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RESEARCH ARTICLE

A study of catalytic effect and premiceller catalysis on the surfactant catalysed oxidation of some amino acids by acidic permanganate

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Abstract

A kinetic study of oxidation of amino acids i.e. glycine, L-Alanine, L-Valine and L-Leucine 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. Premiceller catalysis of the reaction carried out in each amino acid has also been studied.

Introduction

Sodium lauryl sulfate (NaLS) is an organic compound with the formula $CH_3(CH_2)_{11}OSO_3Na$. 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].

Premiceller catalysis

Careful survey of the literature reveals that the miceller effect on oxidation of L-isomers of amino acids by permanganate is very much scanty. Premiceller 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 premiceller aggregates at concentration below the critical micellization concentration (CMC).

When the concentration of surfactant is smaller than that of its CMC is known as premiceller concentration. Many researchers have proposed the formation of premiceller 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 premiceller aggregates occurs in the bulk solution[6].Fendler[7] has given following relationship for premiceller relation.

$$\log(\frac{k_b - k_{bw}}{k_{bm} - k_b})$$

Where w = bulk phase, m= miceller phase
k_b = Rate constant of backward reaction.
k_{bw} = Rate constant of backward reaction in bulk phase.
k_{bm}= Rate constant of backward reaction in miceller phase.

$$[M] = \frac{(C_D \ - cmc)}{N}$$

N=aggregation 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 premiceller 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 CMC[9-12] which is able to catalyse the reaction.

A kinetic model analogous to Dill model[13,14] to explain the premiceller catalytic phenomenon on the basis of positive–cooperativity has been suggested by Piszkiewicz[15].The model accommodates the plot of $\log(k_{obs} - k_o)/(k_m - k_{obs})$ against log[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.

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 ± 0.1^0C. 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 $<2^0$C) in the optic cell. The values of the absorbance due to unreacted permanganate at given times were read out directly from the spectrophotometer.

RESULT AND DISCUSSION

The effect of variation of surfactant concentration:

In all the four amino acids, it has been observed that with the increase in the concentration of sodium lauryl sulphate, the pseudo first order rate constants also increases. It is true in both the stages. The experimental result have been recorded in the Table-1.The plots of k_1 (and k_1^l) against [NaLS] gave straight lines for all four amino acids(Figure-1.3,2.3,3.3 and 4.3)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 $\log[(k_{obs} - k_o)/(k_m - k_{obs})]$ against log [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.

Catalytic action of surfactant and Observation about premiceller catalysis.

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 Moeluyn-Hughes[19] and Chourey[20] that in the presence of catalyst the uncatalysed and catalysed reactions proceed simultaneously.

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:

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

Where k_1 and k_o are pseudo first order rate constant in presence and in absence of NaLS. Thus values of k_c and k_c^l, the catalytic constant for first and second stages have been determined, which are found fairly constant. Results

have been summarized in Table-2.The pseudo first order velocity constant k_1 and k_1^i obtained from variation of NaLS concentration, have been plotted against NaLS concentration are found straight lines[21] (Figure-1.3, 2.3, 3.3 and 4.3) confirming, the catalytic activity of surfactant in the present study.

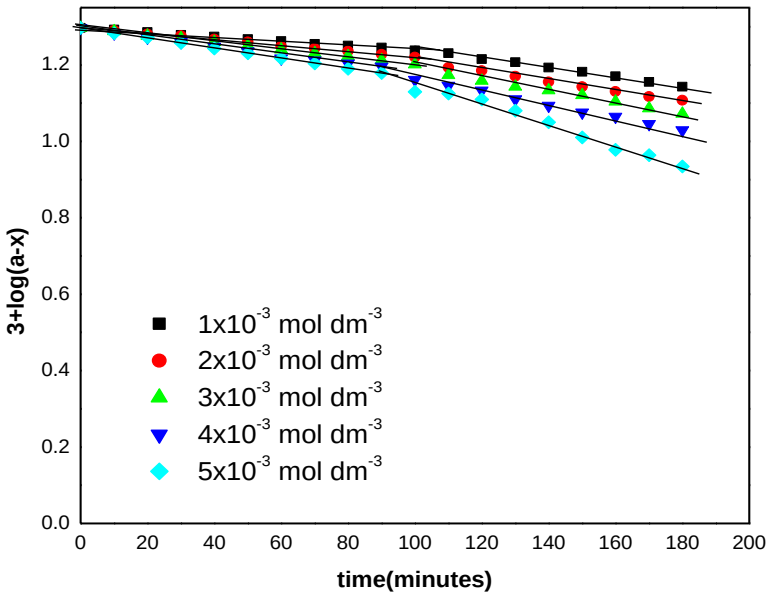

Figure-1.1:-variation of surfactant concentration for glycine

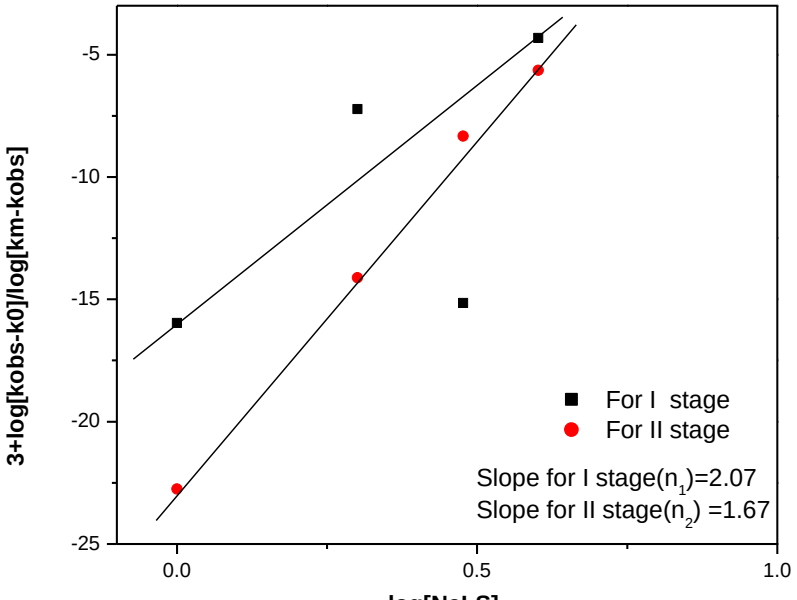

Figure 1.2:-Piszkiewicz plot for Glycine

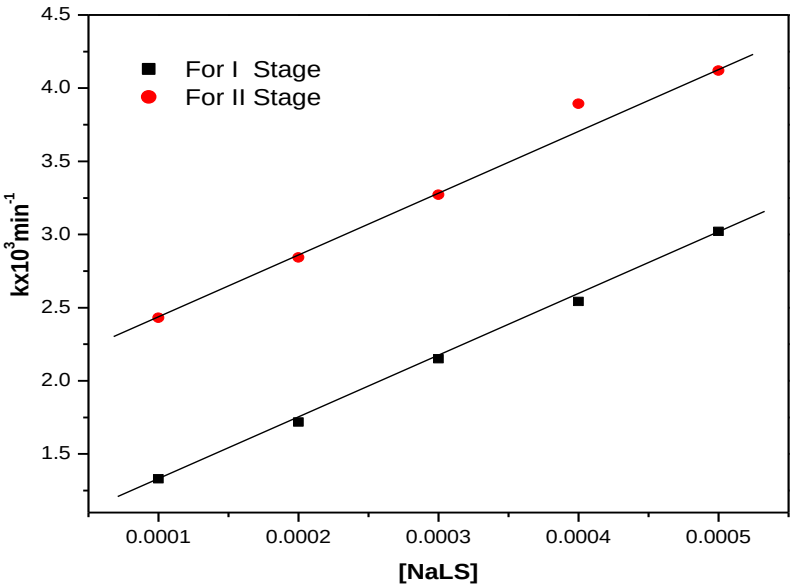

Figure-1.3:-Rate constant(k) against [Surfactant] for glycine

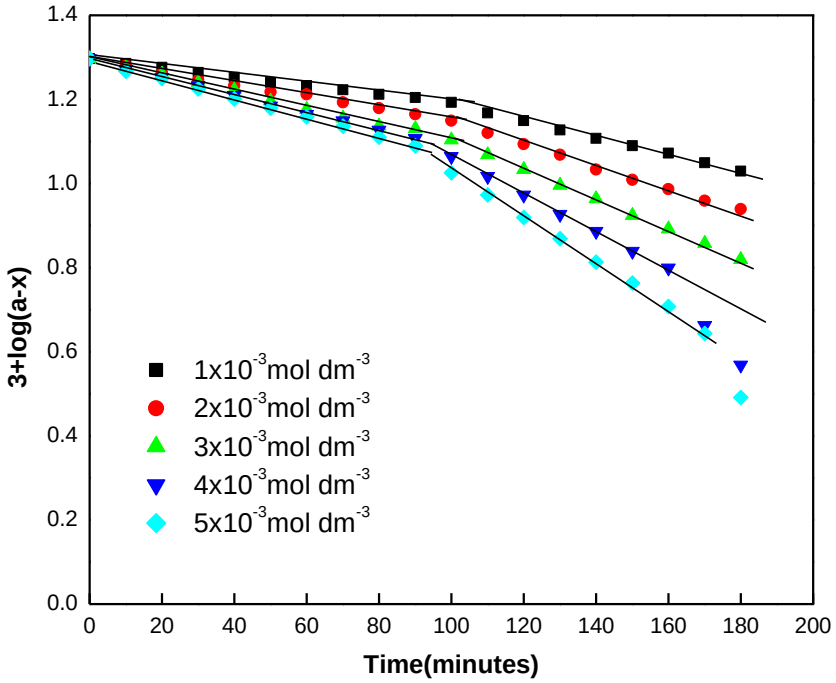

Figure-2.1:-variation of surfactant concentration for L-Alanine

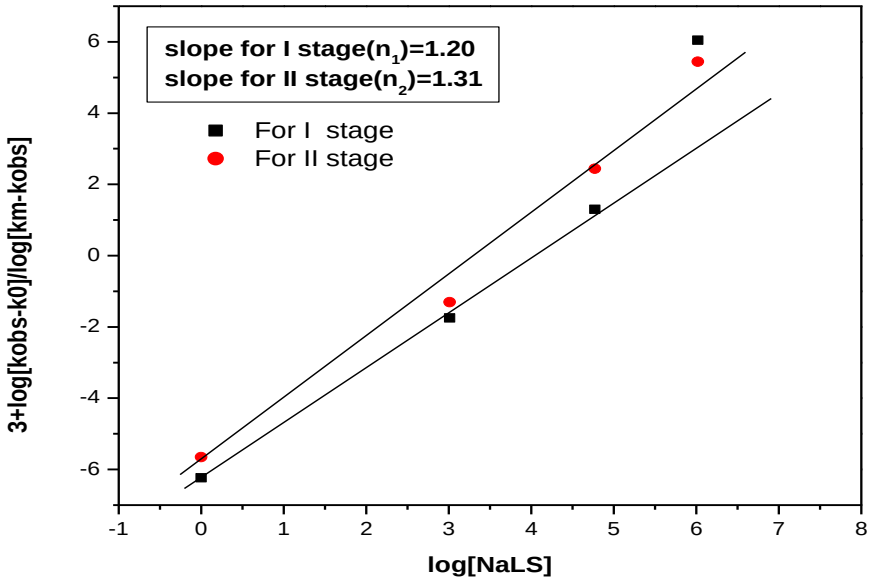

Figure 2.2:-Piszkiewicz plot for L-Alanine

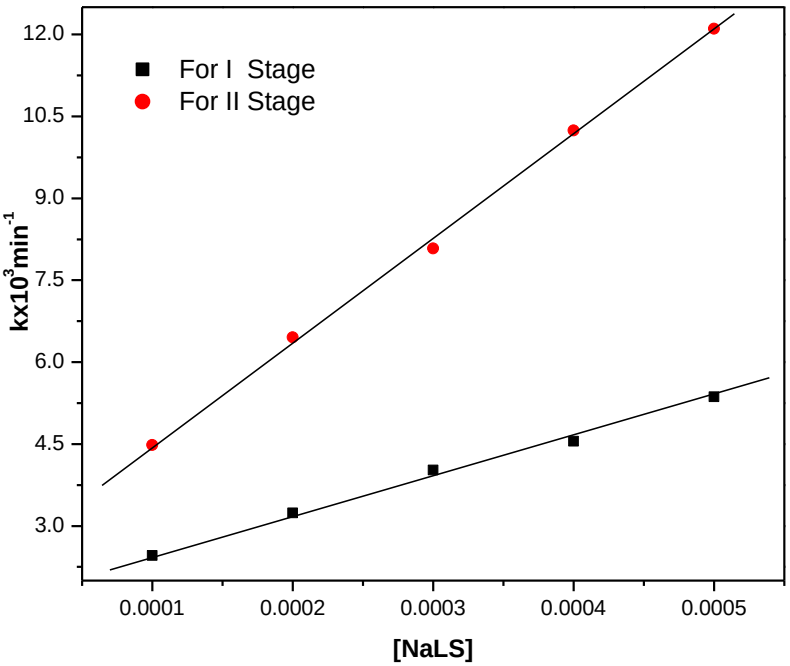

Figure-2.3:-Rate constant(k) against [Surfactant] for L-Alanine

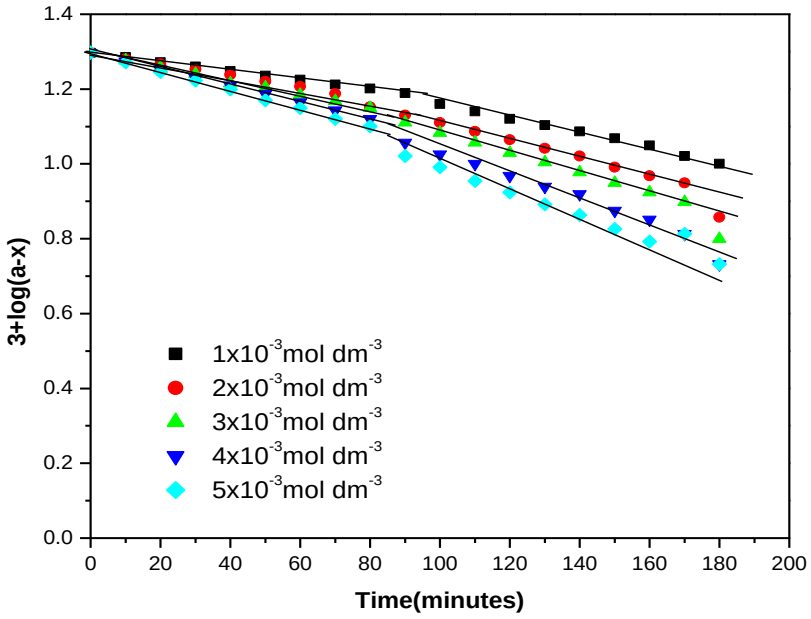

Figure-3.1:-variation of surfactant concentration for L-Valine

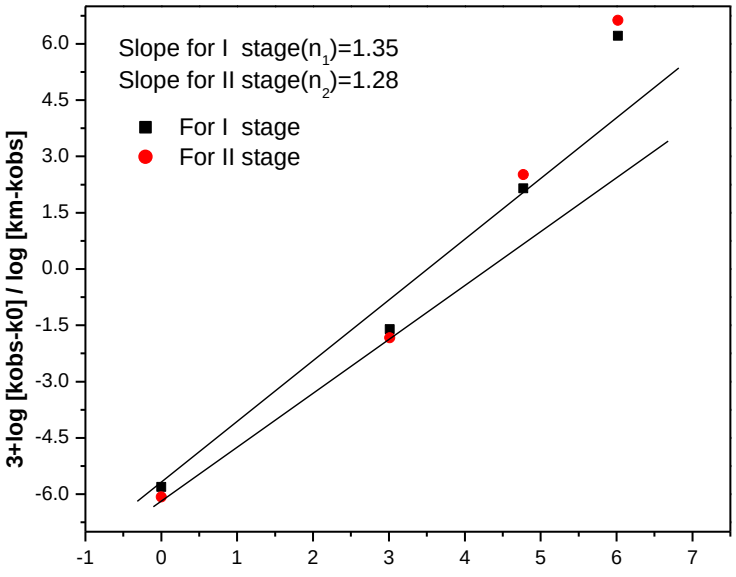

Figure-3.2:-Piszkiewicz Plot for L-Valine

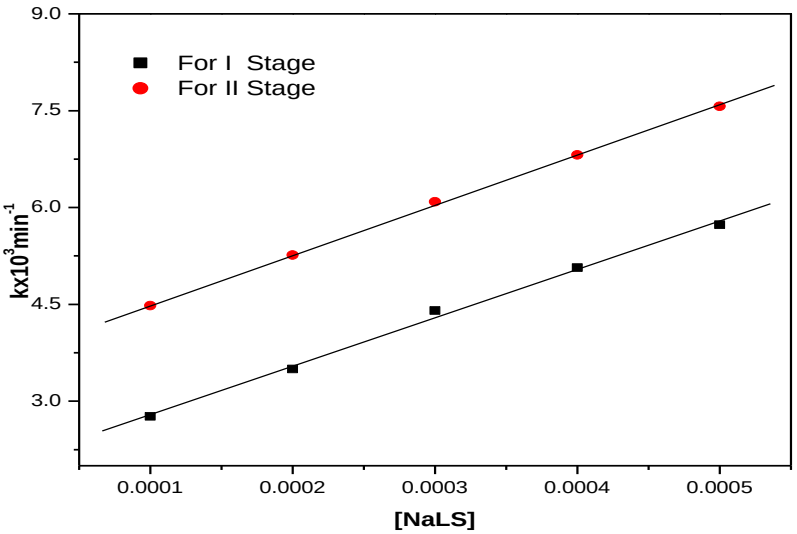

Figure-3.3:-Rate constant(k) against [Surfactant] for L-Valine

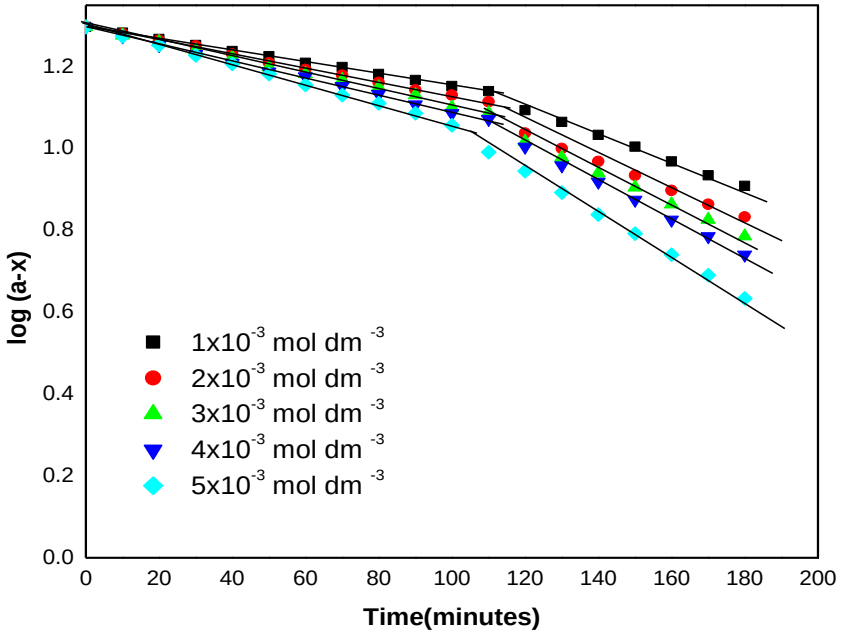

Figure-4.1:-Variation of surfactant concentration for L-Leucine

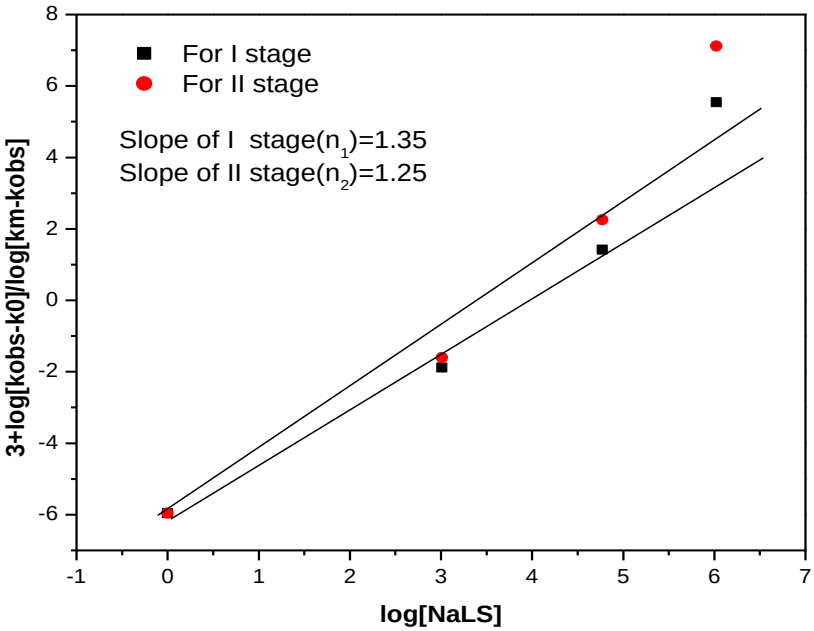

Figure-4.2:-Piszkiewicz Plot for L-Leucine

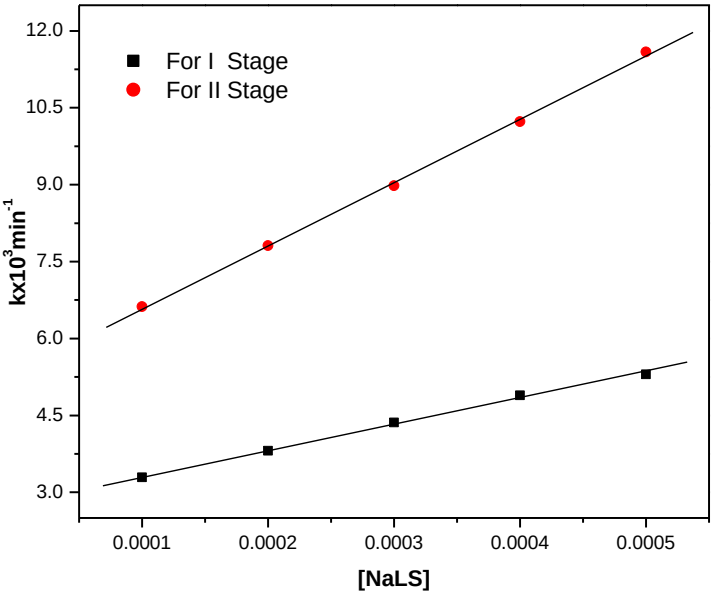

Figure-4.3:-Rate constant(k) against [Surfactant]for L-Leucine

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 $1X10^{-4}$ mol dm^{-3} to 5 X 10^{-4} mol dm^{-3}.The reported CMC (Critical Miceller Concentration) of this surfactant is 8.12 X 10^{-3} M at 25^0C.Literature survey reports that the catalysis below CMC is also feasible[22,23,24] which is known as premiceller catalysis.

In the present investigation a kinetic model i.e. Piszkiewiez model can be applied to establish the premiceller phenomenon the concentration of sodium lauryl sulphate is well below the critical miceller concentration. This is action in term of premiceller catalyst has also been observed with simultaneous determination of catalytic constant k_c and k_c^l as given above.Applying Piszkiewiez model[15], graphs were plotted between $\log[(k_{obs} - k_o)/(k_m - k_{obs})]$ against log [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 Piszkiewiez plots have been reported in the Table-3.These values are well in the range for the expected value of premiceller catalysis i.e. between 1 to 6 , however for the miceller catalysis this value should be more than 20.

Hence positive cooperativity index (value n) between 1-6 obtained graphically, established the phenomena of premiceller 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 hydrophobisity. 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 miceller 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 conductive to reactions. Considerable evidences[31,32,33] are available to show that the concentration of the reactant into a small bulk at the miceller 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 that uncharged reactants[31-34] is supported the present work.

SUMMARY TABLE.1

Rate constants (in 10^{-3} min^{-1}) for variation of [NaLS]

$[KMnO_4]$ = $1X10^{-3}$ mol dm^{-3} $[H_2SO_4]$ = 2 mol dm^{-3}

Temp. = 303K

[NaLS] mol dm^{-3}	**[Glycine]** 0.1mol dm^{-3}		**[L-Alanine]** 0.1mol dm^{-3}		**[L-Valine]** 0.01mol dm^{-3}		**[L-Leucine]** 0.01mol dm^{-3}	
	For I Stage k_1	For II Stage k_1^l	For I Stage k_1	For II Stage k_1^l	For I Stage k_1	For II Stage k_1^l	For I Stage k_1	For II Stage k_1^l
$1x10^{-4}$	1.33	2.44	2.45	4.48	2.76	4.47	3.29	6.62
$2x10^{-4}$	1.71	2.84	3.23	6.45	3.49	5.26	3.81	7.81
$3x10^{-4}$	2.15	3.26	4.02	8.08	4.40	6.09	4.36	8.98
$4x10^{-4}$	2.54	3.86	4.54	10.23	5.06	6.81	4.89	10.23
$5x10^{-4}$	2.91	4.27	5.36	12.10	5.73	7.56	5.30	11.59

SUMMARY TABLE.2

Various Catalytic constants (k_c X 10^{-3}Litre $mole^{-1}$ min^{-1})

$[KMnO_4]$ = 1X10^{-3} mol dm^{-3} $[H_2SO_4]$ = 2 mol dm^{-3}
Temp. = 303K

	[Glycine] 0.1mol dm^{-3}		**[L-Alanine]** 0.1mol dm^{-3}		**[L-Valine]** 0.01mol dm^{-3}		**[L-Leucine]** 0.01mol dm^{-3}	
[NaLS] mol dm^{-3}	For I Stage k_c	For II Stage k_c^l	For I Stage k_c	For II Stage k_c^l	For I Stage k_c	For II Stage k_c^l	For I Stage k_c	For II Stage k_c^l
1x10^{-4}	3.03	4.37	7.88	18.13	7.32	8.09	5.15	12.66
2x10^{-4}	3.41	4.18	7.83	18.92	7.33	7.96	5.15	12.25
3x10^{-4}	3.74	4.19	7.83	18.03	7.90	8.06	5.26	12.06
4x10^{-4}	3.78	4.71	7.19	18.92	7.59	7.86	5.27	12.19
5x10^{-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**

SUMMARY TABLE-3

Positive cooperativity Index (Premiceller catalysis)

Amino acids	Positive cooperative Index from the Piszkiewiez model group (n between1-6)	
	n_1=For first stage	n_2=For second stage
Glycine	2.07	1.67
L-Alanine	1.20	1.31
L-Valine	1.35	1.28
L-Leucine	1.35	1.25

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-Luecine > 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 premiceller catalysis.

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References

1. http://www.chm.bris.ac.uk/motm/SLS/SLSh.htm
2. Zhang, Y. Li, J.Liv, X. and Zeng ,X.(**2002)** : *J.Disp.Sci.Tech.* ,23(04) : 473-481
3. Cerichelli, G. and Mancini, G. (**1994)** : *Langmuir*, 10 : 3982-3987.
4. Imae, T. and Ikeda, S. (**1987) :** *Colld Poly.Sci.* , 265: 1090.
5. Uzeki, S., Ikegawa, T., Takahashiti, T. and Kuwamura, T. (**1988)** : *Langmuir* , 4:1079.

6. Uzeki, S. , Ikegawa, T., Inokumer, A.and Kuwamura, T. (**1989)** : *Langmuir* , 5:222**.**
7. Fendler, F.H. and Fendler, E.J. (**1975)** : *Cata.Mice.Macromole.Mole.Agg*., *J.Am.Chem.Soc.* New York : 20**.**
8. Cui,X. and Mao, S. (**2008)** : *Langmuir* , 24(19): 10771-10775.
9. Bruice, T.C., Katzh, Endler, J. and Fedor, L. (**1968)**: *J.Am.Chem.Soc.* , 90: 1333.
10. Mukerjee, P. and Mysels, K. (**1955)**: *J.Am.Chem.Soc*. , 77: 2937**.**
11. Nagar, V. (**1989)** : *Ph.D.Thesis* ; V.Univ. , Ujjain.
12. Radhakrishnana, A. (**1992)** : *Ph.D.Thesis* ; V.Univ., Ujjain.
13. Dill, K.A. and Flory, P.J. (**1980)**: *Proc.Natl.Acad.Sci.*, 77: 315.
14. Dill, K.A.and Flory, P.J. (**1981)**. : *Proc.Natl.Acad.Sci.* , 78: 676.
15. Piszkiewiez, D.J. (**1977)** : *Am.Chem.Soc.* , 99: 1550-1557.
16. Behera, G.B., Mishra, S.S.and Samantaray, S. (**1982)** : *Ind.J.Chem.* , 21A:1063-1065.
17. Behera, G.B., Mishra, S.S. and Pughari, M. (**1982)** : *Ind.J.Chem.* , 21B: 558-560.
18. Vogel, A.I. (**1964) :** "*A Text book of Quantitative Inorganic Analysis*", Longman and Green,282.
19. Moelwyn-Hughes, E.A. (**1947) :***"Kinetics of Reactions in solutions",*Oxford University press,297-298.
20. Chourey, V.R. (**1984)** : *Ph.D.Thesis* ,V.U.Ujjain.
21. Reddy, A.S. and Reddy, J.N. (**1981) :** *Ind.J.Chem.* , 20A: 608.
22. Menger, F.M. and Portnoy, C.E. (**1967)** : *J.Am.Chem.Soc.* , 89: 4698.
23. Pare, B., Kaur, P., Bhagwat, W.and Fogliani, C. (**2004)** : *J.Korean Chem.Soc.*, 48(2): 201.
24. Raghavan, R. (**1980)** : *Ind.J.Chem.* ,19A: 322-324.
25. Mukerjee, P.and Mysel, K.J. (**1971) :** *"Critical Micelle Concentration of Aqueous Surfactant System"*, Nat.Stand.Ref.Data Ser(U.S.), 36.
26. Kishimoto, S.and Sumida K. (**1974)** : *Chem.Pharma.Bull.* ,22: 1108.
27. Sarsan, G. (**2003)** : *Asian J.Chem.* , 15(01): 133
28. Analseu, R.A.G. (**1976)** : *J.Phys.Chem.* , 56: 966
29. Bunton, C.A. and Wolfe, B. (**1933)** : *J.Am.Chem.Soc.* , 95: 3742
30. Behime ,M.T.A., Fullington, J.G.and Cordes, E.M. (**1965)** : *J.Am.Chem.Soc.* , 87: 266
31. Bunton, C.A., Rivera, F. and Sepulveda, L. (**1978)** : *J.Org.Chem.Soc.* , 43: 116
32. Cuccoria, I.M., Schroter, E.M. and Monteiro, P.M. (**1978)** : *J.Org.Chem.Soc.* , 43: 2248
33. Bunton, C.A. (**1978)** : *J.Am.Chem.Soc.* , 100:5420
34. Finicls, A.and Genesle, P. (**1978)** : *J.Org.Chem.* , 49:12