

Positive Cooperativity Index of the Micellar Catalysed Oxidation of Amino Acids by Acidic Permanganate

Vijay R Chourey¹, Nameeta Bende²

Department of Chemistry, Govt. Holkar Autonomous Science College, Indore-17(M.P), INDIA

Abstract: *The spectrophotometrical study of oxidation of i.e. glycine and L-isomers of three amino acids have been done in the presence of surfactant i.e. sodium lauryl sulphate (NaLS) and sulphuric acid by potassium permanganate. A Kinetic investigation of oxidation of amino acids by acidic permanganate has been carried out spectrophotometrically. The reaction is reported as linear double stage process, first stage is followed by second fast stage. The surfactant used in the reaction is an anionic surfactant. Its catalytic effect on the rate of reaction has been observed carefully. Positive cooperativity Index of the reaction have also been calculated.*

Keywords: Sodium Lauryl Sulphate, Spectrophotometer, L-Isomers, Positive cooperativity Index.

1. Introduction

An anionic surfactant- Sodium lauryl sulfate (NaLS) is an organic compound with the formula $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$. It is an anionic surfactant used in many cleaning and hygiene products. The salt is of an organosulphate consisting of a 12-carbon tail attached to a sulphate group, giving the material the amphiphilic properties required of a detergent. Being derived from inexpensive coconut and palm oils, it is a common component of many domestic cleaning products^[1].

Premicellar aggregation behavior is one of the important properties to understand the self assembly of surfactant in aqueous solutions. It is well known that the some surface-active agents form premicellar aggregates at concentration below the critical micellization concentration (CMC).

When the concentration of surfactant is smaller than that of its CMC is known as premicellar concentration. Many researchers have proposed the formation of premicellar aggregates and their catalytic action. The effect of Sodium Dodecyl Sulphate (SDS) micelles and premicelles on the reversible alkaline fading reactions of crystal violet and malachite green were studied by Zhang et al^[2].

The role of premicellar assemblies upon cyclization of O-(W-Haloalkoxy)phenoxide ions was studied by Cerichelli et al^[3]. Imae et al^[4] reported that the surface tension verses concentration curves of a non-ionic surface active dye in aqueous methanol solutions have two clear break points, which indicates two step micellization of the molecules. Uzeki et al^[5] showed that crown ether surfactants have several break points on surface tension verses concentration curves and proposed that the formation of premicellar aggregates occurs in the bulk solution^[6]. Fendler^[7] has given following relationship for premicellar number $N=60$ (17) per SDS micelle. Xiaohong et al^[8] confirmed by HNMR studies that in case of sodium dodecyl sulphate and CTAB that when the concentration are lower than 'CMC' there are oligomers (Premicelles) formed in these two surfactant system. It has been defined as premicellar concentration

(PMC) and presence of premicelles have found to influence the rate of reaction.

There are extensive evidences from the other system that some aggregation of surfactant is present below CMC⁹⁻¹² which is able to catalyse the reaction.

A kinetic model analogous to Dill model^[13,14] to explain the premicellar catalytic phenomenon on the basis of positive-cooperativity has been suggested by Piszkiwicz^[15]. The model accommodates the plot of $\log((k_{\text{obs}} - k_0)/(k_{\text{lim}} - k_{\text{obs}}))$ against $\log[\text{surfactant}]$, which is linear and gives the slope 'n' an empirical constant and a measurement of positive cooperativity. Behera et al^[16-17] has also reported the same model is the case of sodium lauryl sulphate (NaLS) catalysed reaction of meta and para substituted benzoate and phenacyl bromide. They have also observed the same in the influence of O-substituents in anionic surfactant catalysed reaction of benzoate ions with phenacyl.

2. Material and Methods

All reagents used were of AnalaR and G.R. grade. Permanganate solution was prepared and tested as given by Vogel^[18]. Doubly distilled water was used to prepare all the solutions.

Kinetic experiments were carried out in a thermostat in which the temperature is controlled within $\pm 0.1^\circ\text{C}$. The reactions were usually followed upto 70% of completion. The reaction was initiated by adding requisite amount of pre equilibrated solution of permanganate to an equilibrated mixture of substrate (amino acids), surfactant, metal ion (MnSO_4) and sulphuric acid solutions. The zero time of the reaction was noted when half of the permanganate solution was added. The total volume of the reaction mixture was always kept 50 ml.

All kinetic measurements were conducted under pseudo first order conditions where the amino acid was maintained in a large excess over the permanganate ion concentration.

Kinetic studies was performed by using Systronics 106 spectrophotometer at 525 nm i.e. at absorbance maximum of permanganate. It was verified that there is no interference from other reagents at this wavelength. 2 ml of the aliquot of reaction mixtures were withdrawn at known intervals of time and the reaction was quenched by adding it to a known excess of ice-cold distilled water (temperature $\lt; 2^{\circ}\text{C}$) in the optic cell. The values of the absorbance due to unreacted permanganate at given times were read out directly from the spectrophotometer.

3. Result and Discussion

It has been observed that with the increase in the concentration of sodium lauryl sulphate, the pseudo first order rate constants also increases. in both the stages in all the four amino acids. Increasing the surfactant concentration should eventually lead to all the substrate being associated with the micelle. For amino acids, increasing concentration of surfactant also increase the affinity with substrate to incorporate the substrate.

Further the plots of $\log\left[\frac{k_1 - k_0}{k_0 - k_{-1}}\right]$ against $\log [\text{NaLS}]$ were also found to be linear (Figure-1.2,2.2,3.2 and 4.2).Above discussion confirms its role as a positive catalyst in oxidation reaction.

It is well known that surfactant form micelles and appear as catalyst in number of chemical reactions. Its catalytic effect has also been indicated in present cases too. It has been pointed out by Moelwyn-Hughes^[19] and Chourey^[20] that in the presence of catalyst the uncatalysed and catalysed reactions proceed simultaneously.

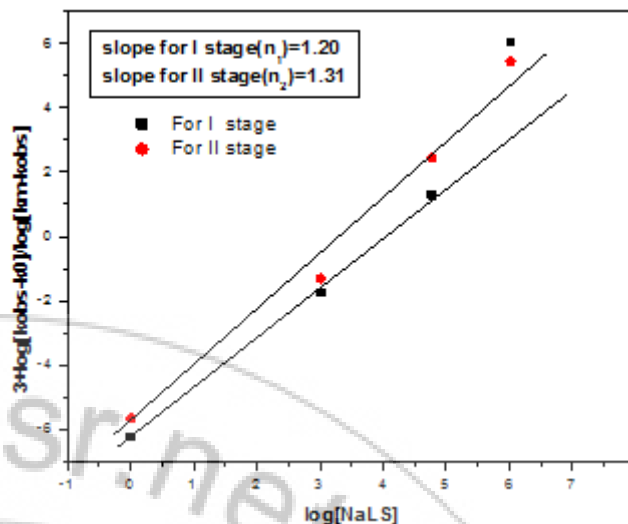


Figure 2.2:-Piszkwicz plot for L-Alanine

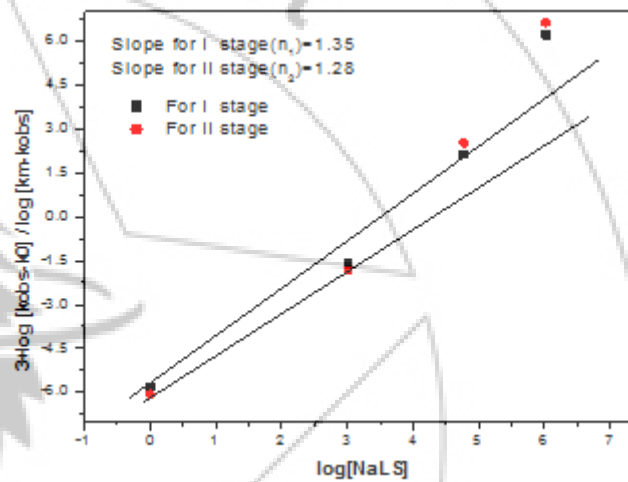


Figure 3.2:-Piszkwicz Plot for L-Valine

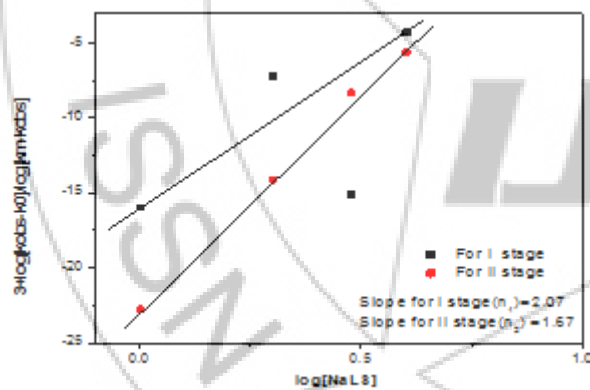


Figure 1.2:-Piszkwicz plot for Glycine

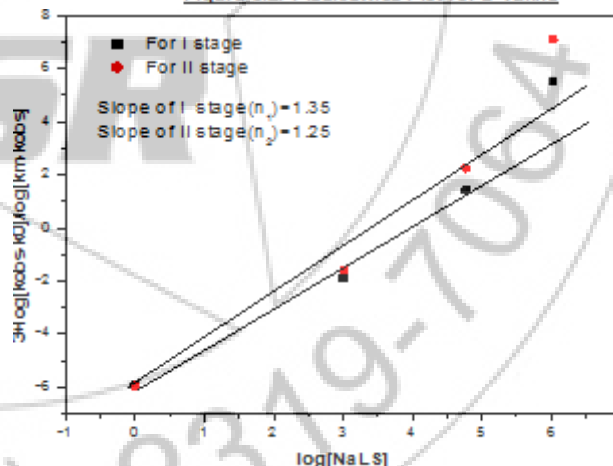


Figure 4.2:-Piszkwicz Plot for L-Leucine

In the present study, it has been found that value of the rate constant is directly proportional to the concentration of the catalyst [NaLS] therefore, catalytic constant k_c can be obtained using equation:

$$k_c = \frac{(k_1 - k_0)}{[\text{NaLS}]}$$

Where k_1 and k_0 are pseudo first order rate constant in presence and in absence of NaLS. Thus values of k_c and k_c^{\pm} , the catalytic constant for first and second stages have been determined, which are found fairly constant. Results have been summarized in Table-1.

The oxidation reactions of all four amino acids have been found to be catalysed by addition of sodium lauryl sulphate as discussed above. The reaction rate increases with the increase in the surfactant concentration from $1 \times 10^{-4} \text{ mol dm}^{-3}$ to $5 \times 10^{-4} \text{ mol dm}^{-3}$. The reported CMC (Critical Micellar Concentration) of this surfactant is $8.12 \times 10^{-3} \text{ M}$ at 25°C .

Literature survey reports that the catalysis below CMC is also feasible^{[22]-[24]} which is known as pre-micellar catalysis.

Table 1: Various Catalytic constants ($k_c \times 10^{-3} \text{ Litre mole}^{-1} \text{ min}^{-1}$)

$[\text{KMnO}_4] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{H}_2\text{SO}_4] = 2 \text{ mol dm}^{-3}$
Temp. = 303K

[NaLS] mol dm ⁻³	[Glycine] 0.1 mol dm ⁻³		[L-Alanine] 0.1 mol dm ⁻³		[L-Valine] 0.01 mol dm ⁻³		[L-Leucine] 0.01 mol dm ⁻³	
	For I Stage k_c	For II Stage k_c	For I Stage k_c	For II Stage k_c	For I Stage k_c	For II Stage k_c	For I Stage k_c	For II Stage k_c
1×10^{-4}	3.03	4.37	7.88	18.13	7.32	8.09	5.15	12.66
2×10^{-4}	3.41	4.18	7.83	18.92	7.33	7.96	5.15	12.25
3×10^{-4}	3.74	4.19	7.83	18.03	7.90	8.06	5.26	12.06
4×10^{-4}	3.78	4.71	7.19	18.92	7.59	7.86	5.27	12.19
5×10^{-4}	3.77	4.53	7.39	18.87	7.40	7.79	5.04	12.47
Average	3.60	4.33	7.62	18.58	7.51	7.95	5.17	12.32

Table 2: Positive cooperativity Index

Amino acids	Positive cooperative Index from the Piszkievitz model group (n between 1-6)	
	n_1 =For first stage	n_2 =For second stage
Glycine		
L-Alanine	2.07	1.67
L-Valine	1.20	1.31
L-Leucine	1.35	1.28
Glycine	1.35	1.25

In the present investigation a kinetic model i.e. Piszkievitz model can be applied to establish the pre-micellar phenomenon the concentration of sodium lauryl sulphate is well below the critical micellar concentration. This is action in term of pre-micellar catalyst has also been observed with simultaneous determination of catalytic constant k_c and k_c^{\ddagger} as given above. Applying Piszkievitz model^[15], graphs were plotted between $\log \left[\frac{k_{obs}(k_{obs} - k_2)}{(k_{obs} - k_{obs})} \right]$ against $\log [\text{NaLS}]$ in each case. Linear graph were obtained (Figure-1,2,2.2,3.2 and 4.2). The slope value n_1 and n_2 for first and second stage process obtained from the Piszkievitz plots have been reported in the Table-3. These values are well in the range for the expected value of pre-micellar catalysis i.e. between 1 to 6, however for the micellar catalysis this value should be more than 20.

Hence positive cooperativity index (value n) between 1-6 obtained graphically, established the phenomena of pre-micellar catalysis. This value also supports the substrate promoted micellization^[24]. There are extensive evidences from other system^{[22]-[27]} and Behera et al^[16] has also reported the kinetic model for sodium lauryl sulphate (NaLS) catalysed reactions of meta and para substituted benzoate and phenyl bromide showing that some aggregation of surfactant is present below CMC that catalyse the reaction.

The catalysis depends upon the charge, type of reaction and reactant hydrophobicity. Following view and suggestions supports the rate enhancement due to the surfactant molecules. Micelles have a dynamic structure such that the

monomers are exchanging rapidly with micelles in the micro second time range and vice versa^[28].

The relation between the rate and surfactant concentration can be explained in terms of the distribution of reactants between the aqueous and micellar pseudo phases which can be perturbed by added solutes^{[28]-[29]}. According to Behime^[30], micelles of surfactant can catalyse bimolecular reactions by bringing reactants together in an environment conducive to reactions. Considerable evidences^{[31]-[33]} are available to show that the concentration of the reactant into a small bulk at the micellar surface is a major source of rate enhancement.

Finicls^[34] explained it in terms of free energy of activation that the free energy transition state might be lowered due to the formation of micelle, thereby accelerating the reaction. Finally in any chemical reaction, if a protonated substrate is involved then it should be expected that an anionic surfactant should catalysed the reaction, because the positivity charged substrate may get adsorbed over the anionic surface rather than uncharged reactants^{[31]-[34]} is supported the present work.

4. Conclusion

The presence of surfactant increases the rate of reaction. On the basis of kinetic results and observations it has been confirmed that oxidation of amino acids are catalysed by H^+ ion and the reaction rate also enhanced in the presence of micelles. The catalytic constant also increases with the increase of concentration of sodium lauryl sulphate. The order of reactivity of amino acids in presence of surfactant in both the stages is given as:-

L-Lucine > L-Valine > L-Alanine > Glycine

The Positive cooperativity Index i.e. (value n) is in between 1 to 6 in case of all L-isomer of amino acids for first and second stages processes shows the phenomenon of pre-micellar catalysis.

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Author Profile



Dr. Vijay R. Chourey, Doctorate in Chemistry from Vikram University, Ujjain has gained almost three decades of teaching experience in colleges affiliated to various universities. He has carried out research in the field of chemical kinetics, homogeneous catalysis and reaction mechanism. He has guided number of research scholars and published over thirty research papers in National and International Journals of repute and article to his credit. He has co-authored a book at graduate level published by Shiva Prakashan, Indore. He has been a member of the board of studies and convener / member of academic bodies of autonomous colleges. Presently he is Head of Department of Forensic Science at Govt. Holkar Autonomous Science College, Indore.



Dr. Nameeta Bende received Ph.D. degrees in Chemistry from Govt. Holkar Science College, D.A.V.V. Indore, India. She has been awarded the Young Scientist Fellowship from MPCOST, Bhopal in Indian Institute of Technology (IIT), Indore. She has been presented 15 research papers in International and National Conferences.