MICELLAR CATALYSIS IN THE OXIDATION OF DL–VALINE BY SODIUM N–CHLORO–4–METHYL BENZENESULPHONAMIDE

Y. R. KATRE*, S. K. SOLANKI, GHANAT K. JOSHI and SANGEETA PATIL

Kalyan Mahavidyalaya, BHILAI NAGAR – 490006 (C.G.), INDIA.

ABSTRACT

The kinetic investigation of oxidation of DL–valine by sodium N–chloro–4–methyl benzene sulphonamide (Chloramine–T) CAT in the presence of the detergent, sodium dodecyl sulphate (NaDS) has been studied by varying the concentration of the reactant. The reaction rate is inhibited by adding NaDS (anionic surfactant). The reaction is more favorable in acidic range (pH 4–6). The reaction is first order with respect to oxidant and zero order with respect to substrate concentration. The positive effect of chloride ion, Hg^{2+} and solvent (methanol) has been observed. The various activation parameters and K/N value has been calculated. The probable reaction mechanism consistent with the observed laws has been proposed.

Key words: DL–Valine, Sodium N–Chloro–4–methyl benzenesulphonamide, Micelle

INTRODUCTION

The kinetic investigations of various organic reactions catalysed or inhibited by dilute aqueous solutions of surfactants have been reported[1–5]. The chlorination of anilines with chloramines–T catalysed by sodium lauryl suphate has been reported by Venkatsubramaniam et al.[6]. At lower pH, chlorination was drastically retarted due to the anionic micelle so formed. The plot of observed rate constant vs detergent gives a sigmoid type curve. They compared the resemblence of surfactants with enzymatic activities. Mahadevappa et al.[7] studied the oxidation of arginine and histidine by chloramines–T (CAT) in acidic medium. They have shown that reaction rates are very sensitive to acid concentrations and follows the rate expression.

$$\frac{-d\,[CAT]}{dt} = k'\,[CAT] = k''\,[CAT]\,[Arg]\,[H^+] + k'''\,[CAT]\,[Arg]\,[Cl^-]^{0.6}$$

$$-d\,\frac{[CAT]}{dt} = k'\,[CAT] = k''\,[CAT]\,[H^+] + k'''\,[CAT]\,[Cl^-]^{0.6}$$

---

* For correspondence
e–mail : kumjos_gha@yahoo.co.in

The work on the oxidation of amino acids has received considerable attention of number of workers[8–10]. In the present work, we report the possibility of micellar inhibition/catalysis and other features of the reaction with amino acid.

EXPERIMENTAL

Materials

NaDS was purified by the method of Duystee and Gurnwald[11]. Phosphate buffer solutions were prepared by standard procedure[11]. CAT was purified and dissolved in doubly distilled water and stored in black coated bottle to avoid any photochemical decomposition. Amino acid and all other reagents viz. Potassium chloride, Mercuric acetate were also of Analar or equivalent grade and their solutions were also prepared in doubly distilled water. After the addition of all reagents, the final pH of the reaction solutions was measured.
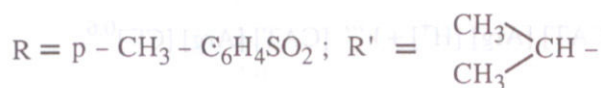
Kinetic measurements

The reaction was carried out under pseudo first order conditions, by keeping a large excess of the amino acid over oxidant CAT. The pH of the reaction solution and temperature ($\pm$ 0.1K) was kept constant. Concentration of CAT was estimated iodometrically at known time intervals. The rate constants were evaluated from the plots of log [oxidant] vs time. The rate constants presented are mean of duplicate runs and have reproducibility with in $\pm$ 4% (Table 1).

Stoichiometry and product analysis

The stoichiometric study of the reaction indicates that in the given experimental condition; one mole of amino acid consumed two moles of CAT. p–Toluene sulphonamide in the reaction mixture was identified by paper chromatography using benzyl alcohol saturated with water as solvent with 0.5% vanillin in 1% HCl solution in ethanol as the spray reagent (R_f = 0.91). Nitriles were detected by their colour reaction with hydroxylamine and ferric chloride[12].

The product analysis of the reaction computes the stoichiometry of the reaction as follows:

$$R'-CH\,(NH_2)\,COOH + 2\,RNCl\,Na \longrightarrow R'CN + CO_2 + 2\,RNH_2 + 2\,NaCl$$

$$R = p - CH_3 - C_6H_4SO_2\,; \quad R' = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH -$$

RESULTS AND DISCUSSION

Dependence of rate on oxidant and substrate

The kinetics of oxidation of DL–valine by CAT in anionic micellar system was investigated at several initial concentrations of reactants under pH–state conditions (pH 5.5.). In the excess

of substrate and fixed surfactant (see Table 1), plots of log [CAT] vs time have linearity; thus, indicating a first order dependence of rate on CAT (Fig. 1). The pseudo–first order rate constants k' for varying initial concentration of CAT are given in Table 1. At lower concentrations of amino acid, the reaction shows fractional order dependence on amino acid whereas at higher concentrations, the reaction depicts a zero order dependence on amino acid (Table 1), suggesting the formation of a reactive species viz. Cl^+ or H_2OCl^+ in a rate determining step. Hence, the rate expression can be given as –

$$\frac{-d\,[CAT]}{dt} \propto \frac{k\,K\,[CAT]\,[S]\,[H^+]}{1 + K\,[S]}$$

where is rate constant and K is equilibrium constant.

Table 1. Effect of reactant concentration on the rate of oxidation of amino Acid by chloramine–T in NaDS micellar system in buffer of pH 5.5, Temp. 308 K

$[NaDS] = 8.0 \times 10^{-3}$ mol dm^{-3}

10^4 [CAT] mol dm^{-3}	10^3 [Valine] mol dm^{-3}	10^4 k sec^{-1}
5.0	2.5	8.05*
5.0	2.5	5.18
4.0	2.5	5.12
2.5	2.5	5.13
2.0	2.5	5.16
1.0	2.5	5.23
5.0	2.5	3.10
5.0	5.0	3.18
5.0	10.0	3.51
5.0	15.0	3.70
5.0	20.0	3.85

* in absence of surfactant

Dependence of rate on surfactant concentration

From number of considerable evidences, it can be shown that micelle surface is a major source of rate variation in bimolecular reactions. The rate study measurements made at different concentrations of the surfactant keeping the other factors constant shows that added sodium dodecyl sulphate inhibits the reaction rates (Table 2). The plot of k_{obs} vs [surfacant] shows a
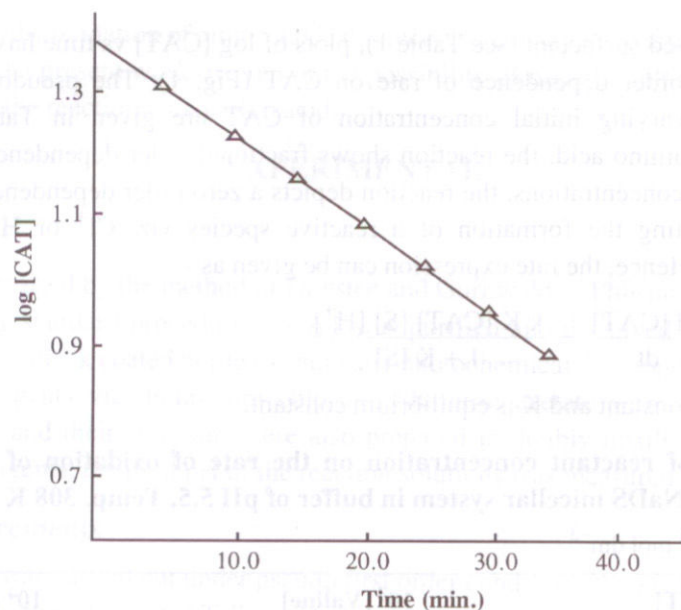
Fig. 1

curvature (Fig. 2). It is interesting to note that the effect of the surfactant on the reaction rate is maximum, in the concentration range $(0.2 \times 10.0 \times 10^{-3}$ M), whereas, CMC value is 8.0×10^{-3} mol.dm^{-3}. It means the surfactant is active even below its CMC value. This might be due to formation of submicellar aggregates at lower CMC value [13,14].

Table 2. Effect of surfactant on the rate of oxidation of amino Acid by chloramine–T in buffer of pH 5.5, Temp. 308 K

[CAT] = 5.0×10^{-4} mol dm^{-3} [Valine] = 2.5×10^{-3} mol dm^{-3}

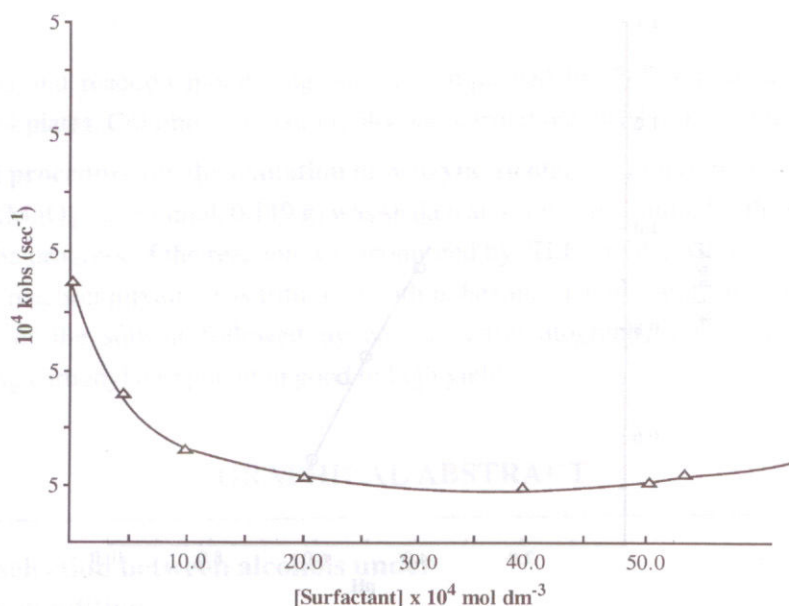| 10^4 [NaDS] mol dm^{-3}	10^4 k sec.$^{-1}$
0.0	8.05
0.5	6.67
1.0	5.60
2.0	5.20
4.0	5.15
5.0	5.35
10.0	5.18
50.0	5.20
80.0	5.18
100.0	5.16

Fig. 2

Dependence of rate on pH

The present study, both in presence and absence of the surfactant shows retardation in the rate with increasing pH values (Table 3). The order dependency on hydrogen ion concentration calculated from the slope of the plot of logarithm of rate constant against pH (Fig. 3).

Table 3. Effect of pH on the reaction rate in the presence of surfactant NaDS

[Valine] = 2.5×10^{-3} mol dm^{-3} [NaDS] = 8.0×10^{-3} mol.dm^{-3}

[CAT] = 5.0×10^{-4} mol dm^{-3} Temp. = 308 K

pH	10^4 k sec^{-1}
4.0	8.48
5.0	5.69
5.5	5.18
6.0	3.59

Dependence of rate on mercuric acetate

The reaction rates were studied in the presence of mercuric acetate. It was observed that in both the cases i.e; presence and absence of the surfactant, there is an increase in the reaction rate with increase in mercuric acetate–concentration (Table 4). The above observation can be explained in the view of complex forming tendency between Hg^{2+} and amino acid. This
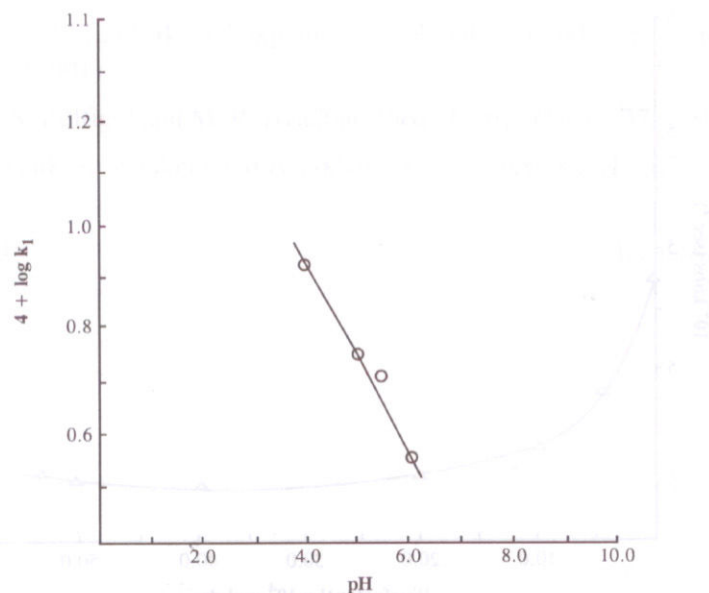
Fig. 3

complexing tendency of Hg^{2+} with amino acid lowers the inhibition produced by the surface of the anionic micelle.

$$R' - CH(NH_2)COOH + Hg^{2+} \rightleftharpoons R' - CH(NH_2) \underset{COO^-}{\overset{NH_2}{\diagdown}} Hg^+ + H^+$$
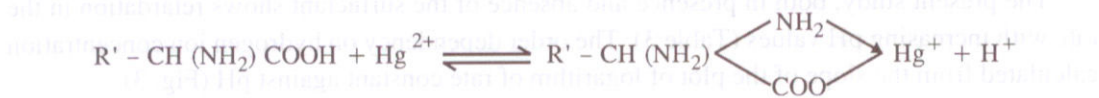
Table 4. Effect of mercuric acetate on the reaction rate in the presence of surfactant NaDS at pH 5.5 and temp. 308 K

[Valine] = 2.5×10^{-3} mol dm^{-3} [NaDS] = 8.0×10^{-3} mol.dm^{-3}
[CAT] = 5.0×10^{-4} mol dm^{-3}

10^5 [Mercuric Acetate] mol.dm^{-3}	10^4 k sec^{-1}
–	5.18
2.5	6.16
10.0	8.60
25.0	10.6
30.0	11.3

Dependence of rate on chloride ion concentration

The rate study measurements were made at different (Cl$^-$) while pH value and ionic strength were kept constant (Table 5). From the data, it has been observed that reaction rate

increased with the addition of chloride ions. This observation is very consistent with of Orton rearrangement of organic haloamides[15].

Table 5. Effect of Cl⁻ on the rate of oxidation of amino acid by chloramines–T in micellar system

[CAT] = 5.0×10^{-4} mol dm^{-3} [NaDS] = 8.0×10^{-3} mol dm^{-3}

[Valine] = 2.5×10^{-3} mol dm^{-3} Temp. = 308 K   pH = 5.5

10^3 [Cl] mol dm^{-3}	10^4 k sec^{-1}
–	5.18
10.0	7.17
50.0	11.1
80.0	15.3

Effect of ionic strength

Neutral salts like sodium perchlorate and sodium sulphate were used to vary ionic strength of the solution and it was observed that there is no effect on the reaction rate of changing ionic strength.

Dependence of rate on solvent

The reaction rate was also studied in different water–methanol mixtures. It was observed that an increase in methanol concentration slightly accelerates the rate of the reaction (Table 6). This observation is very consistent with the fact that CMC values increases in the presence of methanol[16] i.e. micelle formation is lowered. Hence, rate of the oxidation of valine has been increased, (as the micelle formation retarts the process).

Table 6. Effect of solvent (methanol) on the rate of oxidation of amino acid by chloramines–T in micellar system

[CAT] = 5.0×10^{-4} mol dm^{-3} [NaDS] = 8.0×10^{-3} mol dm^{-3}

[Valine] = 2.5×10^{-3} mol.dm^{-3} Temp. = 308 K   pH = 5.5

Methanol (% v)	10^4 k sec^{-1}
–	5.18
1.0	7.00
3.0	7.53
5.0	8.46
30.0	9.44

Dependence of rate on temperature

Various Arrhenious parameters were calculated from the rate measurements at different temperatures. The data so obtained are summarized in Table 7. These values of activation parameters are comparable with those obtained in other cases of chloramines–T oxidation reactions, which follow similar types of reaction mechanisms.
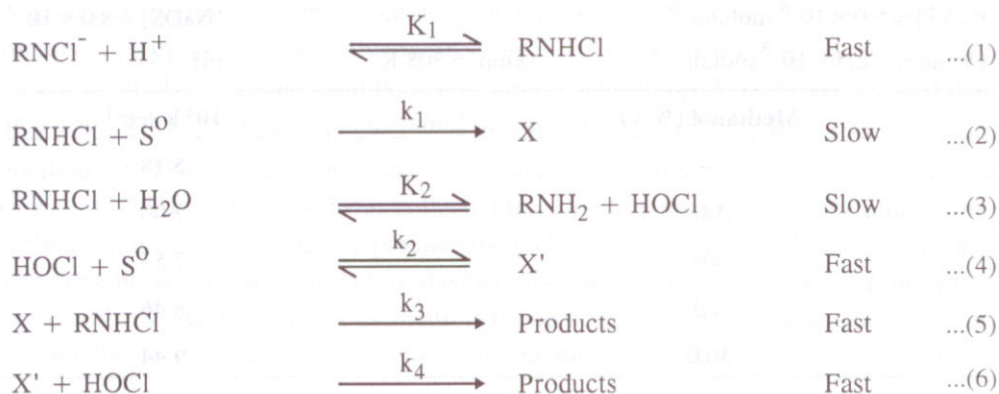
Table 7. Kinetic and thermodynamic parameters for the oxidation of valine by CAT in NaDS micellar system in buffer of pH 5.5

$10^4 k*$ sec^{-1}	5.18
Ea kJ mol^{-1}	82.35
pZ dm^{-3} mol^{-1} sec^{-1}	$5.58–10^{10}$
ΔS JK^{-1} mol^{-1}	-10.30
ΔH kJ mol^{-1}	79.88
ΔG kJ mol^{-1}	80.07

* The rate constant values at 308 K

In aqueous solutions, various oxidizing species may be chloramine–T itself, p–toluene sulphochloramide and hypochlorite ion. Chloramine–T ionizes into the anion RNCl$^-$. The anion picks up a proton in acid solution to give the free acid (N–chloro–p–toluene sulphonamide) as an enhancement in the reaction rate was observed with the decrease of pH value or increase of H$^+$ of the solution. Although the free acid has not been isolated but there is experimental evidence for its formation in acid solution. The acid so formed can under go disproportionation or hydrolysis producing the species RNCl$_2$ and hypochlorous acid, but RNCl$_2$ speices is less probable because experimental observations indicate first order dependence with respect to [CAT]. Since the species RNHCl and HOCl are strong electrophiles, it is more probable that

SCHEME

$$RNCl^- + H^+ \xrightleftharpoons{K_1} RNHCl \qquad \text{Fast} \qquad ...(1)$$

$$RNHCl + S^o \xrightarrow{k_1} X \qquad \text{Slow} \qquad ...(2)$$

$$RNHCl + H_2O \xrightleftharpoons{K_2} RNH_2 + HOCl \qquad \text{Slow} \qquad ...(3)$$

$$HOCl + S^o \xrightleftharpoons{k_2} X' \qquad \text{Fast} \qquad ...(4)$$

$$X + RNHCl \xrightarrow{k_3} \text{Products} \qquad \text{Fast} \qquad ...(5)$$

$$X' + HOCl \xrightarrow{k_4} \text{Products} \qquad \text{Fast} \qquad ...(6)$$

these are responsible for the oxidation of amino acid under the specified conditions. It is also well known that valine (S) can exixts as the anion (S⁻), zwitter ions (S⁰) or the cation (SH⁺) depending on the pH of the medium. In acid solution, majority of valine species are the cation and the zwitter ion. Considering the latter to be the reactive species, the given scheme has been proposed to account for the oxidation of valine at low pH value (acidic range).

Applying the condition for the intermediates and approximation, the rate laws (7) and (8) can be otained for valine (S) assuming that RNHCl and HOCl are the reactive species, respectively.

$$\frac{-d[CAT]}{dt} = K_1 k_1 [CAT][H^+][S]^0 \qquad \qquad ...(7)$$

$$\frac{-d[CAT]}{dt} = \frac{K k_2 [H_2O][CAT][H^+]}{1 + k_2 [H_2O]} \qquad \qquad ...(8)$$

The variation of ionic strength of the medium has no effect on the reaction rate, thus indicating the participation of uncharged species in the rate determining steps (slow). Addition of the solvent (methanol) increases the rate. It indicates dipole–dipole nature of the reacting species in the rate determining steps.

The effect of Cl⁻ on the oxidation of valine can be explained by considering the follwing reaction step –

$$RNHCl + Cl^- \qquad K_3 \rightleftharpoons X'' \qquad \qquad Fast ...(9)$$

The intermediate X'' species may hydrolyse giving HOCl, which interacts directly and rapidly with the substrate (valine) as observed in zero order dependence on the substrate concentration.

Theoretical treatment of micellar effect

To discuss the rate dependence on surfactant, a mathematical model proposed by Bruice *et al.*[17] is applicable. It considers that a substrate, S and n, number of surfactant molecules D, aggregate to form catalytic micelles D_nS; which may further give the products.

$$nD + S \xrightarrow[\text{Oxidant}]{K_D} D_nS$$

Oxidant $\Big| k_w$ $\Big| - k_m$

Products
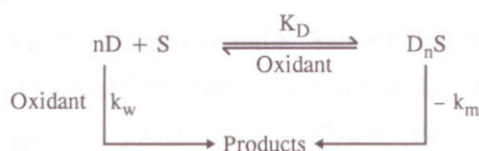
where K_D is the binding constant of the micelle with substrate, k_m and k_W are the rate constant in presence and absence of micelle, respectively.

The rate expression from the above scheme may be given as follow:

$$k_{obs} = \frac{k_m [D]^n + k_w K_D}{K_D + [D]^n} \qquad ...(10)$$

where, k_{obs} is first order rate constant. After rearranging the above expression, the expression obtained is –

$$\log \left[\frac{k_{obs} - k_w}{k_m - k_{obs}} \right] = n \log [D] - \log K_D \qquad ...(11)$$

This equation shows linear ralationship between $\log \left[\dfrac{k_{obs} - k_w}{k_m - k_{obs}} \right]$ and $\log [D]$ (Fig. 4). The

slope value n is called the index of co–operativity. The inhibition effect due to NaDS can be accounted for by the model suggested earlier. The above model is useful to evaluate the substrate–micelle binding constant through an equation of the form–

$$\frac{1}{k_w - k_{obs}} = \frac{1}{k_w - k_m} + \frac{N}{(k_w - k_m) \, K \, (D - cmc)} \qquad ...(12)$$
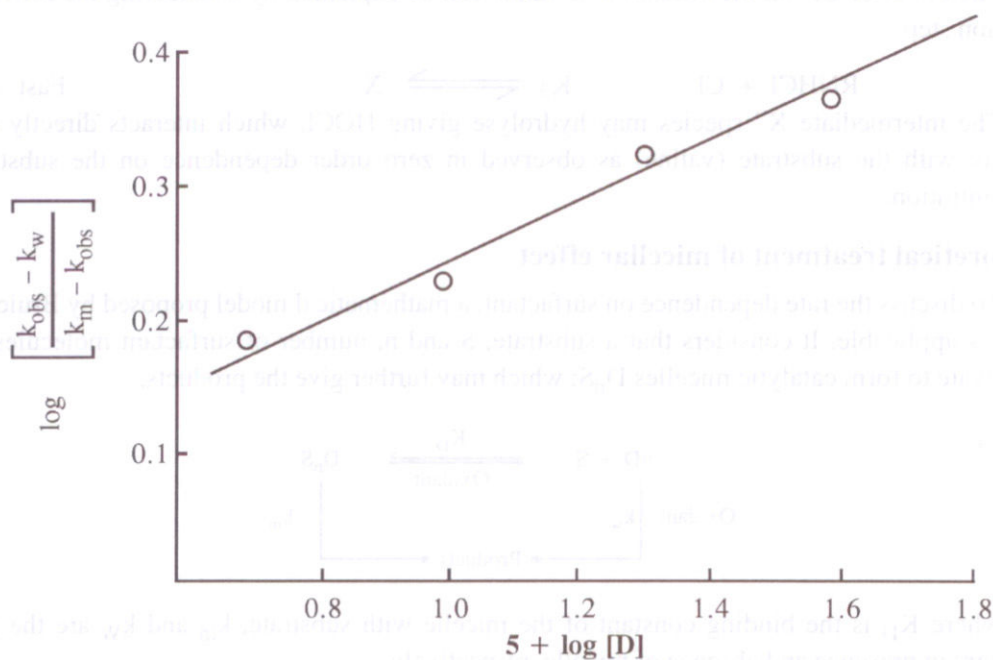

Fig. 4

The value of binding constant K/N calculated for NaDS–valine is 297. This value shows that the rate of oxidation of amino acid, when adsorbed on to micelles, is almost zero. It is responsible for inhibitory action of the anionic micelle derived from NaDS. Hence, it is concluded from these results that the pseudo phase model of micelles explains satisfactorily the effect of micelles on the reaction rate of oxidation of amino acid by chloramine–T.

ACKNOWLEDGEMENT

REFERENCES

1. J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems, Academic Press, New York (1975).

2. K. L. Mittal, "Micellization, Solubilization and Microemulsion", Vol. 2, Plenum Press, New York, (1977).

3. C. A. Bunton, "Reaction Kinetics in Aqueous Surfactant Solutions", Catal. Rev. Sci. Eng., **20**, 1, (1979).

4. K. L. Mittal, "Solution Chemistry of Surfactants", Vol. 1 and 2, Plenum Press, New York, (1979).

5. Grahm, Cairns, Smith and Shaukat Rasoal., J.C.S. Perkin Trans–II, **10**, 1007 (1977).

6. N. Venkatsubramaniam et al., Indian J. Chem, **19A**, 322, (1980).

7. D. S. Mahadevappa K. S. Rangappa and N. M. MadeGowda, Indian J. Chem., **20A**, 263 (1981).

8. Vibha Nagar, S. K. Solanki and V. R. Shastry, Proc. Indian Acad. Sci. (Chem. Sci.), **106 (4)**, 887 (1994).

9. K. S. Rangappa, K. Manjunatha swamy, M. P. Raghavendra and N. M. MadeGowda. Int. J. Chem. Kine., **34(1)**, 49, (2002).

10. Neeti Grover, Neetu kambo, Upadhyay and K. Santosh. Indian J. Chem. **41**, 2482, (2002).

11. M. James, "Practical Physical Chemistry, J.A. Churchil Ltd. London (1967).

12. S. Soloway and A. Lipschietz., Anal., Chem., **22**, 898 (1952).

13. E. Bishop and V. J. Jennings, Talanta., **1**, 197 (1958).

14. C. M. Straks and C. Liotta, "Phase Transfer Catalysis" Principles and Techniques, Academic Press, New York (1976).

15.   E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, (1964). p. 650

16.   L. Panda, and G. B. Behra, J. Indian Chem. Soc. XII, 48 (1985).

17.   R. Bruice, and E. H. Cordes, J. Am. Chem. Soc., **89**, 4695 (1968).