CHAPTER 1

INTRODUCTION

Introduction

Kinetic study is an important aspect of chemical reactions, as it gives knowledge about, (1) how fast the reactants get converted into products, (2) the relation between reaction rate and the properties of the reacting system and (3) the pathway (mechanism) by which the reactants may be assumed to get transformed into products. Thus the very objective of studying kinetics of chemical reaction is to understand the chemical processess In addition to its contributions to the understanding of fundamental chemical processes, it has a lot of technological applications also, for example, in industry, biochemical studies, space technology etc. Thus the study of chemical kinetics provides an opportunity to understand the processes connected with the society.

Ester hydrolysis

A large number of organic reactions have been subjected to kinetic studies, of which ester hydrolysis is one of the important reactions. The mechanism of ester hydrolysis is well understood.

Hydrolysis of esters as such has been found to be very slow process. A number of catalysts have been used to catalyse these reactions, for example, acid - base, metal ions and surfactants to name a few.

Esters of amino acids are found to be important biological compounds, and the hydrolysis of these esters evoked great interest among scientists[1-4]. Regarding the hydrolysis kinetics of aminoacid esters, the base hydrolysis is best understood: There excists an equilibrium between protonated and unprotonated aminoacid esters at neutral medium and the rate expression can be written as

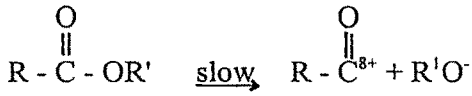
$$- d[ester]/dt = k_1 [E][OH^-] + k_{III} [EH^+][OH^-]$$

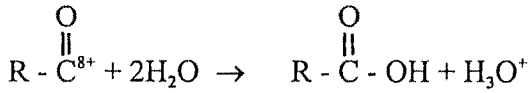
where E and EH^+ represents the protonated and unprotonated formsof ester. Metal ions as well as surfactants can catalyse the hydrolysis of amino acid esters, which may be influenced by pH and temperature of the medium.

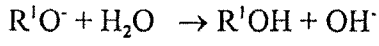
Acid-base catalysis

The hydrolysis of esters can occur through general and specific acid catalysed and base catalysed mechanisms. The specific mechanisms involved in carboxylic ester hydrolysis are discussed in detail in literature[5-12]. In both cases, i.e. the acid catalysed and base catalysed hydrolysis of esters in aqueous medium, there is a nucleophilic attack on the carbonyl carbon atom and an electrophilic attack on the alcoholic oxygen atom. The mechanism for base and acid hydrolysis of carboxylic esters may be shown as below,

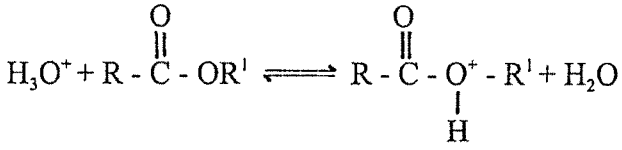
a) Base catalysed hydrolysis

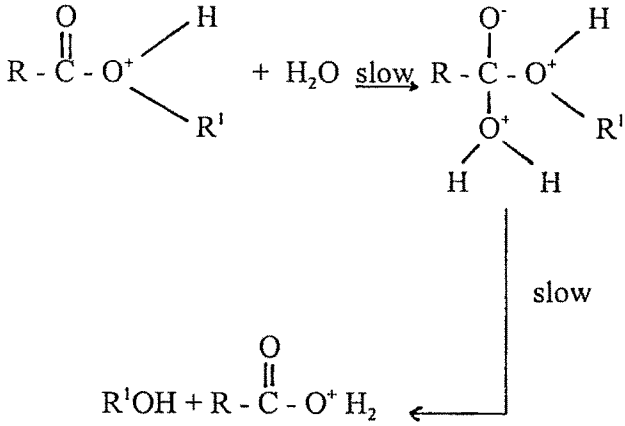






b) Acid catalysed hydrolysis



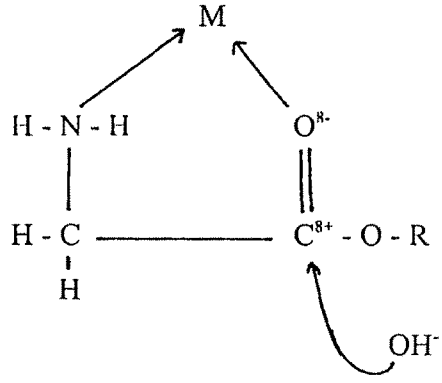


Metal/Metal complex catalysis:

The metal ions have an important role to play in biochemical reactions. Enzymes catalyse the biochemical reactions and it was observed that nearly one third of the enzymes have metal ions associated with them[13]. Metal ion activates the organic molecule or substrate. When an organic molecule gets coordinated to the metal ion, it undergoes several changes which can significantly change its reactivity. The attachment of the organic molecule to the metal ion causes a polarization in the electron density of the organic molecule towards the metal ion, which leads to greater acidity of the ligand[14]. Further, the lowering of the electron density on the ligand, due to coordination with metal ion, makes it more susceptible for nucleophilic attack. A number of studies of metal catalysed reactions have been carried out to explain the catalytic activity of metalloenzyme in the bio-chemical reactions[15]. It has been shown that the hydrolysis of aminoacid esters, are facilitated in presence of metal ion.

The metal ion promoted hydrolysis of aminoacid esters has been a subject of continuing interest among scientists for many years[16-17]. In 1952, Kroll [18] discovered that the hydrolysis of aminoacid ester was catalysed by metal ions. Many of these reactions provide simple models for much more complex metal enzyme[19] reactions. The mechanism (of hydrolysis in this case) has been discussed in literature.

Metal ion forms a chelated complex with aminoacid and this leads to a considerable reduction in the carbonyl stretching frequency. Kroll initially suggested that such chelated ester species were involved in the metal-ion-catalysed hydrolysis of aminoacid esters as shown below:



Following the work of Kroll, a number of studies on simple aminoacid ester hydrolysis were reported.[18,20,21] However, the results obtained from these studies were not satisfactory, i.e. the interaction between the buffer employed and the metal ion ester complex were not clearly discussed in these studies. Some workers failed to study the pH dependance of the reaction [20] and there was failure to control the pH [21]. Further studies in this subject [22-25] showed only order of magnitude agreement, though the uncertainity from the earlier studies regarding the nature of the nucleophile has been resolved. The studies of metal ion promoted hydrolysis of aminoacid esters have also been carried out with a variety of substrates, in which some of the esters are capable of forming chelate ring, without any involvement of the carbonyl group of the ester [13,26-27].

Hydroxyl ion has been shown as the predominant nucleophile in aminoacid ester hydrolysis, inspite of the reaction being studied at pH 5, and the evidence for nucelophilic attack by water has been reported[22] Reaction at high pH, lead to precipitation of metal hydroxides, due to the low formation constants of the metal complexes [18,20].

In biological system, the metal ions are not found in free form, but they are attached to a carrier ligand. Therefore, study of aminoacid ester hydrolysis in presence of metal complexes is also biologically important[28,29]. Even in the case, where ternary complex is formed, the role of metal ion is direct, i.e bringing the polarization of the substrate and facilitating nucleophilic attack on it. The carrier ligand has some specific roles to play. In some cases, the heavy mass of the carrier ligand with hydrophobic groups reduces the dielectric constant of the medium[30] and thus affect the rate of reaction. In order to mimic the natural enzymes, a number of studies have been carried out using metal ions bound to suitable carrier ligands[31,32]. It is known that no model enzyme can compensate with natural enzymes in the rate of reaction[28]. However, the model enzymes help in carrying a more exhaustive study of the relation between the structure of the model system and its reactivity. Such studies cannot be carried out with natural enzymes Thus the artificial models help us in having a better understanding for the functions of the enzyme[30].

Micellar catalysis:

Micelles are well known for its catalytic activity in organic reactions[33-42]. Micelles are formed as a result of aggregation of surfactant monomers.

Surfactants:

Surfactants are substances which possess a hydrophobic carbon chain and a hydrophilic head group. Depending on the charge of the headgroup, they are classified into cationic (eg Decylammonium bromide: $-CH_3(CH_2)_9N^+H_3Br^-$), anionic (eg. Sodium decyl sulfonate - $CH_3(CH_2)_9\ SO_3^-\ Na^+$), non-ionic (eg - Polyoxyethylene (3) decanol :- $CH_3(CH_2)_9O(CH_2CH_2O_3)$ and zwitterionic (eg - N-Dodecyl-N, N-dimethylglycine : - $CH_3(CH_2)11\ N^+\ (CH_3)_2\ CH_2COO^-$) surfactants.

These surface active agents are amphiphilic substances or amphiphiles as their molecules possess distinct region of hydrophobic and hydrophilic character. Since the polarity of the distinct regions of these substances varies greatly, these substances have also been referred to as amphipathic or polar-nonpolar molecules. When surfactants dissolve in aqueous medium, it forms molecular aggregates or micelles[43]. Thus critical micelle concentration (CMC) and aggregation number (N) are two important characteristics of surfactants.

Critical Micelle Concentration (CMC):

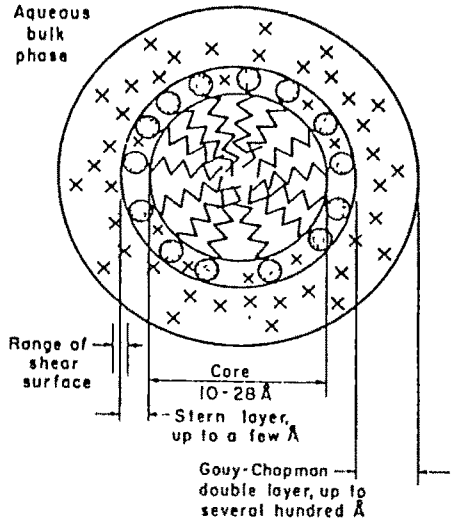
The physical properties of surfactants differ from other non-amphipathic molecules in one major aspect, the abrupt changes in their properties (eg. surface tension, conductivity,. viscosity etc.) above a certain critical concentration[44]. Above this concentration, the surfactant monomers associate to form larger units, named "micelles" and the concentration at which this association occurs is "Critical Micelle Concentration". Each surfactant molecule has a characteristic value of CMC at a given temperature and depends on the hydrophobicity of hydrocarbon chain[45] nature of head group[46], counter ions[47] pH [48], presence of additives[49] etc. The presence of an additive in the solution can modify

the micellization process through specific interaction with surfactant molecules and by changing the solvent nature[50-53].

Aggregation Number : The total number of surfactant monomers present in one micelle is termed as aggregation number[54] and it can be determined by steady state flourescence quenching method[55-57]. Like CMC, aggregation number also depends on the concentration of surfactant, presence of additive and temperature. The aggregation number determines the size and geometry of the micelle and since the effectiveness of micellar catalysis depends on micellar size and geometry [58], information on aggregation number, N, is required for meaningful interpretation of kinetic data.

Shape of Micelle

It is generally assumed that, micelles at concentration not much higher than the critical micelle concentration (CMC) are roughly spherical in shape[59-60]. A two dimensional representation of an ionic spherical micelle[61] is shown below:



The amount of water in the micellar interior varies from surfactant to surfactant and the water can penetrate into micellar surface only upto a distance of approximately 3 to 6 carbon atoms[62,63]. The interior or core of the micelle has genrally been inferred to be hydrocarbon like [64,65].

Duynstee[66] has explained the importance of study of micellar catalysis in the theoretical and practical field. Micelle can catalyze an organic reaction by bringing the

reactants together in its small volume through electrostatic as well as hydrophobic interactions.

The knowledge of critical micelle concentration (CMC), i e the narrow range of concentration at which, the micelles become detectable[67] and the aggregation number (N) are important in micellar catalaysis In quantitative investigations of micellar catalysis, it is desirable to determine the binding constant for the formation of substrate-micelle complex From the values of CMC and aggregation number, it is often possible to determine the association or binding constant [43] Many research workers have explained the catalytic activity of micelle on the basis of the value of binding constant K [68-78]

Micellar catalysis resembles the enzyme catalysis in many ways., Aqueous micellar systems mimic the micro environment of enzymes. A large amount of research work have been carried out in the past, on chemical model systems for specific enzymatic interactions [79,80]

The living cell contains a large number of particles composed of aggregates of molecules [81]. Thus the life processes, proceed mainly within complicated assemblage of molecules rather than in the free solution, where control of the reaction would be difficult[43]. Therefore a knowledge of chemical behaviour, inside the molecular aggregates is essential to understand these highly organised biological process. Naturally occuring micellar systems, such as phospolipids and bile salts, as well as synthetic surfactants affect the rate of numerous chemical reactions[82-85]. The carboxylic ester hydrolysis in micellar medium, due to its simplicity with respect to enzymatic processes, have served well as model systems in investigations of micellar effects[86] on reaction rates.

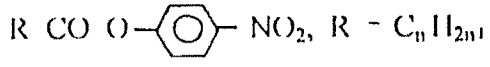
It has been shown that, generally, anionic micelles retard and cationic micelles enhance the rate of carboxylic ester hydrolysis in alkaline medium [43] Anionic micellar systems have been found to increase the rate of the acid catalysed hydrolysis of esters[87-89] where as non-ionic surfactant, either decrease or have insignificant effects on the rate constants for hydrolysis of carboxylic esters In many reactions, where micelle is used as a catalyst, when buffer is used in the system, substantial rate inhibitions have been observed[90-92], therefore, the influence of buffers in micellar medium have been examined carefully in some studies [92], and it is desirable to avoid the use of buffers and electrolytes

or keep the concentrations of such additions as low as possible wherever their use is necessary [93].

Micelle can be regarded as a microreactor, that influences reaction rates and equilibrium by taking up reactants and providing a medium different from that of the bulk and can influence the rate by either increasing or decreasing the rate or by making alteration in the reaction pathway.

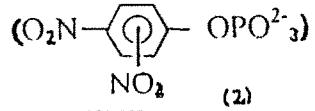
Different Approaches on Micellar rate effect

The development of ideas on micellar rate effects and the role of submicroscopic assemblies are discussed in detail in literature.[94-96]. Early treatments of micellar effects on chemical reactivity were generally based on Hartley's approach to explain the effects of colloidal assemblies on indicator equllibria [96-99]. Menger and Portnoy[100] studied the inhibition of reaction involving p-nitrophenyl alkonates, (1)



(1)

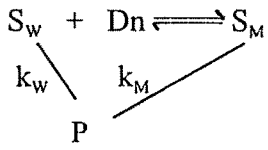
and OH^- ion by anionic micelles and shown that it followed the transfer of ester from water to anionic micelles, because micellar bound ester was relatively unreactive due to repulsion of OH^- from the micellar surface. This quantitative model was also applied to spontaneous hydrolysis of dinitrophenyl phosphate dianions (2)



(2)

catalysed by cationic micelles [101-102]. These dianions were found, strongly bound to cationic micelles and are more reactive at the micellar surface than in water[103-104]. This is also because of the lower polarity of the micellar pseudophase [105-106].

The scheme for pseudophase model that had been applied to inhibition [95-96,100] was as follows:



S_w substrate in water

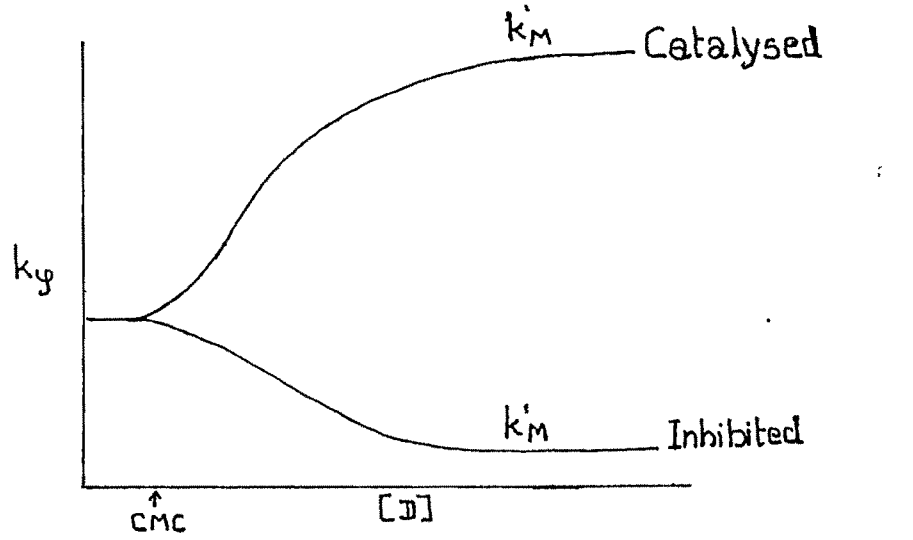
S_M substrate in micelle

$$K_S = \frac{[S_M]}{[S_W][Dn]} \quad (1)$$

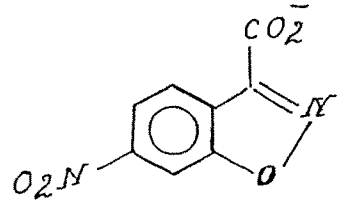
$$k_\psi = \frac{k'_W + k'_M K_S [Dn]}{1 + K_S [Dn]} \quad (2)$$

K_S is the binding constant for substrate micelle complex and k'_W and k'_M are the first order rate constants in aqueous and micellar phase

Inhibition and enhancement in the rate of reaction with concentration of surfactant is depicted as



The pseudophase model does not depend on the location of substrate in the micelle, provided that, movement within the micelle is much faster than the chemical reaction. A lot of work have been done in the past to examine the catalytic effect of micelle on reaction rate using pseudophase models. Heterolyses, which do not require direct intervention by water have been studied in detail. For example Decarboxylation of 6-nitrobenzisoxazole - D-carboxylate ion (3)



(3)

was not incorporated in to anionic micelles, but bind to cationic micelles[107-108].

Therefore, the rate is that in water or aqueous phase. The hydrogen bonding solvents strongly inhibit reactions by solvating and thereby stabilizing the transition state[109]. The rate constant of reactions for which water acts as a nucleophile were also examined[110-113]. The rate of some reactions are sharply decreased by decrease in solvent polarity or water content [114]. Water can also play a role by nucleophilic participation at the reaction centre and by hydrogen bonding with anionic residues [115,116].

Bimolecular reactions:-

The effect of ionic micelle on the rate of bimolecular reactions are determined by the increase in concentration of reactants within the small volume of micellar stern layer[117]. The apparent rate constants in micellar solutions may be either larger[118] or smaller[119] than the rate constants in water, showing both catalytic as well as inhibition effects were important by the micellar systems. The simple distribution model equation (2) fits data for spontaneous reactions and also for micellar inhibited reactions provided that $k_M \rightarrow 0$ and equation (2) reduce to [96]

$$k_\varphi = \frac{k'_w}{1+K_S\,[Dn]} \qquad (3)$$

However, this equation could not apply to micellar rate effects on bimolecular rections in which the values of rate constant k_φ go through maxima with increasing surfactant concentration [120] The general problem of micellar catalyzed bimolecular reactions can be treated by estimating the distribution of reactants between water and micelles and the first order rate constant is given by

$$k_\varphi = \frac{k_W\,[N_{UW}] + k_M K_S\,[N_{UM}]}{1 + K_S\,[Dn]} \qquad (4)$$

When N_{UW} and N_{UM} are the concentration of solution in aqueous and micellar phase [121].

The distribution of substrate between water and micelle can be determined by direct measurement for some ions[122-124]. To compare the rate constants at aqueous and micellar pseudophase, some workers have selected a value for the volume of the reactive region (molar volume of micelle) [121]. But in certain cases where the reaction occurs at the micellar

surface, the molar volume (Vm) has been considered as an arbitrary region at the micellar surface [125]. The value of molar volume of micelle has to be assumed and may depend on the nature of the reaction [126,127].

Theoretical Models of Ion binding

The first theoretical approach to this interionic competition is the Pseudophase Ion Exchange Model developed by Romsted [120] based on analogies with ionic binding to surface of ion exchange resins

Pseudophase Ion Exchange Model (PPIE model)

The basic assumption of this model is that the site of reaction at the stern layer is saturated with counter ions[120] and the competition between reactive and unreactive anions (i.e. Nu^- and X^-) can be described by eqn. [125,128]

$$k_x^{Nu} = \frac{[N_{uW}]\,[X_M]}{[N_{uM}]\,[X_W]} \qquad (5)$$

This model fits a number of bimolecular reactions of anions in cationic micelles.

Chaimovich, Quina et al used this model with cubic equations, to treat reactions of OH^- in buffered solutions, in which the buffer anion competes for the micelle[129]. They showed that the concentration of OH^- at the micellar surface depends not only on the pH of the aqueous pseudophase but also on the concentration of unreactive ions, including that of buffer.

Limitations of Simple Ion exchange model

Even though, the PPIE model could be used satisfactorily in fitting kinetic data for most of the studies, it has some major problems which are not fundamental in nature. For example, β the degree of counter ion binding on micelle, is almost not independent of the nature of the counter ion[120,127,130]. For hydrophilic-anions in cationic micelles β appears to increase with increasing anion concentration on micellar surface and the k value also

increases with surfactant concentrations[131] In absence of any added reactive ion i.e the surfactant counter ion itself is a reactive ion, the equation for k_φ as per PPIE model is

$$k_\varphi = \frac{k_W (\alpha[Dn] + CMC) + k_M K_S (1-\alpha) [Dn]}{1 + K_S [Dn]} \qquad (6)$$

This equation predicts that k_φ will increase with increase in surfactant concentration and for fully bound substrate, where Ks [Dn]>> 1,

$$k_\varphi = k_M /3 \qquad (7)$$

Therefore k_φ should reach a limiting value of k_M β. This prediction is fulfilled for some reactions[132]. But this approach is found to be less satisfactory for reactions involving highly reactive ions like OH^-. This drawback could be overcome by finding out the actual values of degree of micellar disassociation 'α' (β =1-α) [127]. The data can also be fitted by assuming that, the concentration of reactive counter ion (eg. OH^-) at the micellar surface follows Langmuir isotherm[133]. Elimination reactions of DDT and related compounds were examined in mixtures of OH^- in CTAB or CTAOH and found fitted with Langmuir model[134-135]. In some studies, the ionic concentrations in the aqueous pseudophase are replaced by mean ion activities[136] The concept of strictly localized reaction region at the micellar surface have been questioned by some workers and a different approach based on the thermodynamics of ionic interactions with colloidal surfaces has been developed[137]. This model differs from the other in treating the micellar rate enhancements, it has not been applied to spontaneous reactions or to bimolecular reactions in mixtures of reactive and inert ions.

In some cases, where highly hydrophobic counter ions were present, the rate continues to rise even after complete substrate incorporation within the micellar pseudophase [138] and an additional rate contributing reaction across the water-micelle boundary was assumed, to explain this phenomena[139-142]. Subsequently, Bunton et al[131] showed the simulation of kinetic data by a mass action law, which was extended by Rodenas[125,143-144] to systems containing mixture of counterions A number of studies have been done using Coulombic (spherical cell) models[145-146], which are analogus to those

previously employed to calculate micellar properties[147-148] to simulate micellar effects on kinetics and equillibria.

Coulombic models of Ion Binding

The role of Coulombic forces in directing ion micelle interactions was mentioned in earlier studies [94,96,100]. The surface electrical potential of an ionic colloid (eg. micelle) has been calculated from classical electrostatics and the treatment involves solution of the Poisson Boltzman equation (PBE) based on the cell model[149-150]. The specific ion binding was written in terms of Volmer, Langmuir or similar isotherms. The Pseudophase concept was retained, and the distribution of substrate between water and micelles was written in terms of pseudophase model In this case, substrate was assumed to be located uniformly in a shell of fixed width at the micellar surface The rate constant for micellar reaction in which OH^- is involved can be written as shown below [151-152].

$$k_\psi = \frac{k_W [OH^-_W] + k_2^m K_S [Dn] [OH^-]\Delta}{1 + K_S [Dn]}$$

$[OH^-]$ →Molar concentration of OH^- which is distributed uniformly within the shell of width Δ. k_2^m → The second order rate cosntant for reaction in micellar phase.

However, it is more difficult to develop criteria for the selection of the value of the shell width Δ, and the quality of the fits of kinetic data is not very sensitive to the value of Δ for micellar catalysed ionic reactions because, the concentration of counterions falls very sharply with increasing distance from the micellar surface, so that ions that are very close to the micellar surface are responsible for most of the reactions.

A number of studies using functional micelle (i.e. introduction of a reactive group in to a surfactant usually at the head group) have been reported[153-154]. The pseudophase model has been used satisfactorily to explain the rate of reaction with a functional micelle[155-157].

The Pseudophase Ion Exchange model in general, explains many features of micellar rate effects and it has been applied to a variety of colloidal assemblies, namely

vesicles[158], microemulsion[159-161], ammonium ions[162-163] and reverse micelles[164-165]. Altogether it is generally accepted that for bimolecular reactions the surface of assembly/micelle is the main source of rate enhancement, which is an important concept of PPIE model. Despite, having some drawbacks, the PPIE model, still considered as most effective treatment for micellar rate effect Several studies suggest that the PPIE assumption of a constant, net degree of counterion binding (β) and the degree of micellar dissociation (α) is not true[166-167] and the PPIE model could be employed satisfactorily for most of the reactions by determining the actual values of α which is assumed to be constant in its original form The PPIE model considers the total volume of micelle as a separate phase, uniformly distributed in the aqueous phase, and the reaction occurs in both phases and is capable of predicting most ionic micellar effect on reaction rate and equillibria over a wide range of experimental conditions, such as pH, surfactant concentration etc.[168-169].

Mixed Surfactants Systems

Mixtures of surfactants are preferred in most practical applications to that of single surfactant due to the difficulty in preparing chemically and isomerically pure surfactants. The performance advantage often results from mixing different surfactant types.

The knowledge of CMC for the formation of micellar aggregates in solution provides a useful measure of the strength of interactions between different surfactant types. When same type of surfactants mixed, they behave ideally[170] and in case of different surfactant types, significant deviation from ideality and much longer effects can be observed. For example, the non-ideal cationic-anionic mixture of $C_{10}TAB$ and $C_{10}SO_4$, the CMC at a 1:1 molar ratio is approximately an order of magnitude lower than expected for an ideal mixture[171]. Such non-ideal effects provide evidence of synergism and can be exploited in different practical applications[172-174] such as detergency, oil recovery etc The behaviour of mixed surfactant system have been discussed in literature[171,175].

The interaction of cationic surfactant with other surfactants to form mixed micelles are mainly related to two sources The first, is hydrophobic effect. In this case, the

amphiphilic surfactant molecules, consist of both hydrophobic tail and hydrophilic head group, undergo self association to form large aggregates in equilibrium with surfactant monomers. Since the hydrophobic effect is not specific to head group, this effect favours the formation of aggregates of randomly mixed surfactant molecules with their hydrophobic chain in the interior of the aggregate and the hydrophilic head groups at the surface in contact with the aqueous solution. This effect applies equally to both pure and mixed systems of surfactants, which lead to "ideal" mixtures of surfactants in the aggregate

The second part involves some interactions between unlike head groups of different surfactants in the aggregate itself, which causes an excess free energy of mixing related to "non-ideal" mixing in the aggregate. Due to such interactions within the aggregate, there may be significant changes in the behaviour of the overall surfactant solution. Significant excess heats of mixing are observed in the formation of non-ideal mixed micelles [176-178] whereas for ideal mixing process, the excess heat of mixing must be zero by definition.

A number of studies [179-181] suggest that, the primary basis of non-ideal mixing behaviour is electrostatic interaction between the surfactants head groups in the aggregate For example, very large deviations from ideality are observed for cationic and anionic surfactants [182-184], while mixtures of surfactants with like charges behave ideally[185-188]. For ionic-non-ionic mixed surfactant systems, charge seperation based on the composition of the aggregate and relative head group size seems to play the dominant role in determining the strength of interactions, with relatively little effect seen for differences in the chemical structure of non-ionic surfactant itself [181].

Metal Complex Catalysed Hydrolysis of aminoacid esters in micellar medium

A few research work have been cited in literature, in which metal or metal complex catalysed hydrolysis of esters has been carried out in presence of surfactants[189-191]. Most of these studies were used as a model system for much more complex metallo-enzymes which involve intramolecular nucleophilic attack

As it is explained earlier, the metal complexes as well as surfactants can catalyse the aminoacid ester hydrolysis. The metal or metal complex can facilitate the nucleophilic

attack (OH^- attack) on ester, by forming a mixed ligand or ternary complex with it. The surfactant can also bring the nucleophile (OH^-) and the aminoacid ester together by electrostatic and/or hydrophobic interaction. So far, no research work has been cited in literature where kinetic study has been carried out to illustrate the combined influence of these two catalytic systems. Therefore, with a curiosity, to see the combined effect of these two catalysts on the rate, the present study was taken up

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