SUMMARY

Kinetics of simple as well as metal ion, catalysed hydrolysis of aminoacid esters have been a subject of continuing interest among research scientists.[1] Many of the metal complex catalysed reactions provide simple models for much more complex reaction for metalloenzymes such as carboxypeptalase A, Loucine amino peptielase etc. The study of organic reaction in micellear environment is one of the important field of research in recent years.[2,3] Micellear catalysis is highly specific and the environment provide by micelle is sufficiently different from aqueous environment. Micellear aqueous systems may mimic the micro-environment of enzyme[4,5]. Thus the study of metal complex catalysed organic reactions in micellear medium is also important[6] In the present thesis, an effort is made to understand and explain the kinetic behaviour of hydrolysis of some aminoacid esters in presence of surfactants, as well as the metal/metal complex catalysed environment which may have some similarity to biological conditions

Chapter 1 is the review of the work done in organic reactions, especially ester hydrolysis, catalysed by metal complexes and surfactants An introduction to micellear catalysis and different aspects in micellar rate effect including theoretical models have been described

Chapter 2 deals with the materials used and the methods applied in the present investigation. Rate of hydrolysis of different glycine esters in acidic, basic and neutral aqueous media were studied using pH stat method. Experiments were carried out in presence and absence of metal, metal complex and surfactant under different conditions such as various concentrations of surfactant, different temperatures, pH etc Following materials were used:

Esters used	Glycine methyl ester (MeGly)
	Glycine ethyl ester (EtGly),
	Dimethyl glycineethyl ester (diMeGly)
	Phenyl glycine methyl ester (PhGly)

Metal ions	Cu^{2+}, Fe^{3+}, Zn^{2+} and Mn^{2+}
Ligands	2,2'Bipyridyl (bipyl)
	O-phenanthrolene (O-phen)
	Diethylene triamine (DET)
Surfactants	CTAB (cationic)
	SDS (anionic)
	Brij 35 (non-ionic)

Conductivity and surface tension methods were used to determine Critical micelle concentration (CMC) of the surfactants and the aggregation numbers were obtained from fluorescence method

Chapter 3 describes the results and discussion of the study of glycine ester hydrolysis in presence of surfactants and metal/metal complexes and both The pH effect on the rate of hydrolysis in presence and absence of surfactant has been estimated, using a wide range of pH (pH 4→11) Kinetic study in presence of CTAB showed an enhancement in the rate at high pH and an inhibition at lower pH An exactly opposite effect is noted in presence of SDS For Ethyl glycinate, the rate enhancement was about 5 times with SDS at pH 4 Electrostatic interaction between charged micelle and the reactants may be the reason for this catalytic effect.

At high pH, increase in concentration of CTAB, increased the rate initially, but reached a limit well above CMC and thereafter remained unaffected by CTAB concentration Similar, but opposite effect was observed for inhibition at low pH Anionic surfactant affected the rate at low and high pH opposite to that of CTAB. However at low and high pH, non-ionic surfactant Brij35 did not show any effect on the glycine ester hydrolysis, as there is no charge on its surface, it could not have any electrostatic interaction

The pH of most of the biological systems is very close to pH 7 Kinetic studies of ester hydrolysis around pH 7 are rarely found in literature So the aminoacid ester hydrolysis in micellar medium around pH 7, has been given due importance, while the concentration of surfactants are discussed The rate of hydrolysis ≈ pH 7 is quite low, due to low concentration of H^+ and OH^- The presence of surfactant, increased the rate to a very small extent With all the surfactants, bell shaped curves were obtained, when rate constant (k) values were plotted against surfactant concentration. The change in concentration of reactants within the micellar pseudophase could be the reason for this phenomena, showing the importance of electrostatic as well as hydrophobic interactions in micellear catalysis Hydrophobic interaction is reflected in the critical micellar concentration (CMC) values of CTAB and SDS in presence of glycine esters which are in the following order

MeGly > EtGly > DiMeGly > PhGly

Observed rate constants in presence of surfactants are often the result of several processes, including the reaction in bulk and micellear phase A number of models have been suggested in literature to explain the kinetic results [2,7,8] of which pseudophase ion exchange model [8] (PPIE model) has been widely used, to explain the kinetic behaviour of ester hydrolysis Several modifications of ion exchange model are cited in literature [9,10] and in this chapter PPIE model modified by Santana et al [10] has been used to explain the hydrolysis pattern in presence of surfactants

The same model is used for cationic, anionic as well as non-ionic micellar media and it is found that the rate phenomena in the present study can be satisfactorily simulated by the model

The combined effect of metal complex and CTAB on the hydrolysis of MeGly, EtGly, DiMeGly and PhGly under various conditions are discussed in section 2 The hydrolysis were carried out at pH 4, pH 5.2 and pH 5 8

Metal or metal complexes enhance the rate at all the pH's studied Cu^{2+} and Zn^{2+} showed slightly higher catalytic activity, probably due to the softness of these metals compare to Fe^{3+} and Mn^{2+} The enhancement in rate due to metal complex at pH 4 and pH 5 8 are smaller than that at pH 5 2 This could be due to the stability factor of metal complex with glycine ester

Metal complexes enhanced the rate of ester hydrolysis at pH 4, about 1 2 times The catalytic activity of metal complex is 20 times in presence of CTAB The reason could be that the pH of the micellear medium is slightly higher due to repulsion of H^+ ions, which favours a more stable metal-substrate complexation Electrostatic repulsion being strong, the overall effect of metal complex and CTAB is inhibition at pH 4 The catalytic effect of metal complex and CTAB taken together was quite high at pH 5 2 It increased the rate to as high as 110 times at this pH which indicates a synergistic effect The mechanism of catalysis by each is not altered by the presence of the other The observed rate constants for metal complex catalyzed hydrolysis of glycine esters in micellear medium have been satisfactorily simulated by PPIE model

Effect of temperature on the rate was similar to that in absence of metal complex The results showed that the mechanism of reaction is not affected by change in temperature from 30-45°C

Some of the hydrolyses were also investigated in presence of cationic - nonionic mixed surfactant CTAB and Brij35 which catalyse the hydrolysis (as it is explained earlier) were used as components of mixed surfactant It is now well established that, in most of the uses and applications, pure surfactants are less efficient than surfactant mixtures The present study shows that, not only the catalytic effect of mixed surfactant is more than that of single surfactant, but also the concentration of mixed surfactant needed for catalysis is very low. An effort is made to explain the observed kinetic results on the basis of micellization of CTAB-Brij35 mixed system

Chapter 4 summarising of the work done and conclusion

A slight enhancement in rate (though it was not significantly high) was observed at ≈pH 7 for all the esters studied, in presence of cationic, anionic as well as non-ionic surfactant Hydrolysis in presence of metal complex and surfactant together showed a definite combined effect (synergistic effect). Metal or Metal complexes were found to be not affecting the mechanism of catalysis by surfactant in the reaction and vice versa A single model (PPIE model) has been used to explain the catalytic activity of micelle in all the cases studied

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