CHAPTER - I

INTRODUCTION

Part-A : Surfactants in Aqueous Solutions.

Homogeneous media are conventionally chosen to investigate the rates, equilibria and mechanism of chemical reactions in solution. But in reality, most of the reactions do not take place in homogeneous solutions, rather they occur at some interfaces. Many industrially important chemical reactions occur on the surface of solid catalysts. The biological reactions take place on the surface of an enzyme which might be bound to cell membrane $^{1-3}$. The properties of the catalytic surfaces are critically dependent upon the detailed surface structure. So, there is a necessity of studying the behaviour of surface active agents in aqueous medium with regard to their properties and structure. The molecule of a surface active agent consists of a long chain hydrocarbon moiety, linear or branched, and a polar or ionic head group. The hydrocarbon portion exhibits hydrophobic behaviour and the polar or the ionic head group is hydrophilic as it strongly interacts with water via dipole-dipole or ion-dipole interactions. Consequently such moieties possessing these dual characteristics are called 'amphiphiles'. They are also called 'detergent'. 
It is essentially the balance between the hydrophobic and hydrophilic parts of the molecule (ion) which imparts special properties to the surface active agents. The surface active agents are also called surfactants, association colloids, colloidal electrolytes, paraffin chain salts, amphipathic compounds and tensides.

**General classification of surface active agents:**

Depending upon the nature of the head groups, the surfactants are usually classified into four major categories such as (i) anionic, (ii) cationic (iii) nonionic, and (iv) zwitterionic.

(i) **Anionic**: Sodium dodecyl sulphate (SDS) \( \left( \text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}^+ \right) \) and sodium dodecanoate \( \left( \text{C}_{12}\text{H}_{23}\text{COO}^-\text{Na}^+ \right) \) belong to this category of surfactants. A large number of this type of surfactants are produced from triglycerides and soaps of long chain fatty acids by saponification.

(ii) **Cationic**: Dodecyl trimethyl ammonium bromide (DTAB) \( \left( \text{C}_{12}\text{H}_{25}\text{N}^+\text{Me}_3\text{Br}^- \right) \) and hexadecyl trimethyl ammonium bromide (HTAB) or cetyl trimethyl ammonium bromide (CTAB) \( \left( \text{C}_{16}\text{H}_{25}\text{N}^+\text{Me}_3\text{Br}^- \right) \) are examples of this group.

(iii) **Nonionic**: Many of these are based on polyoxyethylenes and a typical example is dodecyl oxyethylene glycol mono ether.
(C₁₂H₂₅(OCH₂CH₂)₆OH, often abbreviated as C₁₂E₆ to denote hydrocarbon chain length and ethylene oxide chain length. The head group is larger in length (24Å⁰) than C₁₂ chain (18Å⁰).

Examples of nonionic surfactant with small head groups are dodecyl sulphinyl ethanol (C₁₂H₂₅SOCH₂CH₂OH) and decyl dimethyl amine oxide, i.e. C₁₀H₂₁ - N - Me. The latter compound is nonionic in aqueous solution above pH 7, but at lower pH it remains in cationic form due to protonation at oxygen site. Another very much in use nonionic surfactant is Iso-octyl phenoxy polyethoxy ethanol, which is marketed in the trade name Triton-X-100.

Zwitterionic: An example of this group of surfactant is 3-dimethyl dodecyl amine propane sulphonate.

Many naturally occurring compounds like triglycerides belong to this category of surfactants. Lecithin, available in membrane of animal cells is one such triglycerides.

\[
\begin{align*}
\text{C}_{17}H_{35}\text{COOCH}_2^- \\
\text{C}_{17}H_{25}\text{COO-CH} \\
\text{CH}_2-O-P -O-\text{CH}_2-\text{CH}_2-\text{CH}_2-N-\text{Me}_3
\end{align*}
\]

Lecithin
Lecithin has extremely low solubility in water. Most of the other surface active compounds, discussed above are soluble in water. It is a rough approximation that compounds with chain length > C_{16} are insoluble whereas compounds with chain length ≤ C_{16} are soluble in water.

These substances possess a unique property of being absorbed at various interfaces (air-water, oil-water, water-solid, oil-solid etc.,) and consequently lower interfacial surface energy. So these are called surface active substances.

**Surfactants and Evidence of Micelle Formation:**

In dilute aqueous solutions (10^{-4} M) the behaviour of ionic amphiphiles is similar to that of strong electrolytes. But as the concentration increases, deviation from ideal behaviour occurs. The interfacial tension, electrical conductivity, pH, density, specific heat, temperature coefficients of solubility, viscosity, optical and spectroscopic properties of solution of amphiphiles undergo well-defined but not abrupt changes. This is attributed to aggregation of amphiphiles to form micelles. The concentration at which the association takes place is called critical micelle concentration (C.M.C.).

**Solution properties:** For surfactants having chain length between C_{8} to C_{16}, the plot of surface tension against logarith m of molar concentration gives a curve which displays
break point at certain concentration above which surface tension remains almost constant. We know Gibbs adsorption equation is

$$\Gamma_2 = \frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln a_2} \right)_{P,T}$$  \hspace{1cm} (1)

where $$\Gamma_2$$ is the surface excess, \(\gamma\), the surface tension and \(a_2\) is the activity of solute.

The condition \(\frac{\partial \gamma}{\partial \ln a_2} = \text{Const.}\) \hspace{1cm} (2)

which holds good just prior to the break point indicates the attainment of saturation of adsorption of the surface. But just after the break point, we have

$$\frac{\partial \gamma}{\partial \ln a_2} = 0$$

which gives \(\gamma = \text{constant} \times \ln a_2\). \hspace{1cm} (3)

As \(\gamma\) remains constant, the activity of surface active agent must remain constant. This is attributed to the micellization of the surfactant molecules. Each surface active agent at a given temperature and electrolyte concentration has characteristic value of cmc. A detailed compilation of such values of surfactants is available.

It is a rough approximation that many \(C_{12}\) ionic surface active agents have cmc values of approximately \(10^{-2}\) mol dm\(^{-3}\) and that further addition of two \(-\text{CH}_2-\) groups lowers the value to \(10^{-3}\) mol dm\(^{-3}\).
Solubility of Surfactants

The solubility of a surface active agent in water increases with temperature and the solubility temperature curve exhibits abrupt change at a certain temperature due to micelle formation.

The cmc of a surfactant varies with temperature, cmc equals the solubility at a certain temperature which is known as Kraft temperature.

Thermodynamics of Micellization

Multiple equilibria are envisaged in the micellar solution which may be delineated as given below.

To understand the aggregation of surfactant monomers to form micelles, the case of a nonionic surfactant may be considered. This avoids complications due to electrical effects associated with ionic surfactants. The association of N single molecules, \( S \), to form micelle \( M \) composed of N
monomers can be represented by the equation.

\[ \text{NS} \rightleftharpoons M \]  

for which the equilibrium constant (K) is given by

\[ K = \frac{[M]}{[S]^N} = \frac{C_m}{C_s^N} \]  

The free energy of micellization is then given by

\[ -\Delta G = RT \ln K = RT \ln C_m - NRT \ln C_s \]  

where \( C_m = [M] \) = total concentration of micelles and \( C_s = [S] \) = concentration of surfactant monomer. Free energy required to insert one monomer unit into the micelle is expressed as

\[ -\Delta G^o = -\frac{\Delta G}{N} = \frac{RT}{N} \ln C_m - RT \ln C_s \]  

For many micellar units \( N \) will be of the order of 100 and hence the first term in equation can be neglected and we can then write

\[ \Delta G^o = RT \ln C_s \]  

An assumption that there is phase change on micellization of surfactants when \( N \) is large is usually made. If \( C_s = (C.M.C.) \), then

\[ \Delta G^o_m = RT \ln [C.M.C.] \]  

For the case of ionic surface active agent

\[ \Delta G^o = RT \left(2 - \frac{p}{N}\right) \ln [C.M.C.] \]  

when \( p \) is the effective change on the micelle.
Enthalpy and entropy of micellization: In case of non-ionic surfactant, the enthalpy and entropy of micellization can be calculated by equation (11) and (12)

\[
\Delta H_m^0 = RT^2 \left[ \frac{d \ln[C_{MC}]}{dT} \right]_P
\]

\[
\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0)/T
\]

An alternative and preferable method of determining \(\Delta H_m^0\) is by caloriemetry. Direct caloriemetric studies have demonstrated that there is large decrease in partial molar heat capacity \(C_p\), on micellization of surfactant. Rosen\(^5\) showed that the large negative free energy of micellization \(\Delta G_m^0\) which becomes increasingly more negative as the chain length increases, consists of a small positive enthalpy change \(\Delta H_m^0\) which diminishes slightly with increasing hydrocarbon chain length and a large positive entropy term \((T\Delta S_m^0)\) which becomes more positive as the hydrocarbon chain is lengthened.

In case of mainly non ionic surfactants the positive standard entropy of micellization is the result of hydrophobic effect. Ionic and zwitterionic surfactants are complicated by entropy effects associated with the release of water molecules by surfactant ion upon partial neutralisation of ionic charges by the counter ions when the aggregation occurs. This adds to the positive entropy of micellization, but in such cases, it is not very clear how much is contributed to \(\Delta S_m\) by solvation effect of the head group and how much by water structuring around the hydrocarbon chains.
The free energy change which takes place at higher amphiphilic concentration is believed to be outcome of the changes in water structure and hence the increase of entropy of the systems. In liquid water, water molecules are intermolecularly hydrogen bonded resulting in a flickering Frank-Evans clusters\textsuperscript{6-9}. The long hydrocarbon chain of an amphiphile increases the orderliness of the water molecule by the formation of these water clusters and thus decreases the entropy. But by formation of micelles the hydrocarbon chains of the molecule self associate and the icebergs that are formed around the monomer melt resulting in decrease in orderliness of water molecules causing increase in entropy of the system. This hypothesis has led to the general belief that the micellisation process is predominantly entropy driven\textsuperscript{8-10}.

**Micellization as a kinetic process**

Micelle is a dynamic entity. The rate of formation and break down of micelles can be measured by using pressure jump and stopped flow techniques. The half life for micellar formation or break down is $\sim 10^{-3}$ seconds\textsuperscript{11-13}. The rate of interchange of surface active molecule between micelle and bulk aqueous phase is an important feature. The life time of a surface active molecule in a micelle is of the order of $10^{-7}$ seconds\textsuperscript{14,15}. 
(Schematic representation of structures formed in concentrated solutions of surface active agents, Corkill & Godman 1969)
Two component system: Surface active Agent—water:

The simplest solution of a surface active agent is a two component system consisting of surfactant and water. In dilute solutions, the micelles are distributed at random. But as the concentration increases, various organised and systematized structures appear. Various structures (i.e. hexagonally close packed, spherical units in a body centered cubic arrangement, lamellar phase composed of sheets of molecules in a bimolecular packing with head groups exposed to water layer in between them etc) are formed over definite concentrations and temperature domains. Further details on the phase behaviour of surfactants is beyond the scope of this thesis.

**Micellar Model Structures**:

(a) Some Historical notes about the structural models of micelles — In early 1920, Mc Bain and Salmon investigated the activity of 1 mol dm$^{-3}$ aqueous solution of potassium stearate at 90°C. The concentration of osmotically active material was found to be 0.42 mol dm$^{-3}$. This indicated that at this concentration association units were formed and the name micelle was given to these molecular aggregates. They suggested the formation of two types of micelles i.e. spherical ionic micelles and lamellar neutral micelles (see fig. 1).
Later in 1936, G.S. Hartley, in his work entitled "Aqueous solutions of paraffin chain salts" suggested that the properties of surface active agents could be explained by formation of one type of micelles.

The micelles proposed by Hartley has the following features.

1. The associated units of surfactants are spherical with radius approximately equal to the length of the hydrocarbon chain.
2. It contains approximately 50 to 100 monomeric units of surface active agents.
3. The process of micellization occurs over a very narrow concentration range.
4. The binding of counterions to charged head groups of ionic micelles decreases the mobility of the units with respect to those without having counterion binding.
5. The interior of micelles formed of hydrocarbon chains shows the characteristics of the liquid hydrocarbon which in turn solubilize many organic substances. The micelle structure proposed by Hartley (Oil drop model) forms a basis for recent developments in this area. Recent small angle neutron scattering studies reveals that due to the motion of molecules, the micelle surface is somewhat nonspherical. The light scattering experiment also indicate that in many systems the micelles are not spherical. Debye and Anacker proposed cylindrical model to explain the light scattering
results on the micellized hexadecyl trimethyl ammonium bromide in water. Evidences for disc shaped micelles have also been obtained.

Micelle formation has theoretically been treated by different models such as (1) Phase separation Model, (2) Mass action Law Model and (3) Multiple equilibrium Model (18-22).

**Phase Separation Model**: This model gives a clearest definition of cmc and may be formulated by assuming that chemical potential of the surfactants in micellar state is constant at given temperature and may be adopted as a standard chemical potential, $\mu_m^O$ analogous to standard chemical potential of pure liquid or solid. Equilibrium with surfactant in solution is represented by

$$\mu_m^O = \mu_m^O + RT \ln a_1$$

where $\mu_m^O$ is the standard chemical potential and $a_1$ is the activity of the surfactant monomer in solution. Putting $a_1 = x_1 f_1$, where $x_1$ = mol fraction of the surfactant monomer, $f_1$ = the activity coefficient and taking $f_1 = 1$, the standard free energy of micellization $\Delta G_m^O$ is given by

$$\Delta G_m^O = \mu_m^O - \mu_1^O = RT \ln X_1$$

(13)

For dilute solutions in water at 25°C, the concentration $X_1 = C / 55.5 \text{ mol dm}^{-3}$, where $C$ = molar concentration of the monomer at micellization ($C = \text{cmc}$)

Hence

$$\Delta G_m^O = RT \ln C - RT \ln 55.5$$

(14)
This model does not take into account the possible variation in activity of the surfactant with increase in total concentration of surfactant and considers micelle formation as analogous to a phase separation, c.m.c. is then saturation concentration of the amphiphile in monomeric state whereas the micelles constitute the 'pseudophase'. The phase separation model predicts a sharp change in physico-chemical properties of surfactant solutions around the cmc while a closer analysis of experimental data reveals a smooth transition. So a number of alternative models have been proposed.

**Mass action law Model:** In its simplest form, this postulates an equilibrium between monomers, $S$, and a single micellar species of aggregation number, $N$:

$$NS \rightleftharpoons M_N, \quad K_M = X_N / X_1^N$$

where $K_M$ is the equilibrium constant defined in terms of molefractions of $M_N(X_N)$ and $S(X_1)$. The standard free energy of micellization per mole of monomer $\Delta G_M^0$ is then given by

$$\Delta G_M^0 = -(RT/N) \ln K_M$$

$$= -(RT/N) \ln X_N + RT \ln X_1$$  \hspace{1cm} (15)

For large values of $N$ ($> 50$) and total concentration not greatly exceeding the cmc, the first term is negligible. Eq. (15) thus reduces to eq (13) for phase separation model.
It is an assumption that the association of monomers into micelles is a co-operative process and the aggregates with smaller value of $N$ are unstable. This model permits a simple extension to be made to the case of surfactants which are strong electrolytes in dilute solution but for which the micelles attract a substantial proportion of counterions into an attached layer so that univalent surfactant with aggregation number, $N$, may have an effective charge $p$ units only. The degree of dissociation of the micelle is $p/N$. For such a surfactant, e.g. $\text{Na}^+\text{S}^-$, the aggregation process may be represented by Eq (16) and corresponding association constant ($K_M$) by Eq (17) where $X_i$'s denote the concentration in molefraction scale and activity coefficient assumed to be unity.

$$\text{NS}^- + (N - p) \text{Na}^+ \rightleftharpoons M_p^- \quad (16)$$

$$K_M = \frac{X_M}{X_S X_{\text{Na}}^{N-p}} \quad (17)$$

For ionic surfactants, the standard free energy of micellization ($\Delta G_m^O$) is then given by equation 18 (ref(19)) in absence of added electrolyte

$$\Delta G_m^O / RT = (2 - p/N) \log X^* \quad (18)$$

where $X^* = \text{c.m.c.}$
For many ionic surfactants, the degree of dissociation of micelles is found from the conductivity measurement to be \( \sim 0.2 \), so that typically the standard free energy, \( \Delta G^0_M \), is given by

\[
\Delta G^0_M = 1.8 \, RT \, \ln X^*
\]  

(19)

This shows that for similar values of the cmc, \( \Delta G^0_M \) for ionic surfactant is two orders of magnitude higher than nonionic surfactants. For sodium dodecyl sulphate, cmc = \( 8.2 \times 10^{-3} \) mol dm\(^{-3} \) at 25\(^\circ\)C and \( \Delta G^0_M = -21.85 \) kJ mol\(^{-1} \). Ionic surfactants having cmc values in the range of \( 10^{-1} \) to \( 10^{-3} \) mol dm\(^{-3} \) in water are likely to exhibit significant deviations from ideal behaviour outlined above and for more exact treatment, activity coefficients of the ionic species should be taken into account using Debye-Hückel Theory.

The assumption of a single aggregation number is a simplification, but this approach illustrates well that larger the micelle, the more co-operative is the association. In reality, however, micellar size is not restricted to a single aggregation number but there is a micellar size distribution. So the multiple phase separation model was developed.

**Multiple Phase Separation Model**

The cmc and aggregation number of surfactants especially nonionic ones vary with temperature, and total concentration
A two dimensional schematic representation of the regions of spherical ionic micelle. The counterions (x), headgroups (O), and hydrocarbon chains (-----) are schematically indicated to denote their relative locations but not their numbers, distribution or configuration.

(Fig-2)
of the surfactant which led to the idea of multiple equilibrium model.

This is depicted below

\[ 2S_1 \overset{K_2}{\underset{S_2}{\rightleftharpoons}} S_2, \quad S_2 + S_1 \overset{K_3}{\underset{S_3}{\rightleftharpoons}} S_3; \quad S_{N-1} + S_1 \overset{K_N}{\underset{S_N}{\rightleftharpoons}} S_N \]

These equilibria may also be represented by a series of association reactions of monomers

\[ \overset{K_N}{\underset{S_N}{\rightleftharpoons}} S_1^N \quad \text{with} \quad N = 2, 3, 4 \]

such that

\[ K_N' = \frac{[S_N]}{[S_1]^N} \]

and it follows that

\[ K_N = \prod_{i=2}^{N} K_i \quad \text{or} \quad \ln K_N' = \sum \ln K_1. \]

Associated with these equilibrium constants, there will be a series of standard free energy changes which are conveniently represented by direct values for each species of the standard chemical potential \( \mu_{\text{mic},N}^0 \) per constituent amphiphile molecule (Tanford-1980)

Further discussion is beyond the scope of this thesis.

Considering these models, a schematic two-dimensional diagram of a spherical ionic micelle is represented in Fig. 2. These micelles have average radii of 12-30 \( \text{Å} \) and contain 20-100 monomers. A hydrophobic part of the aggregates form the core of the spherical micelle which acts as the liquid paraffin. The polar headgroups are placed in micelle-water interface; the interface being in touch with and hydrated by water molecules. Some water molecules are entrapped by
the micelle and in some cases part of the hydrocarbon chain may extend up to the aqueous phase. The charged head groups and small counterions of the ionic micelle are located in a compact region known as Stern layer which extends from the core to a few angstroms. The compactness of the Stern layer is responsible for the reduction of the net charge on the micelle. Most of the counterions are, however, located outside the shear surface in the Gouy-Chapman electrical double layer where they are completely dissociated and are able to exchange with ions on the bulk phase.

**Prediction of Critical Micelle Concentration and Standard free Energy Change of Micellization**

Linear relationship exists between logarithm of measured cmc values and number of carbon atoms $n_c$ in the hydrophobic tail of the surfactant. Becher (1976) summarizes such results for nonionic surfactants by the equation

$$\log C^* = 10.3 - 0.5 n_c$$  \hspace{1cm} (20)

For the phase separation model, the following equation holds good

$$\mu_m^0 - \mu_1^0 = \Delta G_m^0 = RT \ln C^* - RT \ln 55.5$$  \hspace{1cm} (21)

So, the empirical equation (20) at $25^\circ C$ becomes

$$\Delta G_m^0 = \mu_{mic}^0 - \mu_1^0 = 1.85 - 2.85 n_c$$  \hspace{1cm} (22)
For n-alkyl betaines, Tanford\textsuperscript{28} suggested the following relationship

\[ \Delta G_m^o = \mu_{\text{mic}}^o - \mu_1^o = 10.56 - 2.98 n_c \] (23)

for standard free energy of micellization\textsuperscript{28}.

**Solubilization in Aqueous Micellar Solution**

Broadly speaking solubilization is referred to as the formation of a thermodynamically stable isotropic solution of a substance normally insoluble or slightly soluble in a given solvent by the introduction of an additional amphiphilic compound or components. Detergents are used to enhance the solubility of organic compounds\textsuperscript{27-33,10}.

There is little solubilization before cmc but after cmc, the increase in solubility varies directly as the concentration of surfactant over a large range which is used in turn to determine the cmc values. The isotropic saturation concentration of solubilizate is called maximum additive concentration (MAC)\textsuperscript{34,10}. The solubility data are expressed as solubility curves or as phase diagrams. The important factors affecting solubilization are structure of surfactant and solubilizate, temperature, added electrolytes and non-electrolytes\textsuperscript{35,36}. But solubilization sites affect the solubilization also. Increase in length of alkyl chain increases solubilization in micellar core and solubilization in hydrophilic part increases with increase of the polar...
hydrophilic group. The structural aspects of solubilizate like polarity, polarizability, chain branching, molecular shape, size and structure also have various effects.

Temperature has an effect on the extent of micellar solubilization which depends on the structure of solubilizate and surfactant. In most cases with increase in temperature as there is increase in micellar site, particularly with nonionic ethoxylated surfactant, there is increase in solubility of the solubilizate.

Added electrolytes increase the micellar size and reduce the cmc, and also enhance the solubilization. Non electrolytes, like alcohols at low concentration, being incorporated into the micelles increase the micelle size and thereby increase solubilization.

The location site of solubilizate required for understanding of micellar catalysis depend upon the hydrophobic and hydrophilic tendencies of the solubilized molecules. There are four different location sites inside the micelle: (i) interior hydrocarbon core (ii) Palisade layer (solute sand-witched between surfactant chains in the micelle, in the palisade layer in which one may distinguish between deep and short penetration) (iii) Outer hydrophilic region of the surfactant, e.g. in the ethylene oxide region of an ethoxylated surfactant (iv) outer micelle surface. Solubilization is a dynamic equilibrium process like micellization.
Various experimental techniques such as (i) U.V and visible absorptions and fluorescence spectroscopy, (ii) proton and flourine magnetic resonance spectroscopy, (iii) electron spin resonance spectroscopy, (iv) X-ray diffraction, (v) potentiometric studies, (vi) distribution measurements, and (vii) reaction rate studies have been utilized to determine the environment of solubilizate in relation to micellar system.

**Micellar Effects on Chemical Reactions**

The study of micellar effects on the kinetics and equilibria of reactions in solutions continue to be an active area of research. Ionic micelles have striking effects on ionization of indicators and their effects were rationalized in terms of Hartley's rules. For example, the protonation of indicators in the presence of anionic micelles which bring the base and hydronium ion together is enhanced and it stabilizes the conjugate acid; the cationic micelles exert opposite effect in such reactions. The early kinetic studies followed two main lines.

1. It was found that reaction rates sometimes changed very sharply when hydrophobic groups in a substrate favoured its micellization. For example, the rate of acid hydrolysis of monoalkyl sulphates is independent of an increase in the length of the n-alkyl group up to n-pentyl, but longer alkyl
groups cause the substrate to micellise and there is then a sharp rise in the reaction rate \( 81,82 \). The rate enhancement is readily understandable in terms of enhancement of concentration of hydronium ion and other cations in the Stern layer of an anionic micelle. Using the same reasoning Kurz et al.\(^{81}\) were able to explain why the reaction with hydroxide ion was inhibited when alkyl sulphates micellized, whereas micellization had little effect on the neutral hydrolysis. There has been many subsequent kinetic studies of the effect of substrate micellization and it has recently been found that the stereochemistry of deamination of optically active alkylamines changes from inversion of configuration to net retention when the amine micellizes\(^{83}\).

2. The micelle can act as a catalyst. In this role, it mimics enzymic catalysts but only to a limited extent and we can also draw analogies for catalysis by micelles and solid surfaces.

Many reactions of fundamental importance occur at interfaces, and the study of micellar catalysis and inhibition is but part of broader kinetic study of reactions occuring at interfaces between aqueous and nonaqueous solvent and in liquid crystals. The study of these systems has been attracting the attentions of the solution kineticist.\(^{85}\) Three major roles of micelles on the kinetics of reactions in solutions can be envisaged.
(a) It can bring the reagents together. For example, an uncharged substrate can be incorporated into a cationic micelle where it will be concentrated in the stern layer of the micelle.

(b) The reagent may be chemically bound to some or all the monomers which make up the micelle and so can be brought to the proximity of the substrate.

(c) A spontaneous unimolecular reaction may occur more rapidly in the micellar pseudophase than in the bulk solution phase. The rate enhancement is akin to solvent effect; for example the rate of unimolecular decarboxylation of some carboxylate ions is mainly increased when the solvent is changed from water to a nonhydroxylic solvent, and when carboxylate ions are incorporated into a cationic micelle. Reaction takes place at the interface of water and relatively hydrophobic micelle and the reaction rate may be governed by hydrophobic interactions which are relatively unimportant for reactions in homogeneous solution where the dominant structural factors depend on steric and electronic effects. So high degree of reagent selectivity for reactions taking place at micellar surfaces different from those in homogeneous solution is expected. The development of specificity for reactions in a normal micelle will depend upon the nature of interface and the manner in which properties can be modified.
Inhibition

The ability of micelles to inhibit reaction is of great practical importance. Solutions of labile solutes can be stabilised by micelles for extended storage. The substrate can be incorporated into micelles which repel the external reagent. Anionic micelles may incorporate an uncharged substrate and protect it from reactions with an anionic reagent. A spontaneous reaction may go more slowly in the micelle than in the bulk solvent phase. Some of the salient features of the reactions taking place in the micellar media are reviewed in the next chapter.
Metal complex undergo different types of reactions. These reactions are broadly classified as

1. Substitution reactions involving metal and ligand.
2. Reactions of co-ordinated ligands.
3. Redox reactions, and
4. Reactions of complex as a whole (Isomerisation and racemization).

We shall take into consideration only the substitution reactions involving metal and ligands. The ligand substitution reactions of co-ordination compounds can be written in generalised form as equation (1), where M is a metal atom and X and Y are ligands.

\[ MX_n + Y \rightarrow \underset{\text{1}}{\text{MX}_{n-1}} Y + X \]

Substitution reactions are either electrophilic (SE) or nucleophilic (SN)\(^{30}\)

\[ \text{SE : } MX + M_1 \rightarrow M + M_1 X \]
\[ \text{SN : } MX + Y \rightarrow MY + X \]

\(M\) and \(M_1\) stand for metals and charges are dropped for convenience. Extensive studies of the nucleophilic substitution reactions of octahedral Co(III) complexes involving the low spin \(d^6\) configurational state of Co(III) have been made. A well-known reaction of this category is shown in eq (4).
The ligand substitution reactions of octahedral Co(III) complexes may broadly follow any of three mechanistic path ways:

(i) Dissociative (D)

(ii) Associative (A)

(iii) Interchange (I)

(i) **The Dissociative path**: It is subdivided into $S_{N1}$ (limit) and $S_{N1}$. The $S_{N1}$ (limit) mechanism is that in which there is definite evidence for the existence of an intermediate of reduced co-ordination number. The $S_{N1}$ mechanism is one which fulfils the requirement of a dissociative process but there is no definite evidence for the existence of an intermediate of reduced co-ordination number. The $S_{N1}$ (limit) $(= D_{N1} + A_{N1})$ consists of two steps. In the first step, the substrate dissociates forming an intermediate of lower co-ordination number and in the 2nd step, the intermediate picks up a new ligand to give the final products. This path may be delineated as follows:

$$\text{CoL}_5 X^{n+} \xrightarrow{\text{slow}} X^- + \text{CoL}_5^{(n+1)}$$

$$\text{CoL}_5^{(n+1)} + Y^- \xrightarrow{\text{fast}} \text{CoL}_5 Y^{n+}$$

The rate determining step is the bond breaking one.
**Associative path or $S_N^2$ mechanism:**

In $S_N^2$ (limit) mechanism, \( ( = A_N + D_N) \), an intermediate of expanded co-ordination number is generated; the rate determining step involves \( (Y) \) and substrate \( (MA_n) \) to generate the intermediate which then dissociates to the product in a subsequent step. But in case of $S_N^2$-mechanism, the rupture of $M-A$ bond and formation of $M-Y$ bond occurs in the transition state with $M-Y$ bond formation taking precedence over $M-A$ bond breaking. Thus, the $S_N^2$ (limit) mechanism involves a two step process. In the first step a transition state is attained from which an intermediate of higher coordination number is formed. The multi-step process is generally represented as:

\[
Y^- + CoL_5X^{n+} \xrightleftharpoons{\text{slow}} ^{(n-1)+} [Y\cdot\cdot\cdot\text{CoL}_5X]\xrightarrow{\text{fast}} [Y-CoL_5X]^{(n-1)+}
\]

**Foot note**

$S_N^1 \text{(limit)} = D_N + A_N; S_N^2 \text{(limit)} = A_N + D_N$;

$S_N^1 = \text{Id} = D_NA_N$ and $S_N^2 = I_A = A_ND_N$;

according to the new nomenclature recommended by IUPAC (ref. 91-a, 91-b).
In this case the entering group plays an important part for determining the energy of activation of reaction.

**Interchange (I) Mechanism**: 

The interchange path (I), associative (Ia) \( = A_N^+D_N^- \) or dissociative (Id) \( = D_N^-A_N^+ \) proposed by Gray and Langford\(^9\) involve one step in which the leaving group moves from inner to outer coordination sphere and the entering group from the outer to the inner coordination sphere of the central metal ion. In Id, bond breaking step predominates whereas in Ia, bond making is significant. The dissociative and associative paths are associated with intermediates of five or seven coordination number which may be square pyramid, trigonal bipyramid or pentagonal bipyramid, octahedral wedge structures, respectively. From the consideration of the ligand field contribution to the activation energy for various transition states it has been found that square pyramid intermediate for \( S_N^1 \) and octahedral wedge for \( S_N^2 \) pathways are expected in substitution reactions of octahedral Co(III) complexes\(^9\).

**Ligand Substitution reactions of Octahedral Co(III) Complexes**: 

Our present work is concerned with micellar effect on ligand substitution reactions of octahedral Co(III) complexes. The ligand substitution reactions of octahedral Co(III) complexes are categorised as follows:
(1) Acid hydrolysis or Aquation
(2) Base hydrolysis
(3) Replacement of cobalt(III) coordinated water by anion-Anation.

The important features and characteristics of these reactions are briefly described here.

**Acid Hydrolysis**: It is the most extensively studied common reaction which can be represented as follows:

\[
(NH_3)_5CoX^2+ + H_2O \rightarrow (NH_3)_5CoOH_2^3+ + X^- \quad (7)
\]

Acid catalysed hydrolysis occurs if the substrate gets protonated at any ligand site and the protonated species undergoes aquation at characteristic rate.

\[
(NH_3)_5CoX^2+ + H^+ \xrightleftharpoons{K_{eq}} (NH_3)_5CoXH^3+ + H_2O \xrightarrow{k} XH + (NH_3)_5CoOH_2^3+ \quad \ldots (8)
\]

With a basic ligand \( X = F^-, N_3^- \) or \( RO_2^- \) acid catalysis is observed.

Metal ions like Hg(II), Tl(I), Tl(III) and Ag(I) catalyse the aquation of halo, azido and thiocyanato cobalt(III) complexes. The bridged binuclear species \( N_5CoXM(n+2)^+ \) are believed to be the catalytic intermediates.
Metal ion catalysed hydrolysis of carboxylato pentaammine Co(III) complexes derived from oxalic, malonic and salicylic acids have been studied. 

Study of steric and electronic effects of non-labile ligands, charge type effects of substrate, isotope and pressure effects on the substitution reactions revealed that $S_{N1}$ or $I_2$ mechanism is dominantly operative for Co(III) complexes.

The substitution of the aquo ligand in the S-bonded sulphito complex, trans-[Co(en)$_2$SO$_3$H$_2$O] by thiocyanate, thiosulphate and azide is also believed to follow dissociative mechanism due to strong trans activation of the S-bonded sulphite ligand.

The recent work of Harris and co-workers on the carbonato and sulphito cobalt(III) complexes in aqueous solutions suggest that the direct addition of CO$_2$ and SO$_2$ to N$_5$-CoOH$_2^{2+}$ occurs to yield stable carbonato complexes and transient O-bonded sulphito intermediate respectively; the latter undergoes internal redox to Co(II) or isomerisation to its sulphur-bonded analogue depending upon N$_5$-moiety attached to Co(III) centres.
Among the rapidly aquating pentammine cobalt complexes perchlorato-pentaammine-cobalt(III) is also included. At 25°C this complex aquates with $k \geq 0.1 \text{s}^{-1}$. Recently the aquation kinetics of sulphamido, p-toluene sulphaamido and p-nitrobenzene sulphonamido complexes of pentaammine-Co(III) ions which are N-bonded to Co(III) centre have also been investigated. The usually large aquation rate constants of these complexes ($k > 0.01 \text{s}^{-1}$ at 25°C) are attributed to N-protonation of $[(\text{NH}_3)_5\text{CoNHSO}_3\text{R}]^{2+}$ followed by facile release of neutral ligand.

Rotzinger et al. studied the kinetics and product distribution of spontaneous cleavage of $[(\text{H}_3\text{N})_5\text{CoOHCo(NH}_3)_5]^{5+}$ ion in the presence of competing anions. The spontaneous cleavage of $[(\text{H}_3\text{N})_5\text{CoOHCo(NH}_3)_5]^{5+}$ ($= M^{5+}$) in $\text{NO}_3^- / \text{ClO}_4^-$ and $\text{NCS}^- / \text{ClO}_4^-$ media follows the rate laws

$$k_{\text{obsd}} = \frac{k_0 + k_{\text{NO}_3}K_{\text{NO}_3}[\text{NO}_3^-]}{1 + k_{\text{NO}_3}[\text{NO}_3^-] + K_{\text{NO}_3}^2[\text{NO}_3^-]^2}$$

(10)

and $k_{\text{obsd}} = k_0 / (1 + a[Y^-])$ respectively.

The rate laws are interpreted in terms of formation of reactive and unreactive ionpairs of $M^{5+}$ with $\text{NO}_3^-$ and $\text{NCS}^-$ respectively. Considerable amounts of $(\text{H}_3\text{N})_5\text{CoY}^{2+}$ ($Y = \text{NO}_3^-$, $\text{NCS}^-$ and $\text{SCN}^-$) arise from ion scavenging by coordinatively unsaturated intermediates in this reaction. The product
distribution functions \( F[Y^+] = \left[ (H_3N)_5CoY^{2+} \right]_\infty / [M^{5+}]_0 \) have been measured and are discussed in terms of alternative modes of formation of the intermediate. Scavenging can occur from the second coordination sphere (i.e. by intramolecular reaction within an aggregate with \( Y^- \)) or, by intermolecular reaction of \( Y^- \) from solution. The reactive species may be unaggregated reactant (or species aggregated with background electrolyte anion \( ClO_4^- \)) and/or aggregates with \( Y^- \). Among the corresponding kinetic schemes only the one involving \( M^{5+} \) as well as \( MY^{4+} \) with \( MY^{4+} \) scavenging \( Y^- \) from the solution and not from the second co-ordination sphere, leads to simplest model to give a satisfactory fit. The reactive intermediates are quite selective for anions (as well as for N terminus of NCS\(^-\), the ratio of N/S product is 4) and this is interpreted as arising from a genuine, co-ordinatively unsaturated intermediate in this spontaneous aquation process.

Curtis and Lawrence synthesised \([Co(NH_2CH_3)_5L]^3+\) with \( L = \) Urea, dimethyl sulphoxide, dimethyl formamide, trimethyl phosphate and acetonitrile based on \([Co(NH_2CH_3)_5(OSO_2CF_3)]-(CF_3SO_3)_2\) as a precursor. The yield was very high. The acid aquation reactions of these cations occur with rate constants at least 70 fold higher than those reported for other pentaammine analogues at 25\(^\circ\)C, rate enhancement being apparently steric in origin. The activation enthalpy for this complex and its pentaammine analogue are similar. Both activation entropies and activation volumes are more positive for penta
alkylamine cobalt(III) complexes. The dissociative (Id) type mechanism operates. Substantially positive values of $\Delta S^\neq$ and $\Delta V^\neq$ for the aquation of these complexes favour insignificant role of incoming water molecule in dissociative transition state.

Interestingly, studies devoted to understanding the medium effects on solvolytic aquation of halogeno amine cobalt(III) complexes have revealed that solvation of the initial states and transition states by mixed solvent media appreciably mediate their reactivities\textsuperscript{100-108}. These studies also sharply focus attention on the solvent structural effects in addition to the electrostatic medium effects with regard to the variations in the rates and activation parameters of the solvolytic reactions under consideration.

It is important to note that solvent perturbations of the initial state and the transition state of the substrates undergoing solvolysis in mixed solvent media can result in changes in associated activation parameters without change in intimate mechanisms\textsuperscript{107,108}.

**Base Hydrolysis**

The reaction between hydroxide ion and cobalt(III) substrate leading to formation of corresponding hydroxo complex is known as base hydrolysis.
\[
(NH_3)_5CoX^{2+} + OH^- \longrightarrow (NH_3)_5CoOH^{2+} + x^-
\]  

At pH > 10 the product is exclusively hydroxo complex. The base hydrolysis of amine complexes of cobalt(III) invariably follows second order kinetics, first order in both \([OH^-]\) and [complex].

The rate law in the simplest form is
\[
\frac{d [\text{complex}]}{dt} = k [\text{complex}][OH^-] \tag{12}
\]
where the concentration terms are written in square brackets.

Chan et al.\textsuperscript{109} suggested a possible Ionpair mechanism in which it was assumed that the hydroxide ion might associate with cobalt(III) substrate and the resulting ionpair would undergo base hydrolysis by either \(S_{N1}\) or \(S_{N2}\) process. The steps shown are

\[
[(NH_3)_5CoX^{2+}] + OH^- \xrightarrow{K_{IP}} [(NH_3)_5CoX^{2+}] \cdots OH^- \quad \text{(Ionpair)}
\]

\[
(NH_3)_5CoOH^{2+} + x^- \xrightarrow{\text{fast}} [(NH_3)_5CoOH^{2+}] \cdots x^- \tag{13}
\]

The rate law for above mechanism may be deduced as
\[
\frac{-d[(NH_3)_5CoX^{2+}]}{dt} = \frac{k_B K_{IP} [OH^-]}{1 + K_{IP} [OH^-]} [(NH_3)_5CoX^{2+}] \tag{14}
\]

The observed pseudo first order rate constant at constant hydroxide ion concentration is given by
This mechanism predicts a nonlinear variation of $k_{\text{obs}}$ with $[\text{OH}^-]$ leading to the limiting value of $k_{\text{obs}} = k_B$ at high hydroxide concentration. Such a phenomenon was claimed to be observed by Chan in case of $[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}$.

Jones and coworkers\textsuperscript{110} observed similar behaviour in base hydrolysis of $[\text{Co(NH}_3\text{)}_6]^{3+}$. But further work on base hydrolysis of $[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+}$ by Buckingham and coworkers\textsuperscript{111} has contradicted the ion pair mechanism proposed by Chan. The investigation of the base hydrolysis of several cis-chloro-bis(ethylenediamine)(amine)cobalt(III) cations, by Hay and Barnes\textsuperscript{112} also discounted the ion pair mechanism proposed by Chan.

The conjugate base mechanism ($S_{\text{N1CB}}$) suggested by Garrick\textsuperscript{112b} has been substantiated by Basolo and Pearson with several experiments\textsuperscript{112a}.

The mechanism is preferably accepted at present because $\text{OH}^-$ assisted deprotonation equilibria of the cobalt(III) ammine complexes are established more rapidly than the rate of loss of $X^-$ from the conjugate bases.
\[(\text{NH}_3)_5\text{CoX}_2^+ + \text{OH}^- \xrightleftharpoons{K} (\text{NH}_3)_4\text{NH}_2\text{CoX}^+ + \text{H}_2\text{O} \]

\[\text{[Co(\text{NH}_3)_5\text{OH}]} \xrightarrow{\text{fast}} (\text{NH}_3)_4(\text{NH}_2)\text{Co}^{2+} + X^- \quad (16)\]

For such a mechanism, the rate law would be

\[-\frac{d[(\text{NH}_3)_5\text{CoX}_2^+]}{dt} = \frac{K_k_a[(\text{NH}_3)_5\text{CoX}_2^+][\text{OH}^-]}{1 + K[\text{OH}^-]}\]

For \(K[\text{OH}^-] << 1\) the above expression reduces to the usual second order rate law. This has been verified for a large number of Co(III) amine complexes containing at least one NH proton. The strongest evidence in favour of such a mechanism is obtained from the fact that the complex containing no acidic proton do not undergo base hydrolysis at high rates. This is true for the complexes of the type \([\text{Co(CN)}_5\text{Br}_3^-\] and \([\text{Co(CN)}_5\text{I}_3^-\) which hydrolyse at a rate independent of pH in alkalline medium.

Trapping experiments\(^{111a,111b}\), oxygen isotope fractionation studies\(^{113}\) and kinetic studies in non-aqueous solvent like DMSO in presence and absence of \(\text{OH}^-\) and piperidine\(^{114}\) provide evidence in favour of conjugate base mechanism.

The conjugate bases of the weakly basic amine complexes such as \(\text{cis[CoN}_4\text{BX}_2^+}\) (B = imidazole, \(X^- = \text{Cl}^-, \text{Br}^-, \text{N}_3^-, \text{NCS}^-, \text{N}_4=2\text{en, trien}\); B = benzimidazole, \(X = \text{Cl}^-, \text{Br}^-, \text{N}_4 = \text{en}\)) in which facible cobalt(III) promoted NH deprotonation of the N-coordinated (tertiary N) imidazole and benzimidazole occurs in solution in mild alkaline pH range. have been characterised by their
absorption spectra and kinetic reactivities. The cobalt(III)
promoted NH deprotonation of some weakly basic amine complexes
\[ \text{cis}[\text{Co(en)}_2BX]^2+ \] (B = anilines, 2-aminothiazole, aminotriazole)
leading to the formation of the respective conjugate bases
have also been postulated to account for high reactivities of
these substrates in mild acidic media.

The mechanism of base hydrolysis of haloamine cobalt(III)
complex is not fully understood. It is known that halo-
macrocyclicaminocobalt(III) complexes undergo base hydrolysis
with rate limiting NH-deprotonation of amine ligand\textsuperscript{115-117}. There is also possibility of competing deprotonations at
different NH sites of the same complex and the resulting
conjugate bases may react at different rates.

Sargeson et al\textsuperscript{118} studied the base hydrolysis of
p-nitrophenyl phosphato pentaammine cobalt(III) cation which
generates p-nitrophenolate ion, p-nitro phenyl phosphate ion
and hydroxo (Phosphoramido) tetraammine cobalt(III) ion.
Product distribution, \(^{18}O\) tracer and \(^{31}P\) NMR studies implied
the participation of amido conjugate base. A competing
conventional base catalysed S\textsubscript{N}CB mechanism for Co-O bond
rupture accounts for the release of p-nitro phenyl phosphate.
The intermediate hydroxo (Phosphoramido) tetraammine complex
is hydrolysed slowly by base to liberate phosphoramidate anion
by the same mechanism. The ester hydrolysis represents a rapid
phosphoryl group transfer from oxygen to nitrogen and it may model some aspects of amine transferase chemistry.

The $^18O$ tracer study by Sargeson and coworker revealed that co-ordinate nitrite ion in $[\text{M(NH}_3\text{)(ONO)}]^2+ \ (\text{M} = \text{Co(III)}, \text{Rh(III)}, \text{Ir(III)})$ rearranges to its nitro form $[\text{M(NH}_3\text{)}^2\text{(NO}_2\text{)}]^2+$ in aqueous base through base catalysed path which was not revealed previously by other workers.

The work of Tinner and Marty on base hydrolysis of halogeno and azido $[2,6 \text{ bis(amino methyl) pyridine}] \ (1-3 \text{ diamino-2-propanol NN'}) \text{ Co(III)}$ ion has shown that the formation of a square pyramid intermediate by amido base was not considered significant in $S_{\text{N1CB}}$ mechanism.

Sargeson and coworkers have studied the base hydrolysis of pentaamminecobalt(III) complexes of urea dimethyl sulfoxide and trimethyl phosphate. $^18O$ tracer studies show that these substrates undergo base hydrolysis very largely ($>97\%$) by Co-O bond rupture. The results support the dissociative ($S_{\text{N1CB}}$) mechanism and also the formation of a shortlived five coordinated intermediate.

Jackson et al critically examined the rate law and product distribution for the base hydrolysis of $[(\text{NH}_3)_2\text{CoX}]^{n+}$ in presence of competing anions, $Y^{m-}$. No relationship was found to support that the product determining step was rate
rate determining, thereby implicating generation of a highly reactive five coordinated intermediate $[(\text{NH}_3)_5(\text{NH}_2\text{Co})]^{2+}$.

A correlation between the ion pairing properties of the strongly associating anions, $\text{SO}_4^{2-}$, $\text{CO}_3^{2-}$, $\text{S}_2\text{O}_3^{2-}$ and $\text{PO}_4^{3-}$ and the rates of the base hydrolysis reactions was attempted. Ion pairing constants for model $[(\text{NH}_3)_5\text{CoX}]^n^+$ ($n = 2, 3$) complexes with $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{PO}_4^{3-}$ were determined independently. Parallel product distribution studies showed no obvious correlation with their ion pairing. The strongly ion pairing $\text{PO}_4^{2-}$ and $\text{CO}_3^{2-}$ are shown to be very poor competitors, $\text{SO}_4^{2-}$ is a weak competitor, and $\text{S}_2\text{O}_3^{2-}$ is a reasonable competitor; poorly ion pairing univalent anions $\text{N}_2^-$, $\text{SCN}^-$, $\text{CH}_3\text{CO}_2^-$ etc. range from very weak to good competitors. Non-the-less anion competition correlates well with the degree of anion hydration consistent with a product determining step involving the penta-coordinate $[(\text{NH}_3)_4(\text{NH}_2\text{Co})]^+$ species and rate determining anion abstraction from the solvent. Rate constant for base hydrolysis of $[(\text{NH}_3)_5\text{CoX}]^n^+$, ($X = \text{Cl}^-, \text{I}^-, \text{NO}_2^-, \text{OSMe}_2$, $\text{SO}_4^{2-}$) in $\text{ClO}_4^-$, $\text{N}_3^-$, $\text{CH}_3\text{CO}_2^-$, $\text{NCS}^-$, $\text{NO}_2^-$, $\text{NH}_2\text{SO}_3^-$, $\text{NO}_3^-$, $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{S}_2\text{O}_3^{2-}$ and $\text{PO}_4^{3-}$ media at $25^\circ\text{C}$, $\mu = 1$ or 3 M, are reported. Rate reductions commensurate with degree of ion pairing of $[(\text{NH}_3)_5\text{CoX}]^n^+$ are observed and the ion pairs are calc. 4-fold less reactive than the free complex. It is shown that the free ion and the ion paired forms of the conjugate base $[(\text{NH}_3)_4(\text{NH}_2\text{CoX})]^{(n-1)+}$, the reactive entity in the base hydrolysis reaction, are comparable in reactivity. Thus the rate reduction rests
largely with diminished acidity of coordinated amine in the ion pair \([(NH_3)_5CoX]^n^+Y^{m^-}\). It is demonstrated that irrespective of the mechanism the ion pairs with \(CO_3^{2-}\) and \(PO_4^{3-}\) and probably with \(SO_4^{2-}\) must collapse inefficiently i.e. the product is largely \([(NH_3)_5CoOH]^{2+}\). Further mixed anion competition studies using \(SO_4^{2-}\), \(S_2O_3^{2-}\), \(ClO_4^-\), \(N_3^-\) demonstrate that the selective ion pairing by \(Y^{2-}\) has no measurable effect on the capture of \(N_3^-\). Both observations provide competing evidence for the intervention of the conjugate base intermediate \([(NH_3)_4(NH_2)Co]^{2+}\).

F.P. Rotzinger\(^{123}\) studied the base hydrolysis of \([Co(NH_3)_5NO_2]^{2+}\) in aqueous LiOH, NaOH and KOH at 25°C and at variable ionic strength. The kinetics depend upon the nature of alkali metal ion. The equilibrium constant for ion pair formation of the reactant at zero ionic strength and first order rate constant for the substitution with the ion pair were determined. In presence of \(NaClO_4\) and \(NaN_3\) the reaction still follows first order kinetics. The ion pairs are formed with \(N_3^-\) and \(ClO_4^-\). The equilibrium constant for ion pair formation of the reactant with \(N_3^-\) and \(ClO_4^-\) and the first order rate constant for nitrite substitution within the ion triplet formed by hydroxide and anion present in the solution are also determined. The ion triplets with poor nucleophile \((ClO_4^-)\) and good one \((N_3^-)\) undergo nitrate substitution at equal rates since the first order rate constant for nitrate substitution
within the ion triplets is independent of nature of anions like ClO₄⁻ and N₃⁻. This behaviour demonstrates the dissociative nature of substitution of the conjugate base or its ion paired forms.

Rotzinger also studied the base hydrolysis of $[\text{Co(NH}_3)_5\text{NO}_2]^2+$ and $[\text{Co(NH}_3)_3\text{OS(CH}_3)_2]^3+$ in aqueous NaOH + NaN₃ media at 25°C yielding the product $[\text{Co(NH}_3)_5\text{N}_3]^2+$ and $[\text{Co(NH}_3)_5\text{OH}]^2+$. The ionic strength dependent competition of OH⁻ and N₃ is described by the charge of the intermediate formed.

The base hydrolysis of Co(NH₃)₃SO₄⁺ studied in NaOH, NaN₃ and NH₃ of definite concentrations and particular temperature leads to an uncharged intermediate. The experimental results are rationalized by postulating two forms of the hexacoordinated intermediates namely

$$[\text{Co(NH}_3)_4\text{NH}_2 \cdots X]^{(n-1)+}$$

and

$$[\text{Co(NH}_3)_4\text{NH}_2 \cdots X, N_3]^{(n-2)+}$$

which yield exclusively hydroxo pentaammine cobalt(III) by water scavenging whereas the ion paired intermediate $[\text{Co(NH}_3)_4\text{NH}_2 \cdots X, N_3]^{(n-2)+}$ forms exclusively azidopentaammine cobalt(III) by collapsing. The lifetimes of intermediate generated in the base hydrolysis of $[\text{Co(NH}_3)_5\text{SO}_4]^+$, $[\text{Co(NH}_3)_5\text{NO}_3]^{2+}$ and $[\text{Co(NH}_3)_5\text{OS(CH}_3)_2]^3+$ were estimated to be > 1600, 190 and 190 ps respectively.
Base hydrolysis of oxalato(amine)(trien)cobalt(III) and salicylato(amine)trienecobalt(III) perchlorate were investigated in presence of added anions imidazole and ethanol amine and also in D$_2$O medium. The reactions followed $S_N^{1,2}$CB mechanism involving Co-O bond fission. The base hydrolysis of the complex in question is about 10 and 45 times faster than analogous ethylene diamine and pentaammine complexes respectively. Retardation of rates of base hydrolysis by added SO$_4^{2-}$ and PO$_4^{3-}$ was attributed to inertness of the ion pairs to base hydrolysis.

Base hydrolysis of $[M(NH_3)_5OSO_2CF_3]^2+$ (M = Co, Rh, Ir, Cr) and $[M(NH_2CH_3)(OSO_2CF_3)]^2+$ (M = Co, Rh, Cr) complexes at 25°C showed that N-methylation of amine ligand caused a marked enhancement of rate of base hydrolysis with $k_{Me}/k_{NH_3}$ of 100 (Co), 150 (Rh) and 800 (Cr); substantial positive activation entropy for base hydrolysis and positive competition results with azide ion in basic solution favoured a dissociative conjugate base mechanism for all such complexes. The variation in the degree of rate enhancement for NH$_3$ and methyl amine compounds and competition studies in base hydrolysis with azide ion chiefly reflect differences in steric interactions due to metal ligand lengths than any mechanistic diversity. Variation in competition behaviour of Rhodium(III), Cr(III), Co(III) appear to reflect the relative life times of the intermediates of reduced
co-ordination number. For these metal centres the variation in aquation rates are much smaller and do not allow in any certainty mechanistic distinctions. Marked acceleration of rates of both acid and base hydrolysis occur consistently for all trifluoro methane sulfonato complexes compared with those of halogen analogues.

In recent times, a rapid progress has been made in the field of research on the base hydrolysis of transition metal complexes in general\textsuperscript{127-132}. The base catalysed displacement of macrocyclic tetramines from their Cu(II) complexes probably involves amine deprotonation but the purpose is to change the configuration of the nitrogen involved in order to generate or lose firmly bound isomer\textsuperscript{133}.

House et al\textsuperscript{134} showed that the initial observation that Cr(III) complexes are considerably less sensitive to base hydrolysis than their Co(III) analogues is reasonably correct. There are no examples so far of cases where Cr(III) complex is more liable towards base hydrolysis than its Co(III) analogue but there are cases where the rate constant differ by a factor of less than 10. The impression given in the literature is that the ratio $k_{\text{Co}} / k_{\text{Cr}}$ does not change much outside the range $10^3$ to $10^4$.

Tobe et al\textsuperscript{135,136} observed in case of base hydrolysis of Rhodium(III) complexes by comparing the leaving group effects,
that the lability decreases along the sequence Cl > Br > I. The effect is smaller and in the opposite direction to that observed for Cr(III) and completely mirrors, the sequence found in uncatalysed aquation. The only attempt at variation in the nature of amines can be found in the dichloro tetramine complexes where the reactivities of cis[Rh(en)$_2$Cl$_2$]$^+$, cis[Rh(cyclen)Cl$_2$]$^+$ and cis[Rh(cyclam)Cl$_2$]$^+$ can be compared. An 800-fold increase in reactivity on going from cyclam to the cyclen complex is not matched in Co(III) system. $k_{\text{OH}} = 2.1 \times 10^7$ M$^{-1}$ s$^{-1}$ and $2.3 \times 10^6$ M$^{-1}$ s$^{-1}$ for cis[Co(cyclen)Cl$_2$]$^+$ and [Co(cyclam)Cl$_2$]$^+$ respectively at 25°C. It has been suggested that cis[Co(cyclam)Cl$_2$]$^+$ complex undergoes substitution by a synchronous deprotonation and chloride expulsion and so can not reflect the big difference in the lability of the two amido conjugate bases.

According to Hay et al$^{37}$ in many cases it is possible to estimate the value of $k_2$ (the rate constant for solvolysis of amido conjugates base) within an order of magnitude of two (to set a lower limit). In case of cis[Co(en)$_2$X] the protons on the nitrogens trans to $X$ are exchanged with medium protons much faster than the cis ones even when $X$ = CN or NO$_2$. From the work of House et al$^{39}$ it is clear that in a typical Co(III) acido amine complex the great sensitivity towards base catalysed hydrolysis lies in the very high lability of the amido conjugate base, where factors of $10^6$ to $10^9$ are common and the
ratio $k_{OH}/k_{aq}$ may rise as high as $10^{12}$ to $10^{13}$ in certain cases. In general this statement applies irrespective of the nature of the leaving group since in the absence of complications such as rate limiting deprotonation the ratio $k_{OH}/k_{aq}$ does not change much as the leaving group is altered. Although early work suggested that the values of $k_1$ for $[\text{Co(NH}_3)_6]^{3+}$ and $[\text{Cr(NH}_3)_6]^{3+}$ were similar recent studies suggest that $k_1$ values for exchange in trans-diacido-tetra ammine Co(III) complexes are at least $10^2$ greater than those for corresponding Cr(III) species. Buckingham et al. investigated the rates of base hydrolysis of (Syn-$[\text{Co(tetren)Cl}]^{2+}$ and $[\text{Co(Me-tetren)Cl}]^{2+}$; $k_{OH} = 518$ and $29 \text{ M}^{-1} \text{ S}^{-1}$ and $25^\circ C$, $\mu = 1.0$ for Syn-$[\text{Co(tetren)Cl}]^{2+}$ and $[\text{Co(Me-tetren)Cl}]^{2+}$ respectively (Me-tetren = 1,8-diamino-3-methyl-2-(2-ethylamino)-3,6-diazaoctane). It was, however, the rate difference by a factor of 18, shown that the complex formed with N-methylated ligand was a different skeletal isomer. This work was not followed up to bring it to a proper conclusion and while ignoring large body of evidence that had built up over the years that the position of the labilising nitrogen relative to the leaving group was much more important than the exchange lability of its protons these authors have finally accepted cis labilisation in order to interpret some of their own results. Marty has resolved the appropriate skeletal isomer of $[\text{Co(dien)(dapo)Cl}]^{2+}$ (dien = 1,5 diamino-3-azo-pentane, dapo = 1,3-diamino propan-2-ol) and have shown that the base hydrolysis of this complex is accompanied by complete racemization while the meridional arrangement of the terdentate ligand is maintained.
One way to introduce competition for five coordinate intermediate is to have a potential chelating ligand bound as a monodentate one in coordination shell of the substrate. In the base hydrolysis of cis[Co(en)(NH₂CH₂CO₂)X]⁺ (X = Cl, Br, glycinate bound through N) the product consisted of the chelated \([\text{Co(en)}₂(\text{NH₂CH₂CO₂})₂]^{2+}\) species (40.8 %) and the monodentates hydroxo species \([\text{Co(en)}₂(\text{NH₂CH₂CO₂})\text{OH}]^{+}\) (59.2 %) when 1.0 M NaOH is used. At lower hydroxide concentration the amount of ring closing is higher (46.1 %). For six membered ring analogue, cis[Co(en)₂(NH₂CH₄H₂C₀₂)X]⁺ the extent of ring closing was also investigated.
References

54. Nakagawa, T. (1968) Yakagaku 17, 204.


