Kinetic studies on the mechanism of the relative catalytic activities of surfactants in the oxidation of amino-acids by chloramine–T

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Abstract. The kinetics of oxidation of amino-acids by chloramine–T in the presence of two different surfactants (cationic and anionic surfactants) in acidic medium has been studied. The kinetic results show that the reaction is fractional and first order with respect to substrate and oxidant respectively. The influence of halides, ionic strength and solvent on the rate has been studied.

The effect of surfactants on the reaction show that the reaction velocity is highly sensitive to the variation of surfactant concentration. The micelle–substrate binding constant (K) and co-operativity index have been calculated indicating the stability of the catalyst substrate micelles (complex) so formed. A probable reaction path has been suggested and discussed in the light of various experimental results and findings.

Keywords. Oxidation; chloramine–T; surfactants; binding constant; co-operativity index.

1. Introduction

Surfactant assemblies whose properties are well understood at the chemical level are used to mimic the desired functions of cell membranes. Compartmentalization of molecules in these membrane mimetic systems may alter initial, transition and product states and could reduce reaction dimensionalities. These, in turn, often lead to reaction rates, products and stereochemistries that are different from those observed in dilute aqueous solutions (Cordes and Dunlop 1969; Cordes and Gitter 1973; Fendler and Fendler 1975; Bunton 1976).

Recently, there has been an increased interest in the influence of micelles and other types of surface active agents on reactions, particularly as aids to synthesis and reaction control. The results clearly demonstrate that the micelles promote chemical reactivity by increasing the local reactant concentrations. An appropriate kinetic analysis for surface reactions in micellar solution is developed and shown to offer a reasonable explanation. The present work on the influence of surfactants on the oxidation of amino-acids by chloramine–T has been undertaken in an attempt to develop a kinetic model analogous to the Hill model describing enzymatic reactions (Tonellato 1979; Fornasier and Tonellato 1980; Katgeri *et al* 1980).

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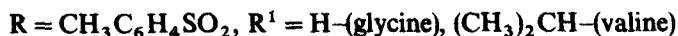
2. Materials and method

Cetyltrimethyl ammonium bromide (BDH) and sodium dodecyl sulphate (Loba Chemie) were used after purification. Distilled acetic acid was used. Aqueous solutions of glycine (Sarabhi Chemicals) and valine (BDH, England) were prepared and standardized by the method available in the literature. All solutions were prepared in doubly distilled water. The method used for the kinetic determination of the reaction rates was performed by using Ostwald's isolation method.

3. Results and discussions

The relative catalytic activities of surfactants on the oxidation of amino-acids by chloramine–T has been studied in the acidic medium.

$$2R\,NNaCl + R^1\,CH\,NH_2\,COOH \rightarrow 2R\,NH_2 + 2NaCl + CO_2 + RCN$$

where
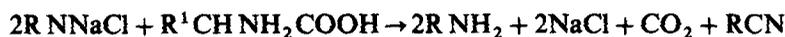
$$R = CH_3C_6H_4SO_2, \quad R^1 = H\text{--(glycine)}, (CH_3)_2\,CH\text{--(valine)}$$

3.1 *Dependence of rate on [CAT] and [amino-acids]*

When the amino acid is in large excess, plots of log $(a–x)$ versus time are linear, indicating first-order dependence on [CAT]. The reaction has fractional order with respect to substrate concertration.

3.2 *Dependence of rate on [surfactants]*

The reaction was studied at different concentration of the surfactants (0.5×10^{-3} mol dm^{-3} to 6.0×10^{-3} mol dm^{-3}) in both the cases. The rate of reaction increases with the increase of [CTAB] and then decreases upto certain limits, while it decreases with the increase of [NaDS] (table 1). This behaviour is in accordance with the micellar catalysis of organic reactions of anion neutral molecular type. With increasing

Table 1. Effect of reactant concentration on rate of oxidation of amino acids by CAT.

(Surfactant) × 10^{-3}	$10^4 \times k$ (s^{-1})		$10^4 \times k$ (s^{-1})	
	NaDS[a]	CTAB[a]	NaDS[b]	CTAB[b]
0·0	1·43	1·41	3·12	3·0
1·0	1·23	1·60	2·90	4·41
1·5	1·17	2·38	2·82	4·60
2·0	1·03	2·06	2·73	5·08
3·0	0·82	—	2·70	4·80
4·0	0·90	2·17	2·59	3·69
5·0	0·93	—	2·64	—
6·0	—	2·06	—	2·45

(a) Glycine; (b) valine [CAT] – 5.0×10^{-3} mol dm^{-3}, [amino acid] – 3.0×10^{-2} mol dm^{-3} AcOH – 30% (v/v), temperature – 308°K
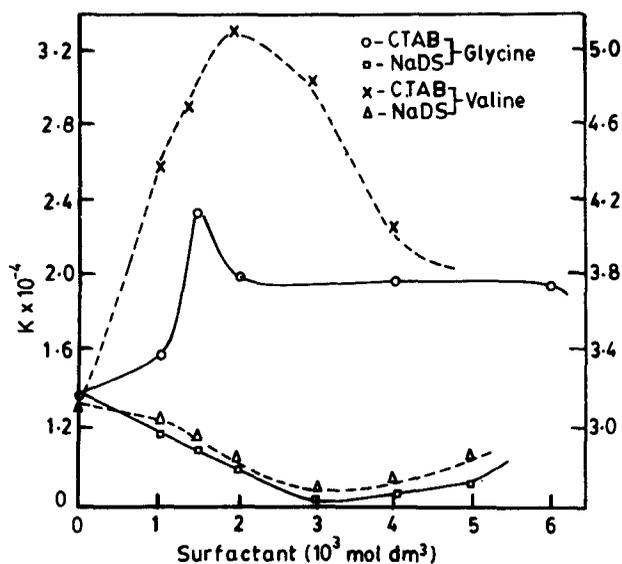
Figure 1. Plot of K v/s [surfactant]; $[CAT] - 5.0 \times 10^{-3}\,mol\,dm^{-3}$, [amino-acid] $- 3.0 \times 10^{-2}\,mol\,dm^{-3}$; AcOH $- 30\%$ (v/v), Temperature $- 308$ K.

concentration of CTAB the relative concentrations of organic substrate and ionic reactants in the Stern layer of the micelle increases rapidly. This tends to accelerate the reaction. The inhibition by NaDs may be due to increasing concentrations of unreactive counter ions and increasing affinity of unreactive counter ions for the Stern layer. Since there is possibility of competition between reactive and nonreactive ions for sites in the Stern layer, the rate of reaction decreases (figure 1).

3.3 *Effects of other parameters*

3.3a *Halides*:   Addition of chloride ions to the reaction mixture has no significant effect on the rate.

3.3b *Ionic strength*:   The rate is unaffected by an increase in the ionic strength of the medium.

3.3c *Temperature*:   The reaction has been studied at different temperatures and the activation parameters have been evaluated in both the cases.

The values of energy of activation show that the reaction is more favorable in the presence of CTAB, as compared to NaDS. The fairly high values of negative $\Delta S^{\#}$ and of positive $\Delta H^{\#}$ in the case of oxidation of glycine and valine in the presence of NaDS suggests the formation of more ordered activated complexes and the transition state is highly solvated (Mahadevappa *et al* 1984).

3.4 *Theoretical treatment of micellar data*

The micellar catalysis or inhibition could be applied theoretically by making certain simplifications and assuming that only one substrate is incorporated into a micelle

Table 2. Activation parameters of amino acids.

| | In the presence of CTAB | | | | In the presence of NaDS | | | |
	Glycine		Valine		Glycine		Valine	
Temperature (K)	308	318	308	318	308	318	308	318
Rate constant k $\times 10^{-4}$	1·50	3·07	1·55	2·96	1·57	3·14	1·60	3·28
Ea (kJ mol^{-1})	52·00 ($\pm$0·66)		52·20 ($\pm$0·60)		56·00 ($\pm$0·44)		59·61 ($\pm$1·00)	59·70 ($\pm$1·00)
$\Delta S^{\ddagger}$	−24·40 ($\pm$0·30)		−25·00 ($\pm$0·22)		−26·00 ($\pm$0·30)		−49·34 ($\pm$0·10)	−50·00 ($\pm$0·10) .
$\Delta H^{\ddagger}$	47·42 ($\pm$0·44)		49·60 ($\pm$0·31)		49·32 ($\pm$0·22)		57·00 ($\pm$0·20)	57·60 ($\pm$0·70)

and that the aggregation number N of the micelle is independent of the substrate On the basis of these concepts the following scheme is proposed.

$$Dn + S \rightleftharpoons DnS$$

$$k_0 \quad \text{products} \quad k_m$$

Scheme 1.

From a system where catalysis is observed at [surfactant] close to CMC, the scheme 1 provides an equation.

The concentration of micelles Dn is given by

$$[Dn] = (C_D - cmc)/N, \tag{1}$$

where C_D is stoichiometric concentration of the detergent;

$$\frac{k_{obs} - k_0}{k_m - k_{obs}} = K(C_D - cmc)/N, \tag{2}$$

where k_m is the maximum rate constant obtained in the presence of detergent.

From the above, the plot of $(k_{obs} - k_0)/(km - k_{obs})$ vs $(CD - cmc)$ is linear in the present case. The values of K/N obtained in the case of CTAB and NaDS were $4·7 \times 10^{-2}$ M, 24×10^{-3} M (glycine), and $5·80 \times 10^{-2}$ M, 25×10^{-3} M for (valine), respectively. The values show that concentration of the reactants in a small volume at the micellar surface is a major cause of rate enhancement or the inhibition of oxidation reactions (Raghavan *et al* 1982).

The catalysis by surfactants (i.e. CTAB or NaDS) can also be explained alternatively by the Piszkiewicz (1977) model. The values of n (called the index of co-operativity) obtained in the present case for glycine and valine in the presence of CTAB and NaDS are 0·85, 1·06 and 0·96, 1·0, respectively. From these values of n it can be concluded that in the case of CTAB the incorporation of the first molecule renders

the association of more detergent molecules difficult. In the case of NaDS, $n = 1.06$ indicating a non-interacting site (Koshland *et al* 1966; Boyer 1970).

Therefore, ionic reactants are attracted by the micellar surface which does not contain any substrate, with a consequent diminution of these at the surface which contains substrate. The micellar-catalyzed reaction thus appears to be analogous to the Hill model for enzyme-catalyzed reaction and this is of importance in the recent advances in the area of molecular biophysical chemistry.

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