CHAPTER 1

INTRODUCTION
A. Oxidation of Carbohydrates

The simple organic compounds from which living organisms are constructed are unique to life and do not otherwise occur on the earth today, except as products of biological activity. These building-block compounds, called biomolecules, were selected during the course of biological evolution for their fitness in performing specific cell functions. They are identical in all organisms. Biomolecules are related to each other and interact in a kind of molecular "game" or logic. The size, shape and chemical reactivity of biomolecules enable them not only to serve as building blocks of the intricate structure of cells, but also to participate in their dynamic, self-sustaining transformation of energy and matter. Biomolecules must therefore be examined from two viewpoints, that of the chemist and that of the biologist.

Living things are composed of lifeless molecules. When these molecules are isolated and examined individually, they conform to all the physical and chemical laws that describe the behavior of inanimate matter.

Carbohydrates are one of the four major classes of biomolecules along with proteins, nucleic acids, and lipids. Carbohydrates are aldehyde or ketone compounds with multiple hydroxyl groups which may be classified as monosaccharides, oligosaccharides, and polysaccharides; the term saccharide is derived from the Greek word for sugar. Monosaccharides are single polyhydroxyaldehyde (known as aldoses, e.g., glucose) or polyhydroxyketone
units (known as ketoses, e.g., fructose), whereas oligosaccharides consist of two
to ten monosaccharide units joined together by glycosidic linkages. Sucrose and
lactose are disaccharides, since they are each made up of two monosaccharide
units. Polysaccharides, as the name implies, may contain hundreds of
monosaccharide units.

Carbohydrates make up most of the organic matter on earth because of
their extensive roles in all forms of life. Carbohydrates serve as energy stores,
fuels, and metabolic intermediates. Ribose and deoxyribose sugars form part of
the structural framework of RNA and DNA. Carbohydrates are linked to many
proteins (glycoproteins) and lipids (glycolipids), where they play key role in
mediating interactions among cells and interaction between cells and other
elements in cellular environment.

Carbohydrates provide the skeletal framework for tissues and organs of
the human body and serve as lubricants and support elements of connective
tissue. Major energy requirements of the body are met by dietary carbohydrates.
They confer biological specificity and provide recognition elements on cell
membranes.

Carbohydrates form the most abundant group of the natural products and
are found in all classes of living organisms. They serve as a direct link
between the energy of the sun and metabolic energy that is required to sustain
life. In organisms, capable of photosynthesis, solar energy is harvested to derive
reaction in which glucose is synthesized from carbon dioxide and water. The
energy stored in “carbon fixation” process then gradually moves upwards into
the food chain. The living organisms that partake the products of photosynthesis
obtain useful energy by oxidizing the carbohydrates back into carbon dioxide
and water through the process of glycolysis and respiration.

In addition to their pivotal role in metabolism, carbohydrates also play an
important role in many organisms. Some examples of the latter type include
cellulose, chitin, lipopolysaccharide, and the bacterial murein, all of which are
derived from repeating sugar units which may have additional cross-linking
components for rigidity. Furthermore, many biotic secondary metabolites such
as cardioglycosides, macrolide antibiotics, and aminoglycoside antibiotics rely
on the sugar components for solubility and activity. In addition, carbohydrates
are used as convenient precursors for the biosynthesis of other important
building blocks such as aromatic amino acids. Carbohydrates also have many
applications in industrial processes. For example, the food industry uses sucrose
as a sweetening agent, a preservative, and a raw material for fermentation.
Starch is used as a raw material for the manufacture of many goods. Cotton is
still one of the most popular fabrics and an important raw material for the textile
industry. Paper and other derivatives of cellulose are important for the
manufacture of packaging materials and plastics.

Glycosides are compounds formed from a condensation between a
monosaccharide, or monosaccharide residue, and the hydroxyl group of the
second residue that may, or may not be another monosaccharide. Glycosides are
found in many drugs and spices and in the constituents of animal tissues.

A knowledge of the structure and properties of the carbohydrates of
physiologic significance is essential to understanding their fundamental role in
the economy of the mammalian organism. The sugar glucose is the most
important carbohydrate. It is as glucose that the bulk of dietary carbohydrate is
absorbed into the bloodstream or into which it is converted in the liver, and it is
from glucose that all other carbohydrates in the body can be formed.

Carbohydrates exert a wide range of functions in living organisms, and
due to the wide distribution of metals and their complex functions for all forms
of life, metal-carbohydrate interactions are a key for understanding bioinorganic
chemistry, and the study of complexation of carbohydrates to metals is one of
the main objectives of carbohydrate coordination chemistry. Metal complexes of
natural carbohydrates have been attracting interest for many years because these
compounds participate in vitally important processes; they are used for
configurational and conformational analysis, determination, and separation of
sugars. Many carbohydrates easily undergo redox processes. Facile oxidation
can abrogate metal binding, particularly so with high oxidation state transition
metals.

The physiological and microbiological activities of carbohydrates depend
largely in their redox behavior. Oxidation of monosaccharides by different
oxidizing agents are, therefore, of special importance due to their biological
relevance.\textsuperscript{9-12} Due to multihydroxy functionality of saccharides they can chelate and coordinate to many metal ions. Besides acting simply as effective chelators,\textsuperscript{13} in many cases they are also reducing agents, \textit{e.g.}, for metal ions such as Ce(IV),\textsuperscript{9} Fe(III),\textsuperscript{10} Co(III),\textsuperscript{11} V(V),\textsuperscript{14} depending on the acidity of the medium.

## B. Cerium(IV) Oxidation of Carbohydrates

In plant and animal tissues cerium is an important metal element,\textsuperscript{15} it combines with most of pivotal living active molecules and plays important physiological function. Cerium(III), the reduction product of cerium(IV), with suited concentration can activate plant growth and improve the metabolism level of sugar and grease. For this reason, various fertilizers and fodder containing cerium(III) are widely applied in China.

Cerium(IV) has been used as an oxidizing agent and an analytical reagent, especially in an acid medium.\textsuperscript{16} Oxidation of organic compounds with cerium(IV) are potentially interesting since cerium(IV) is an unusually strong, one-electron oxidant. Moreover, unique reactions of cerium(IV) with organic compounds can be expected because of specific coordination properties of the ion with various organic and inorganic ligands.

The oxidation of organic substances by cerium(IV) reagents is found to follow different mechanisms, depending on the type of acid media used. The oxidation potential of the Ce(IV)- Ce(III) couple is markedly ligand dependent, \textit{e.g.} the potentials are 1.70 to 1.71, 1.61, 1.44, and 1.28 volts in 1N perchloric,
nitric, sulfuric, and hydrochloric acids, respectively. The oxidation potential in hydrochloric acid is probably low (in negative sense), because reaction at the platinum electrode is not reversible. Increasing the acid concentration from 1N to 8N increases the potential in perchloric acid to 1.87 volts, whereas a decrease to 1.56 and 1.42 volts is observed, respectively, in nitric and sulfuric acids. The increase in potential with increasing perchloric acid concentration is in part attributed to cerium(IV) hydrolysis products. The decrease in potential in sulfuric acid and nitric acid with increasing acid concentration can be attributed to complexing of cerium ions with sulfate and nitrate anions. These predictions have been verified quantitatively for perchloric and sulfuric acid solutions. The standard potential \( (E^\circ) \) in sulfuric acid was calculated to be 1.74 volts when account was made for bisulfate dissociation and the equilibria (Eqs. (1.1)–(1.3)):

\[
\begin{align*}
\text{Ce(IV)} + \text{HSO}_4^- & \rightleftharpoons \text{Ce(SO}_4)^{2+} + \text{H}^+ & K_1 = 3500 \quad (1.1) \\
\text{Ce(SO}_4)^{2+} + \text{HSO}_4^- & \rightleftharpoons \text{Ce(SO}_4)_2 + \text{H}^+ & K_2 = 200 \quad (1.2) \\
\text{Ce(SO}_4)_2 + \text{HSO}_4^- & \rightleftharpoons \text{Ce(SO}_4)_3^{2-} + \text{H}^+ & K_3 = 20 \quad (1.3)
\end{align*}
\]

**Scheme 1.1**

As regards equilibria in the aqueous \( \text{H}_2\text{SO}_4 \) media, the studies by Hardwick and Robertson are very important, but later on Bugaenko and Kuan-Lin have modified the observation made by Hardwick and Robertson who proposed the tri-sulfato species as \( \text{Ce(SO}_4)_3^{2-} \). From the studies of Bugaenko and Kuan-Lin, it was established that the tri-sulfato species is \( \text{HCe(SO}_4)_3^- \).
According to their studies in aqueous H$_2$SO$_4$ media (up to ca. 2 mol dm$^{-3}$) the predominant equilibria are represented by Eqs. (1.1), (1.2), (1.4), and (1.5):

\[
\begin{align*}
\text{Ce(SO}_4\text{)}_2^+ \text{HSO}_4^- & \rightleftharpoons \text{HCe(SO}_4\text{)}_3^- & K_5 &= 0.6 \pm 0.1 \quad (1.4)^{24} \\
\text{HCe(SO}_4\text{)}_3^- + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{H}_3\text{Ce(SO}_4\text{)}_4^- & K_6 &= 2 \pm 1 \quad (1.5)^{24}
\end{align*}
\]

Scheme 1.2

At higher concentrations of H$_2$SO$_4$, the concentration of the H$_3$Ce(SO$_4$)$_4^-$ species increases gradually where a new species H$_4$Ce(SO$_4$)$_4$ has also been suggested. Due to complexation in aqueous H$_2$SO$_4$ media, the tendency of cerium(IV) species to undergo hydrolysis is remarkably suppressed, but in aqueous HClO$_4$ media, hydrolysis leads to Ce(OH)$_3^{2+}$ and Ce(OH)$_2^{3+}$ which further undergo dimerization producing CeO(Ce$^{6+}$.

The cerium(IV) equilibria are important in interpreting oxidation of organic compounds. Kinetic and additional spectral measurements also indicate that the degree of ceric perchlorate association depends on acid concentration. However, a monomer–dimer equilibrium may be an oversimplification, since above pH 0.7 colloidal polymers slowly form. Ceric nitrate equilibria are complicated by dimerization, hydrolysis, and association with cerium(III). This could provide an added complexity in cerium(IV) oxidations where appreciable quantities of cerium(III) are formed.
A good number of studies of the kinetics and mechanism of the oxidation of a variety of organic substrates have been made by cerium(IV) either in sulfuric acid or perchloric acid medium.\textsuperscript{16,33,34} Oxidation of carbohydrates by cerium(IV) has also been a subject of interest,\textsuperscript{9,35–53} especially to find out if the same mechanism is operative in this case, too, as it operates in the case of alcohols, glycols, formaldehyde, \textit{etc}.

Mehrotra\textsuperscript{35,38} investigated the degradation of aldoses by cerium(IV) sulfate in aqueous sulfuric acid. Pottenger and Johnson\textsuperscript{36} studied the mechanism of cerium(IV) oxidation of glucose and cellulose in 1 mol dm\textsuperscript{−3} perchloric acid. The oxidation of D-glucose,\textsuperscript{36,38,40} D-galactose,\textsuperscript{42} L-arabinose,\textsuperscript{42} and L-sorbose\textsuperscript{43} by cerium(IV) has been studied, the reaction generally proceeded to give the corresponding lactones and aldonic acids.

Sala and coworkers\textsuperscript{9,39} reported the oxidative decarboxylation of lactones by cerium(IV) for the synthesis of 2-deoxy-D-erythro-pentose and D-arabinose. Virtanen and coworkers\textsuperscript{47} also studied the oxidation of various aldoses and ketoses by cerium(IV) in perchloric acid and reported the formation of two complexes in each case, one in pre-equilibrium reaction during mixing and other by the dissociation of first one. Sen Gupta \textit{et al}.\textsuperscript{49} investigated the oxidations of aldoses like D-ribose, D-erythrose, and DL-glyceraldehyde and compared the results obtained with that of D-glucose. The results showed that the oxidation of D-glucose, D-ribose, and D-erythrose by cerium(IV) were kinetically similar and DL-glyceraldehyde was oxidized by a different mechanism.
C. Surfactant and Surfactant Micelles

Interfaces are the boundary regions that separate different bulk regions of matter. They have special chemical, physical, and biological properties that have fascinated and drawn the attention of scientists from many different fields. What makes the interface unique is the asymmetry in forces that is experienced by molecules and atomic species located there together with the almost two dimensional geometry of the interface. The chemical composition, the geometrical arrangement of the species, the equilibrium constants, pH, the motion of molecules, the thermodynamics and kinetics of ground- and excited-state chemical change, energy relaxation, and the phases and phase transitions of long chain amphiphilic monolayers are among the fundamental manifestations of the unique characteristics of an interface. The study of chemical reactivity at liquid interfaces occupies an important place in chemistry. Electron transfer, ion transfer, and proton transfer at the interfaces between two immiscible liquids are fundamentally important for understanding processes such as liquid chromatography, phase transfer catalysis, drug delivery problems in pharmacology, and other phenomena in membrane biophysics. The uptake of pollutants by water clouds, an important atmospheric phenomenon, involves reaction such as ionization at the water liquid/vapor interface.

A surfactant (a contraction of the term surface active agent) is a substance that when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a
marked degree the surface or interfacial free energies of the surfaces (or interfaces).\textsuperscript{61}

Surfactants are compounds whose molecules are fitted with pronounced lipophilic and hydrophilic moieties; they are amphiphilic molecules. A process whereby dissolved surfactant molecules react to the repelling action of surrounding water is aggregation to form various kinds of supramolecular structures.\textsuperscript{62}

A wide variety of surfactant compounds can be dispersed in aqueous solution to form organized assemblies, either by spontaneous combination or with the aid of sonication. Their formation can be rationalized in terms of hydrophobic–hydrophilic and electrostatic interactions,\textsuperscript{63} as well as by thermodynamic considerations.\textsuperscript{64,65} Interest in the biological function of some of these assemblies and unusual control of reactivity has prompted a number of structural studies of the different media.\textsuperscript{66–72}

Surfactants find application in almost every chemical industry, including detergents, paints, dyestuffs, cosmetics, pharmaceuticals, agrochemicals, fibres, plastics. Moreover, surfactants play a major role in the oil industry, \textit{e.g.}, in enhanced and tertiary oil recovery. They are also used for environmental protection, \textit{e.g.}, in oil slick dispersants. Therefore, a fundamental understanding of the physical chemistry of surface active agents, their unusual properties, and their phase behavior is essential for most industrial chemists. In addition, an understanding of the basic phenomena involved in the application of surfactants,
such as in the preparation of emulsions and suspensions and their subsequent stabilization, in microemulsions, in wetting, spreading, and adhesion, etc., is of vital importance in arriving at the right composition and control of the system involved. This is particularly the case with many formulations in chemical industry.\textsuperscript{73}

Apart from the traditional use of surfactants, surfactant structures are increasingly being investigated as organic templates to synthesize mesoscopic inorganic materials with controlled nanoscale porosity, which are expected to have applications in electronics, optics, magnetism, and catalysis.\textsuperscript{74}

Surfactants are also utilized in various biochemical methods, such as the purification and analysis of proteins, in analytical methods based on enzymes or immunological techniques, and in cleaning and regenerating chromatographic columns, biosensors, etc. Their ability to hinder protein adsorption is used, both to reduce the depletion of the substance that should be analyzed due to adsorption of the walls of test tubes, etc.,\textsuperscript{75} and to hinder nonspecific adsorption of proteins in, e.g., immunological methods and chromatography.\textsuperscript{76}

**General classification of surfactants**

Numerous variations are possible within the structure of both the head and tail group of surfactants. The head group can be charged or neutral, small and compact in size, or a polymeric chain. The tail group is usually a single or
double, straight or branched hydrocarbon chain, but may also be a fluorocarbon, or siloxane, or contain aromatic group(s).

Since the hydrophilic part normally achieves its solubility either by ionic interactions or by hydrogen bonding, the simplest classification is based on surfactant head group type, with further subgroups according to the nature of the lyophobic moiety. Four basic classes therefore emerge as: the anionics and cationics (which dissociate in water into two oppositely charged species, i.e., the surfactant ion and its counterion), the nonionics (include a highly polar (non charged) moiety, such as polyoxyethylene (—OCH₂CHO—) or polyol groups) and the zwitterionics or amphoterics (combine both as a positive and a negative group).

Examples:

(anionic)

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+ & \quad \text{CH}_3(\text{CH}_2)_{10}\text{COO}^- \text{K}^+ \\
\text{sodium dodecyl sulfate} & \quad \text{potassium laurate}
\end{align*}
\]

(cationic)

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3\text{Br}^- & \quad \text{dodecylpyridinium bromide}
\end{align*}
\]
Surfactants are key components of the organized assemblies used in biological systems. Nonionic surfactants based on carbohydrates are very important in biology. They have potential pharmaceutical (biocompatible formulations), biochemical (extraction of membrane proteins), and medicinal applications. Carbohydrate-based surfactants have water-soluble head group derived from a carbohydrate. This is linked by different functional groups to a hydrophobic part.

Surfactants have particular features that make them attractive in relation to chemical reactivity aspects and for large variety of applications. The application of surfactant based systems as drug delivery vehicles\textsuperscript{77,78} is a growing research area that may develop further in the coming years. It is quite interesting that cationic amphiphiles are now widely used as an effective tool in delivering DNA into cells,\textsuperscript{79,80} even mammalian cells.\textsuperscript{81–85}
Bilayer-forming synthetic surfactants have been extensively used as membrane mimetic models, and some synthetic amphiphiles such as dihexadecyl phosphate or dioctadecylmethylammonium salts have found many different uses in strategic applied areas.\textsuperscript{86}

Aqueous association colloids as reaction media offer alternatives to the use of organic solvents, and there is considerable interest in their use in water as reaction medium; they are attractive candidates in "green" chemistry.\textsuperscript{87–91} For instance, Moss \textit{et al.}\textsuperscript{92,93} observed 1000- to 2000-fold rate enhancements in overall rate constants of hydrolysis of phosphates triesters catalyzed by different iodosocarboxylate ions of varying hydrophobicities in comicelles with CTACl and CTAOH.

Surfactant based reaction media have such kinds of features that make them useful in industrial-scale synthesis and interesting in developing "clean" processes. In fact, they are expected to be nontoxic and nonhazardous, they enhance reaction rates, reactions can usually be carried out under mild conditions, and in favorable cases surfactants can be separated and reused.

Surfactants alone or in combination with a wide variety of other ionic and non-ionic solutes, aggregate spontaneously and with a high degree of cooperativity in solution to form a variety of assemblies (or association colloids) whose structures depend both on solution composition and on the structures of components, primarily the surfactant.\textsuperscript{63,94–96} All surfactant assemblies in homogeneous solution share an underlying organizational structure: a fluid,
hydrocarbon region separated from an aqueous region by an interfacial region with a thickness of the order of the diameter of the surfactant head group.

Largely depending on the molecular architecture of the amphiphile, a wealth of three-dimensional structures can be formed ranging from spherical and rod-like micelles to multilayer structures and to complex biological membranes, whose matrix is a lipid bilayer composed of phospholipids and glycolipids, incorporating proteins. Ionic colloidal assemblies, e.g., micelles, microemulsions, hemimicelles (solloids), bilayers, and vesicles are believed to be mimetic agents for membranes in biological systems. It has also been noted that, there are structural similarities between globular proteins and spherical micelles, and analogies between the catalytic effects of enzymes and functional micelles and between micellar catalysis and phase-transfer catalysis. For these reasons, numerous investigators have focused attention on micelles and reactions in micellar media.

**Micelles, micellar structure and properties**

Normal micelles are assemblies of surfactants, which spontaneously aggregate (micellize) at concentrations greater than critical micelle concentration (cmc) in water and some associated solvents. Micelles are assumed to be spherical, with \(~10^2\) monomers, at low surfactant concentration, but they grow at high surfactant concentrations, especially with added electrolyte, and become rod-like. The growth depends on the length of the hydrophobic group, the structure of the head group, and the added electrolyte. Simple rules
governing the packing of surfactant in micelles and similar assemblies have been proposed that relate the geometry of the assembly to the area of the head group and the length and volume of the hydrophobic residue. The micellar core is oil like, and ionic or polar head groups at the surface are exposed to water.

Micelles have been investigated by an unusually wide variety of techniques including X-rays, nuclear magnetic resonance (NMR), electron spin resonance (ESR), fluorescence, static and dynamic light scattering, calorimetry, and kinetic probes. Micellization is primarily driven by bulk hydrophobic interactions between the alkyl chains of the surfactant monomers and usually results from a favorable entropy change. The overall Gibbs energy of the aggregate is a compromise of a complex set of interactions, with major contributions from head group repulsion and counterion binding (for ionic surfactants). The residence times of individual surfactant molecule in the micelle are typically of the order of $10^{-5}$–$10^{-6}$ s, whereas the lifetime of the micellar entity is about $10^{-3}$–$10^{-1}$ s.

Ever since the discovery of micelles, theoretical models of micelle formation have in some way tried to account for the association–dissociation equilibrium that distinguishes micelles from other colloids. The earliest model is due to Hartley and regards the formation of a micelle as a chemical equilibrium between monomers, counterions and micelles. This model is the so–called Hartley micelle and involves a hydrocarbon–like interior surrounded by polar or ionic head groups. The micelle is pictured as a roughly spherical aggregate
with a radius approximately corresponding to the extended length of the hydrocarbon chain of the surfactant (Fig. 1.1). Micellar head groups and associated counterions are fully hydrated and are found in the Stern layer. Some of the counterions are bound within the shear surface, and many are located in the Gouy-Chapman electrical double layer, where they are dissociated from micelle. This model has quite appropriately been dubbed the mass action (MA) approach \(^\text{114,115}\). The MA approach was followed by the phase separation (PS) model, advanced by Stainsby and Alexander in 1950,\(^\text{116}\) wherein the micelles are treated as a phase separated from that containing the mesomeric species.

A good model is of Gruen, who has described a realistic model of a micelle\(^\text{117,118}\) that involves a rather sharp interface between a dry hydrophobic hydrocarbon core and a region filled with surfactant head groups, some of the counterions, and water, namely the Stern region. This model has been validated using molecular dynamic simulations\(^\text{119,120}\) and is valid for both ionic and nonionic micelles.

The overall structure of micelle is characterized by a situation in which the ionic and polar head groups reside at the surface of the aggregates, where they are in contact with water, with the alkyl chains in the interior of the micelle forming a relatively dry hydrophobic core.\(^\text{121}\) The alkyl chains of micellized surfactant are not fully extended. Starting from the head group, the first two or three carbon–carbon bonds are usually \textit{trans}, whereas \textit{gauche} conformations are likely to be encountered near the centre of the chain. As a result, the terminal
Fig. 1.1: Model of a typical ionic micelle showing the location of head groups (☉), surfactant chains (△△△) and the counterions (+).
methyl moieties of the chain can be located near the surface of the micelle and may even protrude into the aqueous medium.\textsuperscript{122} Consequently, the micellar surface has a definite degree of hydrophobicity. NMR studies have shown that the hydrocarbon tails in a micelle are highly mobile and comparable in mobility to the chains in a liquid hydrocarbon.\textsuperscript{123} The degree of water penetration into the micellar interior has long been a matter of debate. Small-angle neutron scattering studies have indicated that significant water penetration into the micellar core is unlikely.\textsuperscript{124}

\textbf{D. The Pseudophase Model}

Kinetic studies in micellar systems have been in the scope of interest of many researchers for a longtime. The rates of enzymatic, organic, and inorganic reactions have been investigated in the presence of micelles by a great variety of surfactants. The chemical literature in the period 1900–1958 contains a scattering of reports concerning reaction kinetics in aqueous media containing ionic or nonionic surfactants. However, substantial insight into this area was first achieved in 1959 by Duynstee and Grunwald in their study of the effects of cationic and anionic surfactants on the rate of alkaline fading of cationic triphenylmethane dyes.\textsuperscript{125} Since that time, related studies have been appearing at an increasing rate, and interest is still growing.

Association colloids have interfacial regions containing ionic and polar head groups and ionic and polar solutes may be incorporated in this region.
Apolar cores of micelles, which exclude polar and ionic solutes and interfacial regions, are accessible to these solutes and to water. Consideration of the dimensions of head groups and apolar tails indicates that the volume of the interfacial region is approximately half that of the total micelle. Solutions of dilute surfactants are isotropic, but there is extensive physical evidence that they are dispersions of submicroscopic particles which form a micellar pseudophase distinct from the aqueous pseudophase. The interfacial region is highly anisotropic and in ionic micelles there is considerable neutralization of head groups by counterions. The intrinsic heterogeneous character of a micellar solution requires the developments of novel concepts in reaction kinetics since deviations from conventional rate laws applicable to homogeneous systems are frequently observed.\textsuperscript{126–128} In particular, the fact has to be taken into account that compartmentation of the reactants occurs as a consequence of their association with the surfactant aggregates.\textsuperscript{127}

In a homogeneous surfactant solution (above critical micelle concentration) the reactive site of substrate may exist in one or more of the following environments: the micelle interior, the micelle water interface, and the bulk solvent. One of the most important processes leading to the micellar effects on reactions is the solubilization of substrates in micellar interiors. It is possible to solubilize water insoluble substances or to increase the solubilities of slightly soluble ones in aqueous micellar solutions. They penetrate toward the hydrocarbon-like cores of the micelles.\textsuperscript{129–137} Since the solvent molecules penetrate beyond the polar head groups, solute in the solvent phase can interact
both with the nonpolar chains of surfactant molecules and with polar head groups. Thus the micellar phase may be referred to as amphipathic, having affinity for both polar and nonpolar species. Micellar cores behave like an organic phase and the hydrophobic forces play an important role in the solubilization process.\textsuperscript{138}

The pathways and rates of reactions in micelles are affected by how deeply the solubilized species is located within the micelle. Both electrostatic and hydrophobic forces play a role in determining the binding site of a solute inside the micelle, and both the structure of the amphiphile and the solute are of great importance in determining the extent of solubilization and the penetration of solute into the micelles.\textsuperscript{111}

Another fundamental process in micellar catalysis or inhibition is the counterion binding to micelles. Micelles can either attract the reactive ions or repel them depending upon the electrical charge of their head groups. Thus, micelles may bring the solubilized substrates and reactive ions together or keep them apart such that the reactions are speeded up or inhibited. Another way by which micelles can catalyze a reaction is the stabilization of intermediates as bound counterions.\textsuperscript{139,140} Sometimes, even substrates are bound to micelles as their counterions.\textsuperscript{141}

Most kinetic treatments are based on so-called pseudophase model. This model has been generally accepted on the reasonable assumption that for most activated thermal chemical reactions, transfer of material between water and
micelle is so fast that reaction does not perturb the equilibrium distribution of reactants between the pseudophases. This generalization cannot be applied to photochemical reactions, where some steps of the reaction may be very rapid and therefore faster than solute transfer.\textsuperscript{94,142} Provided that equilibrium is maintained between the aqueous and the micellar pseudophases, the overall reaction rate will be the sum of rates in water and in the micelles and will therefore depend on the distribution of reactants between each pseudophase and the appropriate rate constants in the two pseudophases.

Menger and Portnoy\textsuperscript{100} developed a quantitative treatment that adequately described inhibition of ester saponification by anionic micelles. Micelles bound hydrophobic esters, and anionic micelles excluded hydroxide ions and so inhibited the reaction, whereas cationic micelles speeded saponification by attracting hydroxide ions.\textsuperscript{143} Provided that only substrate distribution has to be considered, which is the situation for micelle-inhibited bimolecular or spontaneous unimolecular reactions, Scheme 1.3 shows the substrate distribution and reaction in each pseudophase.\textsuperscript{144}
In the Scheme 1.3, \( D_n \) denotes micellized surfactant, \( S \) is substrate, subscripts \( w \) and \( m \) denote aqueous and micellar pseudophases, respectively, and \( k'_w \) and \( k'_m \) are first-order rate constants. The binding constant, \( K_s \), is written in terms of the molarity of micellized surfactant, but it could equally be written in terms of the molarity of micelles. The concentration of micellized surfactant is that of total surfactant less that of monomer, which is assumed to be given by the cmc.

The experimental rate constant \( k_\psi \) for Scheme 1.3 is a weighted sum of the two constants \( k'_w \) and \( k'_m \)

\[
k_\psi = f_w k'_w + f_m k'_m = f_w k'_w + (1 - f_w) k'_m \tag{1.6}
\]

where \( f_w \) and \( f_m \) are the fractions of substrate in the bulk solution and solubilized in the micelles, respectively. The second version of Eq. (1.6) arises from the recognition that \( f_w + f_m = 1 \). The equilibrium constant, \( K_s \), in Scheme 1.3 can be written as

\[
K_s = \frac{[S_m]}{[S_w] [D_n]} = \frac{f_m [S_i]}{[D_n] f_w [S_i]} = \frac{f_m}{[D_n] (1 - f_m)} \tag{1.7}
\]

where \([S_i] \) is the total substrate concentration.

From Eq. (1.7)

\[
f_w = (1 + K_s [D_n])^{-1} \tag{1.8}
\]

which, on substitution in Eq. (1.6), gives
This equation is similar in form to the Michaelis–Menten equation of enzyme kinetics, although the analogy is limited because most enzymatic reactions are studied with substrate in large excess over enzyme. Equation (1.9) could be rearranged to give Eq. (1.10), which is formally similar to the Lineweaver–Burk equation and which permits calculation of $k'_m$ and $K_s$ provided that $k'_{w}$ is known:  

\[
\frac{1}{(k'_{w}-k_{w})} = \frac{1}{(k'_{w}-k'_{m})} + \frac{1}{(k'_{w}-k'_{m})K_s[D_n]} \quad (1.10)
\]

Equations (1.9) and (1.10) have been applied successfully to micellar catalyzed unimolecular reactions and to many micellar mediated reactions. The observations suggest that the pseudophase model is useful in analyzing micellar catalysis and inhibition. These equations, however, depend on some major assumptions, in particular that the cmc gives the concentration of monomeric surfactant and the rate and binding constants in the micellar pseudophase are unaffected by reactants and products.

E. Statement of the Problem

Cerium(IV) as an oxidant has been employed both in mechanistic$^{16,29,49,145-159}$ as well as synthetic$^{160-162}$ studies despite the fact the speciation of sulfato–cerium(IV) species is still not established
conclusively in sulfuric acid medium. Cerium(III) is the only reduction product of cerium(IV) as the latter is one of a group of metal ion oxidants which apparently react only via one-electron steps. Cerium(III) has been found useful for the plants as well as animals.

Due to very important role of cerium(IV) (as an oxidant), the oxidation of carbohydrates by cerium(IV) has received attention for a long time, but the same in presence of surfactants has not been studied so far.

Effect of organized structures (e.g., micelles being one of them) on the rate of electron transfer reactions has been receiving considerable attention too. A number of interfacial electron transfer processes have been investigated in polyelectrolytes, vesicles and micellar surfaces including photoredox reactions. The interest in this subject arises from the similarity with the biological processes. Therefore, the present work was undertaken to study the effect of surfactant micelles on the kinetics and mechanism of oxidation of carbohydrates by cerium(IV). For this purpose two aldopentoses (D(+)-xylose and L(+)-arabinose), two aldohexoses (D(+)-glucose and D(+)-mannose), and two ketohexoses (D(-)-fructose and L(-)-sorbose) were used. The surfactants used in the study were cationic cetyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulfate (SDS).


References


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