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Effect of Anionic Micelle on the Oxidation of DL-Alanine by Chloramine-T

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Micellar rate enhancement and inhibition are generally treated on the assumption that water and micelles behave as distinct reaction media, *i.e.*, pseudophase. The kinetics of oxidation of DL-alanine by sodium N-chloro-4-methyl benzene sulphonamide (chloramine-T) (**1**) in the presence of the detergent, sodium dodecyl sulphate (NaDS) (**2**) which forms anionic micelles has been studied. The reaction has 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) on the rate is observed. The probable reaction mechanism consistent with the observed laws has been proposed.

Key Words: Oxidation, Chloramine-T, Alanine, Anionic micelle.

INTRODUCTION

The kinetic investigations of various organic reactions are catalyzed or inhibited by dilute aqueous solutions of surfactants[1–5]. The chlorination of anilines with chloramine-T catalyzed by sodium lauryl sulphate has been reported by Venkatsubramanian[6]. At lower pH chlorination is drastically retarded due to the anionic micelle so formed. The plot of observed rate constant *vs.* detergent gives a sigmoid type curve and also compares the resemblance of surfactants with enzymatic activities. Mahadevappa *et al.*[7] studied the oxidation of arginine and histidine by chloramine-T (CAT) in acidic medium. They have shown that reaction rates are very sensitive with acid concentrations (low acid HCl 0.04 to 0.12 M and high acid HCl 0.12 M).

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

EXPERIMENTAL

Phosphate buffer solutions were prepared by standard procedure[11]. Chloramine-T (CAT) was purified and dissolved in doubly distilled water and stored in black coated bottles to avoid any photochemical decomposition. Amino acid and all other reagents, *viz.*, potassium chloride, mercuric acetate were also of AnalaR grade and their solutions were prepared in doubly distilled water.

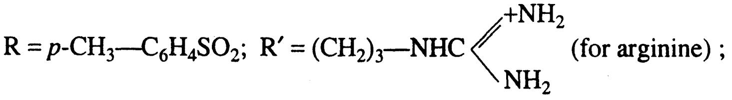
The reaction was carried out under pseudo first order conditions, by keeping a large excess of the amino acid over oxidant CAT. The pH of the reaction solution and temperature (±0.1 K) was kept constant. Concentration of CAT at known time intervals was estimated iodometrically. The rate constants were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

Stoichiometry and Product Analysis

The stoichiometric study of the reactions 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 identifies 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 ($R_f = 0.905$). 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:

$$R'\text{—}CH(NH_2)COOH + 2RNClNa \longrightarrow R'CN + CO_2 + 2RNH_2 + 2NaCl$$



$$R = p\text{-}CH_3\text{—}C_6H_4SO_2;\ R' = (CH_2)_3\text{—}NHC\begin{cases} {}^{+}NH_2 \\ NH_2 \end{cases} \text{(for arginine)};$$

and

$$HC{=}N\text{—}CH{=}C(NH)\text{—}CH_2\text{—}$$

RESULTS AND DISCUSSION

Dependence of rate on oxidant and substrate

The kinetics of oxidation of DL-alanine by CAT in anionic micellar system were investigated at several initial concentrations of reactants under pH-state conditions (pH 5.5). In the excess of substrate and fixed surfactant (Table-1), plots of log [CAT] *vs.* time have linearity indicating a first order dependence of rate on CAT (Fig. 1). The pseudo first order rate constants k′ are constants for varying initial concentration of CAT as given in Table-1. At lower concentrations of amino acids the reaction shows fractional order dependence on amino acid whereas at higher concentration the reaction depicts a zero order dependence on amino acid (Table-1), suggesting a formation of reactive species, *viz.*, Cl^+ or H_2OCl^+ in a rate determining step. Hence, the rate expression can be given as:

$$\frac{-d[CAT]}{dt} = \frac{kK[CAT][S][H^+]}{1 + K[S]}$$

where k is rate constant and K is equilibrium constant.

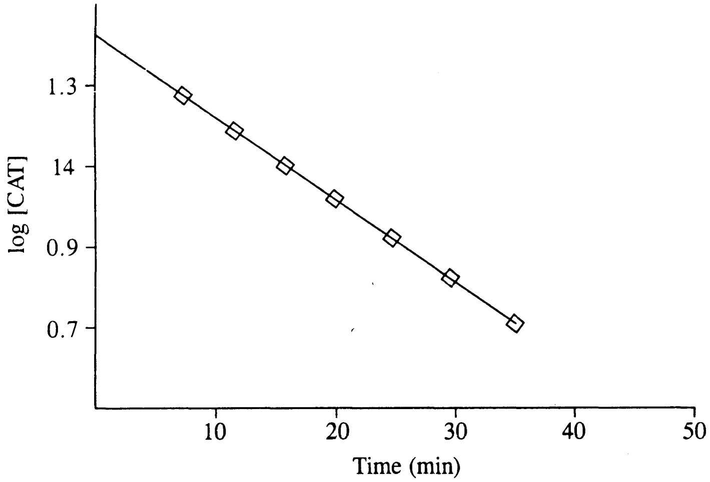


Fig. 1. A plot of log [CAT] *vs.* time

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, TEMPERATURE 308 K)

[NaDS] = 8.0 × 10^{-2} mol dm^{-3}

10^5 [CAT] (mol dm^{-3})	10^4 [alanine] (mol dm^{-3})	R [alanine] (k′ sec^{-1})
50	25	10.31*
50	25	6.90
40	25	6.88
25	25	7.09
20	25	6.92
10	25	6.78
50	25	5.68
50	25	4.39
50	50	4.85
50	100	5.90
50	150	5.98
50	200	6.13

*Values in absence of surfactant.

Dependence of rate on surfactant

From number of considerable evidences it can be shown that micelle surface is a major source of rate variations of 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 plos of k_{obs} *vs.* [detergent] has curved nature (Fig. 2). It is interesting to note that the effect of the detergent on the reaction velocity is maximum, in the concentration range (0.2 to 10.0×10^{-3}), whereas CMC value is 8.0×10^{-3} mol dm^{-3}. It means the detergent is active even below the CMC value, which might be due to formation of submicellar aggregates at lower CMC value[13, 14].

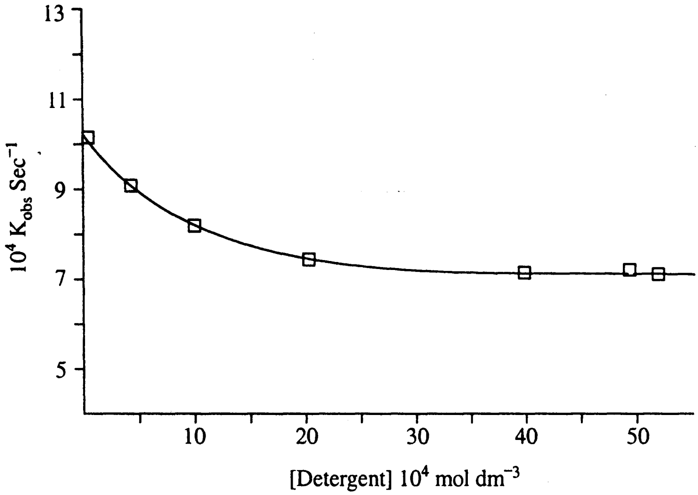


Fig. 2. A plot of k_{obs} *vs.* [detergent]

TABLE-2
EFFECT OF SURFACTANT ON THE RATE OF OXIDATION OF
AMINO ACID BY CHLORAMINE-T IN BUFFER (pH 5.5, TEMPERATURE 308 K)

[CAT] = 50×10^{-5} mol dm^{-3}, [Alanine] = 25×10^{-4} mol dm^{-3}

10^4 [NaDS] (mol dm^{-3})	R [alanine] (k' sec^{-1})	10^4 [NaDS] mol dm^{-3}	R [alanine] (k' sec^{-1})
0.0	10.31	5.0	7.03
0.5	9.20	10.0	6.90
1.0	8.75	50.0	6.92
2.0	7.75	80.0	6.90
4.0	6.86	100.0	6.87

Dependence of rate on pH

The present study, both in presence and absence of the detergent shows the retardation of rate with increase of the pH value (Table-3). The order dependence on hydrogen ion concentration calculated from the slope of the plot of log [k] against pH (Fig. 3).

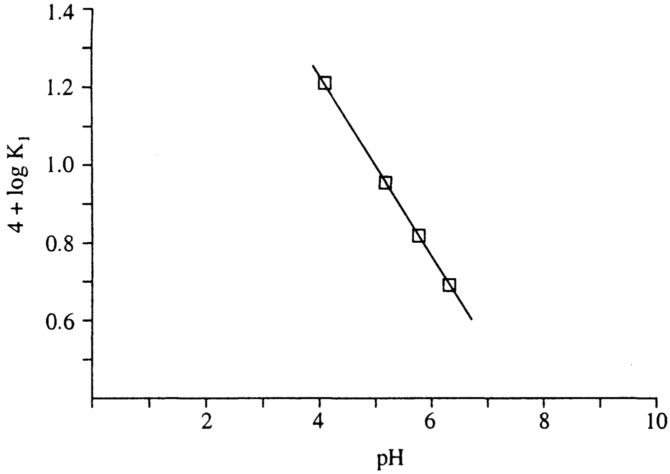


Fig. 3. A plot of log [k] *vs.* pH

TABLE-3
EFFECT OF pH ON THE REACTION RATE IN THE PRESENCE OF SURFACTANT (NaDS)

[Alanine] = 25×10^{-4} mol dm^{-3} [NaDS] = 6.0×10^{-3} mol dm^{-3}
[CAT] = 50×10^{-5} mol dm^{-3} Temperature 308 K

pH	10^4 k sec^{-1}	pH	10^4 k sec^{-1}
4.0	16.90	5.5	6.90
5.0	9.08	6.0	4.87

Dependence of rate on mercuric acetate

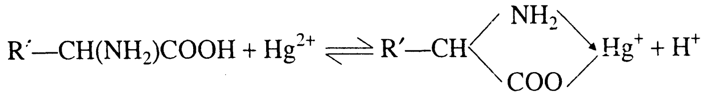
The reaction rates were studied in the presence of mercuric acetate. It was observed that in both the cases presence and absence with increase in mercuric acetate-concentration there is acceleration in the reaction velocity (Table-4).

TABLE-4
EFFECT OF MERCURIC ACETATE ON THE REACTION RATE IN THE PRESENCE OF SURFACTANT AT pH 5.5 AND TEMPERATURE 308 K

[Alanine] = 25×10^{-4} mol dm^{-3} [NaDS] = 8.0×10^{-3} mol dm^{-3}
[CAT] = 50×10^{-5} mol dm^{-3}

10^{-5} [Mercuric acetate] (mol dm^{-3})	10^4 k sec^{-1}	10^{-5} [Mercuric acetate] (mol dm^{-3})	10^4 k sec^{-1}
—	6.90	25.0	12.8
2.5	8.32	30.0	—
10.0	9.21		

The above observation can be explained in view of complex forming tendency between Hg^{2+} and amino acid. This tendency of Hg^{2+} with amino acid lowers the inhibition effect produced by the surface of the anionic micelle.



$$R'\text{—}CH(NH_2)COOH + Hg^{2+} \rightleftharpoons R'\text{—}CH\begin{matrix}NH_2\\COO\end{matrix}Hg^{+} + H^{+}$$

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, the reaction rate increases with the addition of chloride ion. This observation is very consistent with the Orton rearrangement of organic haloamides[15].

TABLE-5

EFFECT OF Cl^- ON THE RATE OF OXIDATION OF AMINO ACID BY CHLORAMINE-T IN MICELLAR SYSTEM

$[CAT] = 50 \times 10^{-5}$ mol dm^{-3} $[NaDS] = 8.0 \times 10^{-3}$ mol dm^{-3}
$[Alanine] = 25 \times 10^{-4}$ mol dm^{-3} Temperature = 308 K

$10^3\,[Cl^-]$ (mol dm^{-3})	10^4 k sec^{-1}	$10^3\,[Cl^-]$ (mol dm^{-3})	10^4 k sec^{-1}
—	6.90	50	11.7
10	8.61	80	16.2

Effect of variation of ionic strength

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

Dependence of rate on solvent

The reaction rate was also studied at 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 increase with the presence of methanol[16], *i.e.*, micelle formation is lowered. Hence, rate of the oxidation of alanine is increased (as the micelle formation retards the process).

TABLE-6

EFFECT OF SOLVENT (METHANOL) ON THE RATE OF OXIDATION OF ALANINE BY CHLORAMINE-T IN MICELLAR SYSTEM

$[CAT] = 50 \times 10^{-5}$ mol dm^{-3} $[NaDS] = 8.0 \times 10^{-3}$ mol dm^{-3}
$[Alanine] = 25 \times 10^{-4}$ mol dm^{-3} Temperature = 308 K pH = 5.5

Methanol (volume %)	10^4 k sec^{-1}	Methanol (volume %)	10^4 k sec^{-1}
—	6.90	5	8.20
1	7.44	30	9.47
3	7.87		

Dependence of rate on temperature

Various Arrhenius parameters were calculated from the rate measurements carried out at different temperatures. The data so obtained are summarized in Table-7. These values of activation parameters are very comparable with those obtained in other cases of chloramine-T oxidation reactions, which follow similar types of reaction mechanisms.

TABLE-7
KINETIC AND THERMODYNAMIC PARAMETERS FOR THE OXIDATION OF ALANINE BY CAT IN NaDS MICELLAR SYSTEM IN BUFFER (pH 5.5)

10^4 (k* sec^{-1})	6.90	ΔS (JK^{-1} mol^{-1})	–14.34
E_a (kJ mol^{-1})	76.49	ΔH (kJ mol^{-1})	75.88
PZ (dm^{-3} mol^{-1} sec^{-1})	7.34×10^9	ΔG (kJ mol^{-1})	76.17

*The rate constant values at 308 K.

In aqueous solution, various oxidizing species may be chloramine-T itself, *p*-toluene sulphochloramide and hypochlorite ion. Chloramine-T ionize into the anion $RNCl^-$. The anion picks up a proton in acid solution to give the free acid (N-chloro-*p*-toluene sulphonamide) as enhancement of the reaction rate with the decrease of pH value on increase of H^+ of the solution is observed. Although the free acid has not been isolated but there is experimental evidence for its formation in acid solution. The acid so formed can undergo disproportionation or hydrolysis producing the species $RNCl_2$ and hypochlorous acid, but $RNCl_2$ species 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 they are responsible for the oxidation of amino acids under the specified conditions. It is also well known that an alanine (S) can exist as the anion (S^-), zwitterion (S^0) or the cation (SH^+) depending on the pH of the medium. In acid solution majority of alanine species are the cation and the zwitter ion. Considering the latter to be the reactive species, the **Scheme** has been proposed to account for the oxidation of alanine at low pH value (acidic range).

Scheme

$$RNCl^- + H^+ \quad \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} RNHCl \qquad \text{Fast} \qquad (1)$$

$$RNHCl + S^0 \quad k_1 \longrightarrow X \qquad \text{Slow} \qquad (2)$$

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

$$HOCl + S^0 \quad k_2 \rightleftharpoons X' \qquad \text{Fast} \qquad (4)$$

$$X + RNHCl \quad k_3 \longrightarrow \text{Products} \qquad \text{Fast} \qquad (5)$$

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

Applying the condition for the intermediates and approximate reasons, rate laws (7) and (8) can be obtained for alanine (S) by assuming that RNHCl and HOCl are the reactive species respectively.

$$\frac{-d[CAT]}{dt} = K_1k_1[CAT][H^+][S]^0 \qquad (7)$$

$$\frac{-d[CAT]}{dt} = \frac{K_1k_1[H_2O][CAT][H^+]}{1 + k_2[H_2O]} \qquad (8)$$

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

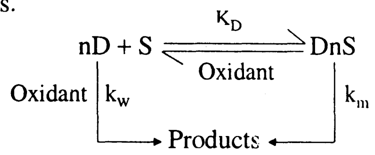
The effect of Cl^- on the oxidation of alanine can be explained by considering the following reaction step:

$$RNHCl + Cl^- \quad K_3 \rightleftharpoons X'' \qquad \text{Fast} \qquad (9)$$

The intermediate X″ species may hydrolyze giving HOCl which interacts directly and fastly with the substrate (alanine) as observed zero order dependence on the substrate concentration.

Theoretical treatment of micellar effect

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



where K_D is the binding constant of the micelle with substrate k_m and k_w are the rate constants in presence and absence of micelle.

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

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

where k_{obs} is first order rate constant. After rearranging the above expression we obtain the expression:

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

This equation shows linearity (Fig. 4) relationship between $\log\left[\frac{k_{obs} - k_w}{k_m - k_{obs}}\right]$ and log [D]. The slope value n is called the index of cooperativity. The inhibition

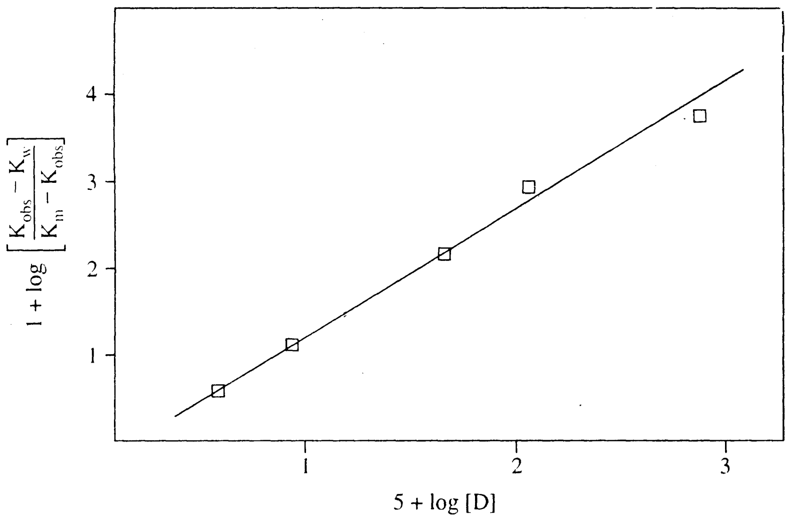


Fig. 4.

effect due to NaDS can be accounted for by the model suggested by Menger *et al.* The above model is useful to evaluate the substrate micelle binding constant through an equation of the form:

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

The values of binding constants K/N calculated for NaDS-alanine is 261. This value shows that the rate of oxidation of amino acids when adsorbed on to micelles is almost zero, which is responsible for inhibitory action of the anionic micelle derived from NaDS. Hence it is concluded from the above results and findings that the pseudo phase model of micelles explains very satisfactorily the effect of micelles on the reaction rate of oxidation of amino acids by chloramine-T.

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THE H BOND

The glue of life, tying molecules together,
Or causing them to split apart.
The atom in the fuel of burning stars,
Lying in between centres of electronegativity,
Bonded to one, and attracted to the other,
The weak force joining the three!
Found in all forms of life, large and small,
Present in the alpha helix, beta-pleated sheets,
The hemoglobin and the catalysts of life,
And in the triple helix of collagen!
And found in the double helix of the DNA.
The tying hands of the fluid of life,
Holding together the units of aqua,
Creating a tension at the surface,
And an increased resistance to flow,
Or a climb up the walls of the capillary.
Supporting the life from hot to cold,
Keeping it warm by not letting them go,
Keeping it cool as they depart.
The crust of ice covering the fluid,
The void of space in the 3-D lattice,
The frozen ones resting on the fluid of life!

The membrane, covering the cell,
Bathed in the fluid of life,
The bonds between aqua and the polar heads,
Forming the bilayer and the micelles.
The H-Bonds dissolving sugar in blood,
Giving the enzymes the globular shape,
And strength to the fibres of proteins!
Would that you know what that is!
The pervading weak force of life!

—Dr. Fazlul Huq