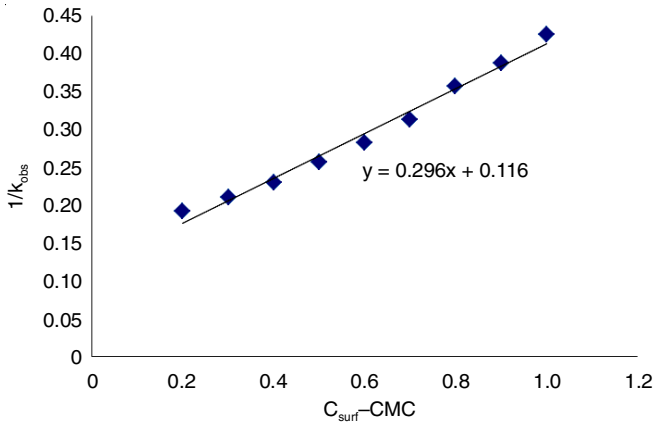


Fig. 11. Plots to confirm applicability of Menger-Portnoy model

To verify the applicability of Menger-Portnoys model to the kinetic data obtained for the TX-100 catalyzed oxidation of ciprofloxacin by chloramine-T in acidic conditions, a graph is plotted between $1/k_{obs}$ and C. Linear plot obtained (Fig. 11) confirms the retardation influence of TX-100 on the title reaction. The calculated value of binding constant K_A has been found to be 2.6.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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