CHAPTER V

KINETICS OF ACYLATION REACTION IN MICELLES AND ALKALINE HYDROLYSIS OF HYDROXAMIC ACIDS IN SURFACANT / POLYMER MIXED MICELLES
KINETICS OF ACYLATION REACTION IN MICELLE AND ALKALINE HYDROLYSIS OF HYDROXAMIC ACIDS IN SURFACTANT/POLYMER MIXED MICELLES

5.0 INTRODUCTION

The development of new heterogeneous catalytic procedures for acylation of organic compounds has become a priority for the chemical industry \(^1\)-\(^2\) and acylation of aromatic compounds over using different catalysts has been the subject of a number of reports \(^3\)-\(^{10}\). Indeed, such a process has been commercialized \(^{11}\)-\(^{12}\).

Acyl chlorides are vigorous acylating agents. They react with water to give carboxylic acids, with alcohol and phenols to give esters, with ammonia and amines to give amides and with carboxylate to give anhydrides. They react with aromatic compounds in the presence of aluminium chloride as catalyst to give ketones.

Acylation is usually carried out in solvent. It requires catalyst in much amount because much of catalyst is removed by the formation of a complex with product.

Several aspects of hydroxamic acid such as their synthesis,
photochemical formation, physical and chemical properties, ionization and structure, analytical and therapeutic applications have been reviewed from time to time. In the previous chapters acidic hydrolysis of hydroxamic acids and nucleophilic substitution reaction of hydroxamic acids have been discussed.

Literature reveals that considerable efforts have been made on the kinetic study of acid or base catalysed hydrolysis of various hydroxamic acids. The use of hydroxamic acids as precursor of Lossen rearrangement is also well investigated. However, the kinetics of acylation of hydroxamic acids using acetic anhydride has not been explored properly. It is possible to achieve acylation of hydroxamic acids with acetic anhydride and solvent (1,4 dioxane) at 55°C over pyidine catalysts. For some potential applications in the fine chemicals/ pharmaceuticals area, however the reactions would need to involve more complex acylating agents.

This chapter is divided into two sections:

[A] Kinetics of acylation reaction in micelles
[B] Alkaline hydrolysis of hydroxamic acids in surfactant/polymer mixed systems
In section A, the kinetics of acylation of hydroxamic acids using acetic anhydride as an acylating agent in non-aqueous medium have been studied spectrophotometrically. The effect of pyridine and cationic surfactants on the rate of acylation has also been reported.

Polymer-surfactant interactions are currently the subject of extensive investigations due to new and specific technological applications. Many papers related to micellar catalysis of hydroxamic acids in the alkaline media have been published \(^{42-56}\). A number of substrate mixed micelle systems involving specifically designed electrostatic and hydrophobic interactions have been the subject of recent investigations. Micellar systems have gained much importance as the micelles themselves serve as nucleophiles or specific catalysis. Various techniques have recently been applied to study the polymer surfactant complexes \(^{57-60}\). Apart from important field of application, kinetics in these systems is of fundamental importance in basic surface and colloid chemistry.

Water soluble polymers interact strongly with surfactants in aqueous solutions. There is much interest in understanding the nature of interactions and its consequences \(^{61-63}\). Polymer-micelle interaction results from an accumulation of relatively, weak binding forces, which makes the association process even more intriguing.
The formation of mixed aggregates of polymer–surfactant has been a subject of intense investigation in recent years \(^{64-69}\). In a number of applications \(^{70-75}\) of importance to chemical, pharmaceutical, petroleum and mineral processing industries, the surfactant molecule are present in solution not alone but along with polymer. Polymer–surfactant (PS) interactions, which is very similar to protein surfactant interactions, has attracted much attention owing to their industrial applications, eg. in paints, coatings, cosmetics, cell fusion protocols \(^{74}\) etc. as well as in other biological systems \(^{75-76}\). The polymer surfactant interaction have been discussed in chapter – II.

However, many intriguing questions remain. In particular, the relationship between the chemical structure of the surfactant and polymer and their propensity for interaction, and also the dominant driving force for interaction are still debated in the literature.

Although application of such interactions are numerous, many problems are still unsolved. Particularly the question of how the polymer–surfactant couples effects the reaction kinetic possess a challenge for chemists. Very little work has been done on the characterisation and its properties on a reaction medium \(^{77-78}\). The base catalysed hydrolysis of p–TBHA and o–TBHA in surfactant–poly (ethylene) glycol (M.W. = 400) systems have also been
investigated. Various combinations (Scheme – I) have been attempted to optimize the kinetics parameters.

I. PEG (M.W. = 400) – CATIONIC SURFACTANTS

PEG (M.W. 400) – RN⁺(CH₃)₃Br⁻ (SURFACTANT)

R = C₁₂H₂₅ (DTAB), C₁₄H₂₉ (TTAB), C₁₆H₃₃ (CTAB)

PEG – C₁₆H₃₃N⁺(CH₃)₃C₇H₇ (CTATs)

II. PEG (M.W. = 400) – ANIONIC SURFACTANTS

PEG (M.W. 400) – C₁₂H₂₅SO₄⁻Na⁺ (Sodium dodecyl sulphate)

PEG (M.W. 400) – C₈H₁₇SO₃⁻Na⁺ (1 – Octane sulphonic acid sodium salt)

PEG (M.W. 400) – C₈H₂₁SO₃⁻Na⁺ (1-Decane sulphonic acid sodium salt)

III. PEG (M.W. = 400) – NON-IONIC SURFACTANTS

PEG (M.W. 400) – C₁₂H₂₅(OCH₂CH₂)₂₃OH (Brij – 35)

Scheme - I

The ethylene oxide functionality is of general interest, as it interacts favourably with a variety of surfactant head groups.
5.1 EXPERIMENTAL

Materials

Hydroxamic acids used in the work were p-nitrobenzohydroxamic acid \([p-\text{NO}_2\text{BHA}]\), p-methoxy benzohydroxamic acid \([p-\text{OCH}_3\text{BHA}]\) and N-Phenylbenzohydroxamic acid \([\text{PBHA}]\). All the hydroxamic acids were prepared by benzoylation freshly prepared and purified by literature procedure \(^{79-80}\). The base used in the experimental investigations were sodium hydroxide (Qualigens). Solvent (1,4 dioxane) used was of MERCK make. Acetic anhydride was obtained from ALLIED, Chemicals, Baroda.

Following surfactants were used without any further purification: Cetyltrimethyl ammonium bromide; CTAB; (SIGMA), Tetradecyltrimethyl ammonium bromide; TTAB; (SIGMA), Dodecyltrimethyl ammonium bromide; DTAB; (SIGMA), Cetyltrimethyl ammonium p-Toluene sulphonate; CTATs; (FLUKA), Sodium dodecyl sulphate; SDS; (SIGMA), 1-octane sulphonic acid sodium salt; (S.D.Fine), 1-decane sulphonic acid sodium salt; (S.D.Fine), poly oxyethylene (23) lauryl ether; BRIJ - 35; (SIGMA).

Polyethylene glycol with molecular weight of 400 (PEG - 400);
[SIGMA] was used for the surfactant / polymer mixed systems. Surfactant solutions of a definite concentration were always freshly prepared by weighing out a certain amount of surfactant and diluting it up to the required volume with double distilled water. The conductance measurements were carried out with a Systronics digital conductometer (Type 304).

Kinetic measurements were made by use of the Systronics UV-VIS spectrophotometer type 108 and Unicam UV2 300 spectrophotometer.

Methods

KINETIC MEASUREMENTS

Kinetics were followed spectrophotometrically by measuring the concentration of the hydroxamic acid by the colour reaction with $\text{Fe}^{3+}$ ions. Beer’s law was shown to hold for formulation of hydroxamate complex under these conditions [at 1:1 ratio of Fe (III) : hydroxamic acid]. In the complex $\lambda_{\text{max}}$ is found to be 520 nm. Addition of various surfactants do not effect the $\lambda_{\text{max}}$. The reaction is as follows:

$$n \quad \frac{R-N-OH}{R'-C=O} + \text{Fe}^{(III)} \rightarrow \left( \frac{R-N-O}{R'-C=O} \right)_n \text{Fe}^{(III)} + n\text{H}^+$$
These complexes of Fe (III) are all kinetic labile. A colorimetric method, based on the formation of purple colour water soluble complex between hydroxamic acid and iron (III) was used for studying the course of reaction in kinetic measurements.

The reaction mixture for the kinetic runs was prepared by quickly mixing the solutions of hydroxamic acids, catalyst and acylating agents, prepared in non-aqueous solvent (1,4 dioxane). The acylation reaction was followed spectrophotometrically by measuring the concentration of hydroxamic acid, after known time intervals. The method was used as hydroxamic acids from quantitative complexes with ferric chloride in hydrochloric acid medium, the optical density of the complexes is then measured at 520 nm by following literature procedure \(^8\). The measurements were carried out at different concentration of the hydroxamic acids and acetic anhydride at 55\(^0\)C in (1,4 dioxane) in presence of pyridine.

5.11 PRODUCT ANALYSIS

Reaction mixtures containing hydroxamic acid (25m moles) and acetic anhydride (25m moles) was allowed to react in non-aqueous medium (1,4 dioxane) using pyridine as catalyst at 303 K with constant stirring for three hours to complete the course of the reaction.
Then, the reaction solvent was removed under vacuum and the residue was poured on ice cold water. The cold reaction mass was neutralised using acetic acid and the obtained solid was filtered washed with water, dried and finally crystallized from aqueous–alcohol. The yield of O-acyl hydroxamate obtained is 80 – 85% at 1:1 stoichiometric condition. The melting point of these hydroxamate are in good agreement with reported in the literature 82-86.

5.2 RESULTS AND DISCUSSION

[A] KINETICS OF ACYLATION REACTION IN MICELLES

Hydroxamic acids is acetylated with acetic anhydride over pyridine to give O-acyl hydroxamate. The reaction rates were determined at different concentration of hydroxamic acids by keeping concentration of acetic anhydride constant. Similarly, the rates were determined at different concentrations of acetic anhydride by keeping concentration of the hydroxamic acids constant. The rate constants were found to be constant (data not shown). Kinetic measurements of acylation of hydroxamic acids have been performed in (1,4 dioxane) in the presence of catalyst pyridine using CTAB. The results are recorded in Table-5.1 and depicted graphically in Figure-5.1. Kinetic measurements were carried out at different concentration of
hydroxamic acids by keeping concentration of acetic anhydride at 328 K in 1,4 dioxane using pyridine as a catalyst [Tables - 5.2 - 5.3].

When hydroxamic acids react with acetic anhydride, the -NH₂ group gets acylated i.e., hydrogen atom of the -NH₂ group is replaced by acyl group and forms O-acyl hydroxamate, (Scheme - II).

\[
\begin{align*}
\text{Hydroxamic acid} & \quad \text{Acetic anhydride} \\
\text{R-C=O} & \quad \text{CH₃-C=O} \\
\text{H-N-OH} & \quad \text{catalyst} \\
\text{CH₃-C=O} & \quad \text{R-C-NH-O-C-CH₃} \\
\text{O-acyl hydroxamate} & \quad \text{CH₃COOH} \\
\text{Acetic acid} & \quad + \\
\end{align*}
\]

Scheme - II

The rates of acylation of hydroxamic acids in 1,4 dioxane medium in presence of pyridine was observed as in the order:

\[\text{BHA} > \text{p-NO₂BHA} > \text{p-OCH₃BHA} > \text{PBHA}\]

1,4 Dioxane is polar aprotic solvent. Pyridine is more basic in
dioxane hence, it catalyse the dissociation of hydroxyl group of hydroxamic acids. Therefore, acylation in presence of pyridine is faster in dioxane medium.

5.21 EFFECT OF CATIONIC SURFACTANT

The effect of cationic surfactant for the acylation reactions of hydroxamic acids (benzohydroxamic, p-nitrobenzohydroxamic, p-methoxybenzohydroxamic and N-Phenylbenzohydroxamic acids) using acetic anhydride in presence of pyridine are shown in Tables 5.1 to 5.3. The \( k' \) value for the reactions with benzohydroxamic acid increases sharply with increasing surfactant (CTAB) concentration in the reaction medium upto \( 8.23 \times 10^{-3} \) M and then decreases upon further addition of CTAB (Figure – 5.1). In the case of \( p \)-nitrobenzohydroxamic, \( p \)-methoxybenzohydroxamic and N-Phenylbenzohydroxamic acids, the \( k' \) value increases upto \( 5.48 \times 10^{-3} \) M, (Figures 5.2 to 5.4).

Micellar kinetics is governed by electrostatic and hydrophobic interaction between micelle and reactants, transition complexes and products. The electrostatic surface potential at the micellar surface can attract or repel reaction species, and a strong hydrophobic interaction can bring about the incorporation into micelles even of reagent that the bear the same charge as the ionic micelle.
TABLE 5.1

EFFECT OF CTAB ON ACYLATION REACTION OF BENZO-HYDROXAMIC ACID, TEMP. = 55°C, IN 1,4 DIOXANE

\[ [\text{BHA}] = 0.0051 \text{ M} \quad , \quad [\text{C}_6\text{H}_5\text{N}] = 0.0055 \text{ M} \]
\[ [(\text{CH}_3\text{CO})_2\text{O}] = 0.005 \text{ M} \]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[CTAB] X $10^{-3}$ M</th>
<th>$10^5 k_\psi / s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NIL</td>
<td>2.79</td>
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<tr>
<td>2.</td>
<td>2.73</td>
<td>21.9</td>
</tr>
<tr>
<td>3.</td>
<td>5.48</td>
<td>39.8</td>
</tr>
<tr>
<td>4.</td>
<td>8.23</td>
<td>63.9</td>
</tr>
<tr>
<td>5.</td>
<td>13.7</td>
<td>54.7</td>
</tr>
<tr>
<td>6.</td>
<td>16.4</td>
<td>50.7</td>
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FIG. 5.1 EFFECT OF SURFACTANT ON ACIDIC HYDROLYSIS OF BENZOHYDROXAMIC ACID

FIG. 6.2 EFFECT OF SURFACTANT ON ACIDIC HYDROLYSIS OF p-NITRO BENZOHYDROXAMIC ACID
TABLE - 5.2

EFFECT OF CTAB ON ACYLATION REACTION OF HYDROXAMIC ACIDS, TEMP. = 55°C, 1,4 DIOXANE

\[ [HA] = 0.0038 \text{ M}, \quad [(C_6H_5)N] = 0.0055 \text{ M} \]

\[ [(\text{CH}_3\text{CO})_2\text{O}] = 0.005 \text{ M} \]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[CTAB] x 10^{-3} M</th>
<th>(10^5 k_{\text{yr}} / \text{s}^{-1})</th>
<th>(p-\text{NO}_2\text{BHA})</th>
<th>(p-\text{OCH}_3\text{BHA})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NIL</td>
<td>3.84</td>
<td>2.69</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>2.73</td>
<td>10.6</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>5.48</td>
<td>18.7</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>9.60</td>
<td>13.0</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>13.7</td>
<td>8.56</td>
<td>2.65</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 5.3 EFFECT OF SURFACTANT ON ACIDIC HYDROLYSIS OF p-METHOXY BENZOHYDROXAMIC ACID

FIG. 6.4 EFFECT OF SURFACTANT ON ACIDIC HYDROLYSIS OF PHENYL BENZOHYDROXAMIC ACID
### TABLE - 5.3

**EFFECT OF CTAB ON ACYLATION REACTION OF N-PHENYL BENZO HYDROXAMIC ACID, TEMP. = 55°C, 1, 4 DIOXANE**

\[
\begin{align*}
\text{[PBHA]} &= 0.003 \text{ M} \\
\text{[(CH₃CO)₂O]} &= 0.005 \text{ M} \\
\text{[(C₆H₅)N]} &= 0.0055 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[CTAB] (\times 10^{-3} \text{ M})</th>
<th>(10^5 k_f / \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.00</td>
<td>0.71</td>
</tr>
<tr>
<td>2.</td>
<td>2.73</td>
<td>2.80</td>
</tr>
<tr>
<td>3.</td>
<td>5.48</td>
<td>4.98</td>
</tr>
<tr>
<td>4.</td>
<td>9.60</td>
<td>3.38</td>
</tr>
<tr>
<td>5.</td>
<td>13.7</td>
<td>3.06</td>
</tr>
</tbody>
</table>
The presence of micellar catalysis is easily explained as an electrostatic effect. The cationic nature of the surfactant favours the presence of base in the micellar medium and accelerated the acylation of substrate associated with the micelle. Increasing surfactant concentration increased the concentration of substrate associated with the micelle along with the increase in the concentration of the inert counterion Br\(^-\) which will compete with base.

### 5.22 MECHANISM AND CONCLUSION

The product is formed in the following three steps.

\[
\begin{align*}
\text{(i)} \quad \text{R-C-NHOH} + \text{B} & \xrightleftharpoons[k_2]{k_1} \text{R-C-NH-O}^- + \text{B}^+\text{H} \\
\text{[S]} & \quad \text{[B]} & \quad \text{[In\(_1\)]}
\end{align*}
\]

\[
\begin{align*}
\text{(ii)} \quad \text{R-C-NH-O}^- + \text{CH}_3\text{-C} & \xrightarrow[k_3]{\text{CH}_3\text{-C}} \text{R-C-NH-O-C-CH}_3 \\
\text{[In\(_1\)]} & \quad \text{[CH}_3\text{-C]} & \quad \text{[CH}_3\text{-C]} & \quad \text{[In\(_2\)]}
\end{align*}
\]
Acylation reaction will add a new contribution in the chemistry of hydroxamic acids. Hydroxamic acids have been suggested to behave either as NH or OH acids depending on solvents. Numerous studies indicate that hydroxamic acids are OH, rather than NH acids in water. Hydroxamic acids ionizes to form hydroxamate ion and attack the carbonyl carbon of acetic anhydride and form O-acyl hydroxamate. Acylation reaction of hydroxamate ions thus studied, proved that hydroxamate ions are effective deacylating agent. On the basis of this aspects, work is in progress to study the deacylation of the carboxylate and dephosphorylation of the phosphate esters.
[B] **ALKALINE HYDROLYSIS OF HYDROXAMIC ACIDS IN SURFACTANT/POLYMER MIXED MICELLES**

The systems discussed in this section are composed of a nonionic polymer i.e., poly (ethylene) glycol, PEG (M.W. = 400) and various cationic, anionic and non-ionic surfactants. Different combinations of polymer-surfactant systems and their effects on the hydrolysis of hydroxamic acids are schematically presented (Scheme - III).

Hydrolysis of Hydroxamic acid (I)

\[
\begin{align*}
R' & - N - OH \\
\downarrow \\
R & - C = O \\
(I)
\end{align*}
\]

- R = C\text{\textsubscript{6}}H\text{\textsubscript{5}} ;  \quad R' = 4 - \text{CH}\text{\textsubscript{3}}.C\text{\textsubscript{6}}H\text{\textsubscript{4}} \quad \text{p-TBHA}
- R = C\text{\textsubscript{6}}H\text{\textsubscript{5}} ;  \quad R' = 2 - \text{CH}\text{\textsubscript{3}}.C\text{\textsubscript{6}}H\text{\textsubscript{4}} \quad \text{o-TBHA}

Solvent = 10% (v/v) 1,4 Dioxane
Temp. = 55°C
Alkaline Hydrolysis (0.1M NaOH)
The influence of non-ionic polymer / cationic surfactant, non-ionic polymer / anionic and non-ionic polymer / non-ionic surfactant systems on the alkaline hydrolysis of p-TBHA and o-TBHA were studied at fixed concentrations of (NaOH = 0.1 M) and 10% (v/v) 1,4 dioxane at 55°C. The results are shown in Tables 5.4 - 5.5. The pseudo-first order rate constants for the alkaline hydrolysis of hydroxamic acids at different polymer - surfactant concentrations are given in Figures 5.5 to 5.9. In case of anionic and non-ionic
TABLE 5.4

EFFECT OF MIXED POLYMER/SURFACTANT SYSTEMS ON THE ALKALINE HYDROLYSIS OF p-TBHA AT 55°C, MEDIUM: 10% (v/v) 1,4 DIOXANE, NaOH = 0.1 M

<table>
<thead>
<tr>
<th>PEG-400</th>
<th>10^5 k_\psi / s^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (v/v)</td>
<td>CTAB</td>
</tr>
<tr>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>5.00</td>
<td>44.7</td>
</tr>
<tr>
<td>10.0</td>
<td>37.8</td>
</tr>
<tr>
<td>20.0</td>
<td>29.6</td>
</tr>
<tr>
<td>40.0</td>
<td>-</td>
</tr>
</tbody>
</table>

k_\psi_{(NIL)} = 7.32 \times 10^{-5} \text{ s}^{-1}
FIG. 6.5: EFFECT OF POLYMER - SURFACTANT [SDS] MIXED SYSTEMS ON THE ALKALINE HYDROLYSIS OF HYDROXAMIC ACIDS AT 55°C

FIG. 6.6: EFFECT OF POLYMER - SURFACTANT [SDS - 3R] MIXED SYSTEMS ON THE ALKALINE HYDROLYSIS OF HYDROXAMIC ACIDS AT 55°C
TABLE 5.5

EFFECT OF MIXED POLYMER/SURFACTANT SYSTEMS ON THE ALKALINE HYDROLYSIS OF o-TBHA AT 55°C, MEDIUM: 10% (v/v) 1,4 DIOXANE, NaOH = 0.1 M

<table>
<thead>
<tr>
<th>PEG-400</th>
<th>10^5 k_f / s^{-1}</th>
</tr>
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<tbody>
<tr>
<td>% (v/v)</td>
<td>CTAB</td>
</tr>
<tr>
<td>0.00</td>
<td>21.6</td>
</tr>
<tr>
<td>5.00</td>
<td>22.0</td>
</tr>
<tr>
<td>10.0</td>
<td>21.8</td>
</tr>
<tr>
<td>20.0</td>
<td>17.0</td>
</tr>
<tr>
<td>40.0</td>
<td>-</td>
</tr>
</tbody>
</table>

k_f(NIL) = 2.70 \times 10^{-5} \text{ s}^{-1}
FIG. 5.7: EFFECT OF POLYMER - SURFACTANT [CTAB] MIXED SYSTEMS ON ALKALINE HYDROLYSIS OF HYDROXAMIC ACIDS AT 55°C

FIG. 5.8: EFFECT OF POLYMER - SURFACTANT [CATIONIC] MIXED SYSTEMS ON THE ALKALINE HYDROLYSIS OF p - TBA AT 55°C
surfactants rate constant increases but in case of cationic surfactant, it was observed that the first order rate constant increases with increasing polymer–surfactant concentration, go through a maxima and then decreases gradually at its higher concentration. The aggregation number of surfactants in presence of polymers, using specific–ion electrode, fluorescence and neutron scattering techniques have been reported in the literature. The reactive ions, OH\(^-\), are substituted by the counterions in the Stern layer, where the reaction is supposed to occur. From all the experimental results it can be concluded that the polymer (PEG – 400) interacts with anionic and non–ionic micelles.

The polymer incorporation in micelles produces an increase in the micellar ionization degree and decrease in the surfactant aggregation number and the CMC value. The polymer incorporation in micelles also produces an apparent inhibitory effect on the acidic and alkaline hydrolysis of hydroxamic acids, compared to the effect found in pure micelles. This effect is related to,

(i) the increase in the micellar ionization degree, related to the micellar surface potential the substrate should overcome to solubilize in the micelle.

(ii) the increase of the volume element where the reaction is supposed to occur, which produces a dilution of the reactants, and
(iii) there is a change of the apparent dielectric constant of the reaction medium.

Several modes of interactions (hydrophobic interaction, dispersion forces, hydrogen bonding, hydration of the polymer and head groups, steric repulsion and electrostatic interactions between surfactant head groups etc.), may contribute significantly. Small changes in chemical structure of the surfactant or polymer may shift the balance of forces and may change which modes of interaction dominate.

In general anionic, non-ionic surfactants interact strongly with non-ionic water soluble polymer and they may play important role in the binding phenomena in systems containing, polymer and surfactants mixtures. Stabilization of the interface between the hydrophobic core and water is considered to be a major driving force for polymer-micelle interaction.

Data in Tables 5.4 and 5.5, show the pseudo-first order rate constants for various reaction systems. The addition of cationic surfactants to non-ionic polymer, poly(ethylene) glycol inhibits the rate of hydrolysis of hydroxamic acids in alkaline media.

Binding of additional substrate to enzyme may increase or
decrease the observed reaction rate and by analogy the co-operativity between the surfactant molecules and the substrates may account for micellar catalysis.

To fit the kinetic results to the theoretical treatment, it is necessary to know the micelle volume, which is difficult as it depends on the polymer location, how many monomeric units are inside the micelles and the polymer concentration solubilized in the micelles. The polymer/surfactant ratio has been taken as 1:1 and the complete solubility of the polymer in the micelle has been considered. Polymer–micelle interaction depends on several properties of the surfactant molecule such as the chemical nature, geometry and charge. Saito and co-workers found that the interactions of neutral polymers with long chain alkyl ammonium cations depend on the counterion species. Also, the weak interaction of neutral polymers with cationic micelles is caused by the large size of the surfactant head groups. Addition of poly(ethylene) glycol to surfactants makes the surface charge density of mixed surfactant/polymer system be lower than that of the single ionic micelle, leads to the decrease of exclusion between ionic head groups of the ionic surfactants. Probably, the size of the head group and the interaction of the head group with the hydration sheath of the polymer are the main reasons for weak interaction of cationic micelles with polymers.
5.3 CONCLUSION

The mechanism of alkaline hydrolysis of hydroxamic acids are given in (Scheme – IV).

Hydroxamic acids react with rate–determining attack of $\text{OH}^-$ on the carbonyl group resulting in a tetrahedral intermediate followed by rapid ring fission.

By proper choice of mixed systems it is possible to enhance the stability, selectivity and sensitivity of analytical reaction. The mixed
systems produce a synergistic effect on the hydrolysis reaction of anionic and non-ionic surfactants. But in case of cationic surfactant, the rate constant increases sharply with increasing polymer concentration in the reaction media and then decreases, upon further addition of polymer. Hence, the mixed system produce a inhibitory effect on the hydrolysis reaction of hydroxamic acids in cationic micellar media.
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