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Effect of metal ion on reaction velocity of surfactant catalysed oxidation of some amino acids by acidic permanganate

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Abstract

The effect of Mn(II) was observed on the rate of reaction of deamination and decarboxylation of some amino acids *i.e.* glycine and L-isomers of amino acids(L-Alanine, L-Valine and L-Luecine) in presence of anionic surfactant (sodium lauryl sulphate) by acidic potassium permanganate. A Kinetic investigation of oxidation of amino acids by acidic permanganate has been carried out spectrophotometrically.The Mn(II) ion taken for experiment in different concentrations in the form of $MnSO_4$ salt. The reaction is reported as linear double stage process, first stage is followed by second fast stage.

Key words: $MnSO_4$,spectrophotometer,surfactant,amino acids.

Introduction

Metal Ion Catalysis :

Metal ion catalysis in organic reactions can be observed in both redox reaction and acid-base reactions. In redox reaction the metal ion exists in more than one oxidation state in solution. Metal ion reaction alternatively with the oxidising and reducing reagents providing easier electron transfer. Literature survey reveals that number of reactions have been studied in presence of metal ion as a catalyst in redox and acid-base reaction.

All metal are Lewis acid and their activity in acid catalysed reactions may be due to the metal ion adding on the substrate in such a way that it can be able to drain electron towards the site of attachment. The greater is the electron sink efficiency of the metal ion, greater will be its activity as catalyst[1].

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Review on the comparative investigation of interaction between metal ions with L-methionine, alanine, leucine, valine and glycine in aqueous solution was presented by Sajadi[2].

Silver (I) catalysed oxidation of alanine by Ce(IV) in perchloric acid medium was studied by Devara[3]. Kinetic study of ruthenium(III) catalysed oxidation of L-alanine by diperiodatoargentate(III) in aqueous alkaline medium reported by Seregar and coworkers[4]. Chemical oxidation reaction are full of illustration of the use of many uni-atomic metallic ions as oxidant e.g. Ag(I),Fe(III),Ce(VI),Cr(VI), Mn(VIII) etc. Shrivastava and co-workers studied the kinetics of Ru(III) catalysed oxidation of glycine and alanine by N-bromoacetamide (NBA) in perchloric acid media[5]. Oxidation of β-alanine by N-Bromophthalimide in the presence of Ru(III) chloride as homogeneous catalyst in acidic medium was investigated by Singh *et al.*[6]. Lamani *et al.*[7] studied the Os(VIII)/Ru(III) catalysed oxidation of L-Phenylalanine by Ag(III) periodate complex in aqueous alkaline medium.

Kinetics of Ceric-Cerium oxidation of organic acids was studied by Maheshwari[8] and of some aromatic aldehydes was reported by Khan[9]. Same type of investigation on some aromatic phenols was observed by Dixit[10].

Oxidation of some aliphatic aldehydes by Thallium(III) was studied by Kothari[11]. Electron transfer reactions of monosaccharides with metal ion was studied by Rawat[12]. Oxidation of alcohols,carbohydrates, aldehydes, ketones ,acids,glycols and other polyhydric alcohols by Cerium(IV) perchlorate was observed by Tambe[13].

Kinetics of electron transfer reaction of thallic(III) Perchlorate with glycerol was studied by Arzare and co-workers[14]. Kinetics and mechanism of electron transfer reactions of Iron(III) perchlorate with aldohexoses in presence Of 2,2'-Bipyridyl was reported by Fadnis and co-workers[15]. Kinetics of oxidation of adonitol by manganese(III) pyrophosphate was observed by Fadnis and coworker[16]. Kinetics and mechanism of oxidation of *L*-arabinose by vanadium(V) and d-xylose by Mn(III) pyrophosphate were studied by Bhatnagar *et al.*[17.18].

Experiment

All reagents used were of AnalaR and G.R. grade. Permanganate solution was prepared and tested as given by Vogel[19]. 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

Table 1. Effect of for Manganese ion on reaction velocity (k x10^{-3} min^{-1})

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

[NaLS]=1X10^{-4} mol dm^{-3} Temp=303K

$[MnSO_4]$	μ	[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_1^1	For I Stage k_1	For II Stage k_1^1	For I Stage k_1	For II Stage k_1^1	For I Stage k_1	For II Stage k_1^1
	*1.000	1.3304	2.4400	2.4588	4.4836	2.7625	4.4799	3.2955	6.6262
3x10^{-4}	1.0012	2.2387	4.8977	3.4857	6.5060	3.6307	5.7543	4.4668	8.9125
4x10^{-4}	1.0016	2.9512	5.7543	3.4315	6.9202	4.0738	6.7608	4.6773	9.7723
5x10^{-4}	1.0020	3.4299	7.0794	3.7416	7.4851	4.2657	7.2443	5.2480	11.220
6x10^{-4}	1.0024	4.0300	8.8799	4.0969	8.0495	4.5708	7.7624	5.4954	12.735
7x10^{-4}	1.0028	4.6773	11.630	4.3936	8.1962	5.1286	8.5113	6.0255	12.882

* indicates concentration/ionic strength of solution without addition of $MnSO_4$

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

Observations and Discussion

Catalytic effect of Manganous Ion(Mn II):

Metal ion catalysis has been investigated by added Mn^{2+} in the reaction mixture.Its varying concentration influence the reaction in great extent[1]. The effect of Mn(II) as a catalyst in the case of oxidation of permanganate is well known[20]. The oxidation of glycine, L-Alanine, L-Valine and L-Leucine by permanagante has also been found to be catalysed by the addition of Mn(II) ions in presence of sodium lauryl sulphate. Result are summerised in the Table 1.

On the basis of literature available[21] and the work performed, the catalysed reaction is proceeds as follows :

$$5\ RCHNH_2COOH + 2MnO_4^- + 6H^- \xrightarrow{NaLS} 5\ RCHO + 3H_2O + 2Mn^{2+} + 5CO_2 + 5NH_3$$

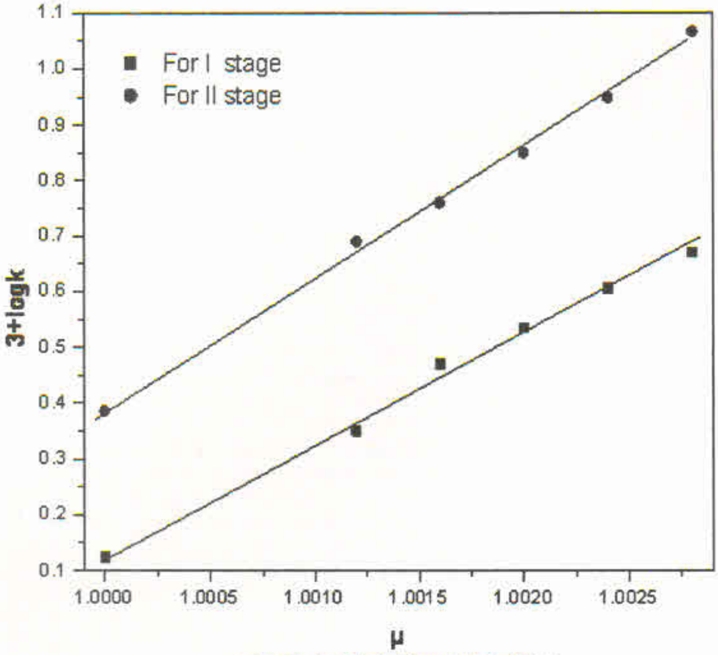

Figure-1:-Variation of [$MnSO_4$]

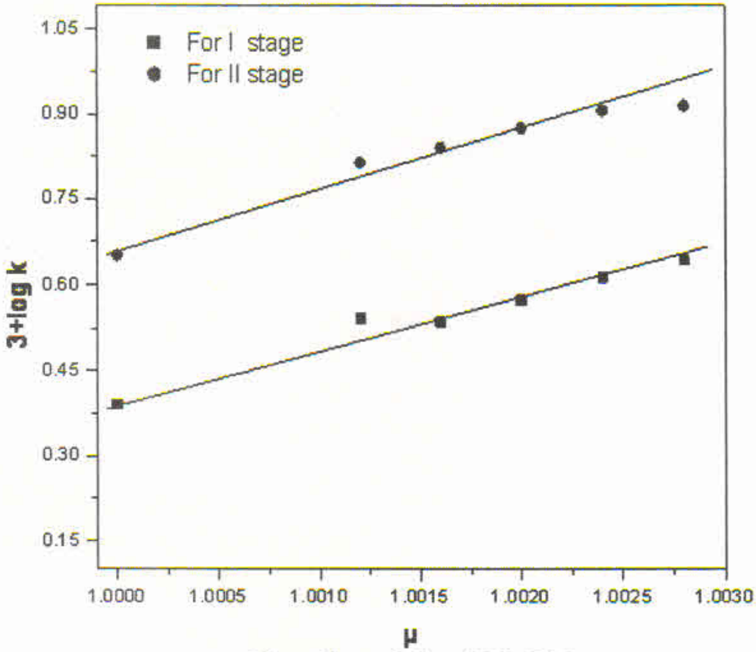

Figure-2:- variation of [$MnSO_4$]

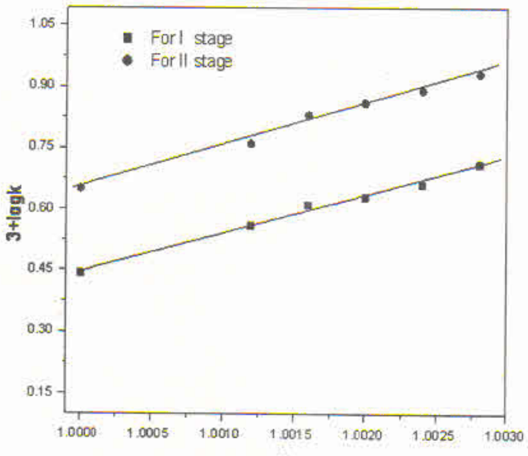

Figure3:-variationof [$MnSO_4$]

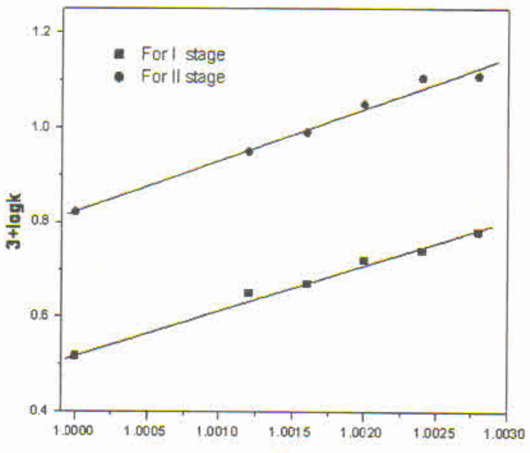

Figure-4:-variation of [$MnSO_4$]

In the present study Mn(II) has been found to exert catalytic effect in presence of surfactant. In the present case there are two possibilities

(i) Either Mn (II) may form a complex with amino acids which may there be oxidized by $HMnO_4$, or

(ii) Mn(II) may react with Mn(VII) to give Mn(III),which may accelerate the rate of the reaction.

$$MnO_4^- + Mn^{2+} \rightarrow MnO_4^{2-} + Mn^{3+}$$

Similar view have also been presented by Waterbury[22], Verma *et al.*[23] and Sahu[24]. They confirmed that it is due to the complex formation. A review on the comparative investigation of interaction between metal ions with L-methionene,alanine,leucine,valine and glycine in aqueous solution was presented by Sajadi[2] is also in our support.

In the given table μ=1.0000 in 'μ' column is the ionic strength without adding the [$MnSO_4$]. To show the effect of ionic strength, on the reaction velocity, the plots of the ionic strength 'μ' against the log k and log k_1^1 have been drawn given in Figures 1 to 4.

Conclusion

The presence of Metal ion (Mn II) 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 metal ion and micelles.The order of reactivity of amino acids in presence of metal ion in both the stages is given as

L-Luecine > L-Valine > L-Alanine > Glycine

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