CHAPTER I: INTRODUCTION

The multiplication of terrorist actions in the recent years is alarming and the detection and detoxification of chemical and biological warfare agents has become one of the highest research priorities in the field of national security and public health\(^1\)-\(^{10}\). Military and terrorist activities may result in air, water and soil contamination with different organophosphorus chemical warfare agents. Hazardously, these compounds act as acetylcholinesterase inhibitors and can be lethal within minutes if inhaled\(^{11}\)-\(^{15}\). When their acute toxicity was discovered, their use was redirected into chemical weapons. With the rising concern of terrorist nerve gas attacks threatening homeland security, trace detection of nerve agents has become increasingly important. Several current lines of research are pursuing the development of catalytic methods for destruction of chemical warfare agents under ambient conditions. It is the goal of this thesis to study deacylation and dephosphorylation reactions in cationic monovalent and gemini surfactants with special bias on carboxylate and phosphate esters. The current state-of-the-art, development of new methodologies and chemistry of detoxifying reactions have been discussed in the sections below.

1.0 DEACYLATION AND DEPHOSPHORYLATION REACTIONS

Over the past several years, a number of theoretical and experimental approaches have been used to address the problem of deacylation and dephosphorylation (Chart-1) reactions\(^{16}\)-\(^{25}\). Deactivation of reactive esters like carboxylate (I), organophosphorus (II) and sulfonate (III) are classical reactions of fundamental importance in chemistry and biology\(^{26}\)-\(^{30}\).
Alkaline Degradation of the Organophosphorus Pesticide Fenitrothion

X. Han, V. K. Balakrishnan and E. Bunce!


Oxime Induced Reactivation of Sarin-Inhibited AChE

J. Wang, J. Gu, M. Feliks and W. A. Sokalski


Determination of the Hydrolysis Kinetics of Alpha-naphthyl Acetate in Micellar Systems and the Effect of HPMC

P. Werawatganone and D. E. Wurster


Decontamination of VX, GD, and HD on a Surface Using Modified Vaporized Hydrogen Peroxide

G. W. Wagner, D. C. Sorrick, L. R. Procell, M. D. Brickhouse, I. F. Mcvey and L. I. Schwartz


Premicellar Accelerated Decarboxylation of 6-Nitrobenzisoxazole-3-Carboxylate I on and its 5-Tetradecyloxy Derivative


Chart 1: Estiolysis of Carboxylate/Phosphate ester

Quantum Mechanical Calculations on the Reaction of Ethoxide anion with Dimethyl methylphosphonothiolate

J. L. Menke and E. V. Patterson


Detection and Protection against Chemical Warfare Agents

L. M. Eubanks, T. J. Dickerson and K. D. Janda


Catalytic Hydrolysis of p-Nitrophenylacetate by Electrospun Polyacrylamidoxime Nanofibers

L. Chen, L. Bromberg, T. A. Hatton, L. M. Eubanks, T. A. Dickerson

The remarkable growth in the field of acylation and phosphorylation reactions has been greatly motivated by the interest in understanding and developing more 'user-friendly' reaction media and catalytic reagents. In view of catalytic cleavage of carboxylate and phosphate esters, detailed fundamental studies on metal ion catalysis\textsuperscript{31-35}, nucleophile-aided hydrolysis\textsuperscript{36-40}, micellar catalysis\textsuperscript{41-45} and enzymatic hydrolysis\textsuperscript{46-50} are in progress.

Developing novel materials for the cleaving of phosphoester and carboxylic ester bonds under mild conditions is urgently required to address the environmental problems. In recent years, increasing attention has been given to the development of novel reaction media for studying the reactivity and selectivity of chemical and biochemical reactions\textsuperscript{51-55}.

1.1 MEDIUM FOR DECONTAMINATION

Decontamination of environmental toxins has been the focus of considerable research for several decades\textsuperscript{56-60}. In particular, chemical warfare agents are of great concern due to proliferation, spurring research into the adsorption and reactivity of chemical warfare agents and their analogues on a variety of materials. A better understanding of the mechanism of the hydrolysis of phosphate and
carboxylate esters is required to address the environmental problems. The accidental or intentional release of toxic organophosphate in the environment is a serious issue and can cost many lives. Pollution due to organophosphates is attributed mainly to improper management of stock piles of expired pesticides, and chemical warfare nerve agents. Most of the organophosphate nerve agents for military use were an outgrowth of the search for effective insecticides. Several techniques have been developed to address the pollution threat posed by organophosphates. They are summarized in Chart-2.

Metallomicelles are micelles comprised of functionalized amphiphiles that contain one or more metal atoms. Those useful for catalysis usually contain a transition metal chelated to a lipophilic ligand. In aqueous solution, the metal ion complex forms the headgroup that interfaces at the Stern region. Metal-catalyzed hydrolytic reactions of carboxylic and phosphate esters have been studied for many years and, in general, these are relatively well-understood processes. These reactions involve catalytically active M\(^{n+}\)-(OH) species where the metal ion serves as: (i) decreasing the pK\(_a\) of the metal-associated HOH so that a M\(^{n+}\)-coordinated hydroxide can be formed at reduced pH; (ii) a bifunctional role for M\(^{n+}\) (OH) acting as a Lewis acid and provider of the coordinated hydroxide to attack the C=O or P=O group; (iii) a possible additional role for the metal ion of promoting accelerated breakdown of any intermediates through coordination of the leaving group to the metal ion.

Microemulsion offers the intriguing capability of cosolubilizing high concentrations of water insoluble and water soluble reactants, and many studies of chemical reactivity in microemulsions have focused on potential large scale applications of these systems as reaction media. Morphologically, they are a microheterogenous phase distribution on a nanometer scale. They are frequently
droplet type of dispersions, either of oil-in-water (O/W) or water-in-oil (W/O). The microemulsion based system is simple, cheap, mild and relatively rapid. The high solubilizing power of microemulsions has lead several groups\textsuperscript{78-85} to use them for the destruction of toxic materials. The highly toxic and very hydrophobic blister agent mustard gas and less toxic model compounds are rapidly destroyed by hydrolysis or oxidation. Their reactions are very rapid in microemulsions that contain hypochlorite ion and tert-butyl alcohol, which generates tert-butyl hypochlorite, the probable oxidant. The high solubility of very hydrophobic chlorosulfides in microemulsions is of key importance in this reaction\textsuperscript{80-84}.

Brembilla \textit{et al.}\textsuperscript{86} reported the effect of polymer microdomains on the catalyzed esterolysis of hydrophobic picolinic esters. They generated hydrophobic microdomains in aqueous solutions by intramolecular coiling of poly(3-hexadecyl-1-vinylimidazolium bromide). The influence of the produced microenvironments on the chemical reactivity of water insoluble reactants was studied. By employing hydrophobic benzimidazoles (IV) in the presence as well as the absence of Zn\textsuperscript{2+} ions, hydrolysis of hydrophobic picolinate esters (V) were studied.

\begin{align*}
\text{R}_1 = & C_{10}H_{21}, \text{R}_2 = H, \text{R}_3 = CH_2OH \\
\text{R}_1 = & C_7H_{15}, \text{R}_2 = H, \text{R}_3 = CH_2OH \\
\text{R}_1 = & C_{10}H_{21}, \text{R}_2 = H, \text{R}_3 = H \\
\text{R}_1 = & H, \text{R}_2 = H, \text{R}_3 = CH_2OH \\
\text{R}_1 = & H, \text{R}_2 = C_{10}H_{21}, \text{R}_3 = CH_2OH \\
\text{R}_1 = & H, \text{R}_2 = H, \text{R}_3 = H \\
\end{align*}

\textsuperscript{n} = 1, 3, 5, 7, 10
However, these polymers and macrocycle-based catalysts have many disadvantages. For example, a number of these systems are not soluble in water. Hence, they exhibit poor solubilization ability of substrates. Water insolubility forces the experiments to be performed in mixtures of organic solvents and water, which cannot be directly correlated with biological enzyme systems, where all reactions take place in aqueous medium. Quite often they exhibit lower binding constants for substrate binding due to their rigid nature. In addition, often these systems show either a lack of turnover capacity or low turnover abilities. To circumvent the above-mentioned problems several groups have focused their attention on using various self-assembling systems as reaction media for these hydrolytic reactions.

Cyclodextrins (CDs) occupy a leading position among the many reagents employed to model the enzymatic cleavage of various toxic substrates. CDs have often been used for such studies because of their marked ability to form inclusion complexes with a wide variety of guests in solution. Their ability to recognize, bind and catalyze the scission of numerous size complementary substrates has been described in many reviews and reports. The cyclodextrin complexes find a wide range of uses in pharmaceuticals, industrial and reaction chemistry. Their ability to modulate reactivity depends on their capacity to complex organic substances. CDs have a unique role in the removal of pesticide residues from contaminated soils, for example, from localized industrial sites. In such a situation, the leaching of the pesticide through rain water, along with other hydrophobic compounds, causes these to localize below the ground water table where they accumulate as DNPLs (dense nonaqueous phase liquids); there they remain virtually immune to degradation through bacterial action over several decades or longer. Now, if a CD solution is pumped from the surface into its constituents and degraded, while the CD solution is recycled upstream. This process is similar to the traditional "pump-
and-treat" procedure using surfactants\textsuperscript{101}. Measurement of binding constants between a given pesticide and available CDs enables one to quantify and optimize this methodology.

Nanotechnology is a highly promising and exciting cross-cutting molecular technology that spans many areas of science and technological application\textsuperscript{102-115}. Nanotechnology is unique in itself. The matter is controlled at the most elementary level like the atom. It makes the use of logical steps that cannot be avoided in the human progress. More than the progress of this technology in a narrowed stream it also signifies the development of a new technology age. Recent advances in nanoscience and nanotechnology have led to a new areas of research interest in employing nanometer-sized particles as an alternative matrix for supporting catalytic reactions\textsuperscript{116,117}. Newly developed magnetic nanoparticles show much promise as a novel addition to the family of catalytic destruction technologies for organophosphate compounds.

Current research is also investigating the potential that individuals with variable activity of certain enzymes important to the metabolism of organophosphates may be more susceptible to their effects. One important enzyme that is under investigation is paraoxonase, which is responsible for the hydrolysis of organophosphates. Several other enzymes have been shown to accelerate the hydrolysis of the G and V agents and related compounds, including organophosphorus pesticides\textsuperscript{118-120}.

Reactivity in association colloids has been extensively studied over the past several decades\textsuperscript{121-130}. The rate enhancements observed in these aggregates are largely the result of increase in the concentrations of reactants in the small interfacial volumes in which the reactions take place\textsuperscript{126-128}. Quantitative treatments
of reactivity in association colloids frequently use the pseudophase model. Bimolecular nucleophilic reactions can be described as illustrated in Scheme 1.1, where $S$ and $Nu$ are the substrate and the nucleophile in water (subscript w) or in the micellar pseudophase (subscript m). $k_{2,w}$ and $k_{2,m}$ are the second-order rate constants for substrate/nucleophile reactions in the aqueous phase and in the micellar pseudophase, respectively, and $K_S$ is the binding constant of the substrate to the micelles based on the concentration of micellized surfactant, defined as the difference in the total concentration of surfactant and the critical micelle concentration (cmc), i.e., $[M] = [\text{surfactant}]_{\text{total}} - \text{cmc}$.

\[
\begin{array}{c}
S_w + M & \xrightarrow{K_S} & S_m \\
\downarrow k_{2,w} & \text{Nu}_w & \text{PRODUCTS} & \uparrow k_{2,m} \\
\end{array}
\]

Scheme-1.1

The second-order rate constant $k_{2,m}$ is written in terms of the local concentration of the nucleophile in units of moles per liter of reaction volume within the micellar pseudophase ($\text{Nu}_m$), which cannot be measured directly. The concentration of the nucleophile can also be taken as a mole fraction of the bound reactive anion to the micellized surfactant, defined as $\text{Nu}_m = \frac{[\text{Nu}_m][M]}{V_m} = \beta V_m$, where $\beta$ is the degree of counterion binding to the micelle and $V_m$ is the molar volume of the reactive region in the aggregate. $V_m$ also relates the apparent, measurable, micellar rate constant, $k_m$, to $k_{2,m}$, (i.e., $k_m = k_{2,m}/V_m$). Thus, formulation of the kinetics of bimolecular reactions under pseudo-first-order conditions ($[\text{Nu}] \gg [S]$) gives eq 1.1. The value of $V_m$ is unknown, so that in order to
estimate $k_{2,m}$ from $k_m$, one assumes a value for $V_m$; typical estimates ranging from $0.14 \, M^{-1}$ (the volume of the micellar Stern layer) to $0.37 \, M^{-1}$ (the volume of the micelles). \(^{137}\)

$$k'_w = \frac{k'_w[Nu] + k_mK_s[M]}{1 + K_s[M]} = \frac{k'_w + (k_{2,w'}V_m)\beta K_s[M]}{1 + K_s[M]} \quad 1.1$$

$$X_m + Nu \quad \overset{K_x^{N_r}}{\longleftrightarrow} \quad Nu_m + X_w \quad 1.2$$

The micellar surface also behaves as a selective ion exchanger, and competition between reactive (Nu) and inert (X) counterions can be expressed as in eq 1.2, in which an empirical ion exchange constant, $K_x^{N_r}$, accounts both for ionic and hydrophobic contributions to the binding. This extension of the pseudophase model has been called the pseudophase ion exchange model or PIE and successfully fits the kinetics of many bimolecular reactions in micellar solutions. In the PIE model, $\beta$ (the degree of counterion association to the micellar surface) is assumed to be constant and insensitive to surfactant and salt concentrations. However, this assumption generally fails for very hydrophilic anions such as $\text{OH}^-$, $\text{F}^-$, or $\text{OOR}^-$, for which the degree of association appears to increase gradually with increasing surfactant concentration.

In the present investigation, the micellization and interfacial properties of some novel surfactants like alkyltriphenylphosphonium bromides and gemini surfactants and the catalytic reactions of toxic esters using $\alpha$-nucleophiles in the presence of these monovalent and gemini micelles have been explored.
1.2 SURFACTANTS

Surfactants are receiving extensive attention in both pure and applied sciences. Surfactant molecules (also called amphiphiles or detergents) unite a polar or ionic head and a nonpolar tail within the same molecule. These molecules are said to be amphipathic, that is, they have distinct hydrophilic (polar) and hydrophobic (nonpolar) regions. The polar region, called the headgroup, may be either neutral, cationic, anionic, or zwitterionic. The hydrophobic tail has one or more chains of varying length, composed usually of a hydrocarbon. Common examples are:

- Polyoxyethylene dodecyl ether, $C_{12}H_{25}(OCH_2CH_2)_{23}OH$ (neutral)
- Cetyltrimethylammonium bromide, $C_{16}H_{33}(CH_3)_{3}N^+Br^-$ (cationic)
- Sodium dodecyl sulfate, $C_{12}H_{22}OSO_3^-Na^+$ (anionic)
- N-dodecyl-N,N-dimethylglycine, $C_{12}H_{22}(CH_3)_{2}N^+CH_2COO^-$ (zwitterionic)

The nonpolar part, which is typically made up of one or more alkyl chains, causes these compounds to be sparingly soluble in water, whereas the polar or ionic part interacts strongly with water. Surfactants are used in chemical, biomedical, pharmaceutical and industrial fields and in many areas of human activity. The vast majority of the surfactants is discharged after use into industrial effluents and/or sewage and may ultimately reach rivers, lakes and oceans. Molecular design of surfactants with varying architectures offers excellent opportunity for tailoring the surfactant self-aggregation behavior and the physicochemical properties of their solutions.

The application of cationic surfactants in high technology and biomedical fields has become very important. A deeper study about the micellization behavior of these surfactants could give important information on the different steps involved in various applications. The results of this physicochemical
Physicochemical aspects and the applications of surfactant solution d on the molecular structure of the surfactants and environmental factors urature, additives etc.). Extensive investigations have been reported in the ure 145-148 dealing with the quaternary ammonium cationic surfactant (VI) and nium based surfactants (VII).

\[
\begin{align*}
\text{CH}_3 & + \text{Br}^- \\
R & \quad \text{N} \quad \text{CH}_3 \\
\text{CH}_3 &
\end{align*}
\]

\[
\begin{align*}
\text{Br}^- & + \text{N} \quad \text{R} \\
\end{align*}
\]

\( \text{R} = \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{OH} \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

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\( \text{Br}^- \)

\( \text{N} \)

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\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)

\( \text{Br}^- \)

\( \text{N} \)

\( \text{CH}_3 \)

\( \text{CH}_3 \)
1.2.1 GEMINI SURFACTANTS

Gemini (dimeric) surfactants are made up of two surfactant like moieties connected at the level of the head groups or on the alkyl chains in close vicinity to the head groups by a spacer group of varying nature and length \(^{153-158}\) (Scheme 1.2). The spacer can be attached directly to the identical ionic groups (A), each of which is in turn bonded to an identical hydrocarbon tail (often the case for cationic surfactants); alternatively, (B) the two identical amphiphiles are joined midway (case of nonionic and anionic gemini surfactants). They constitute a new class of amphiphilic molecules having its own distinct behavior \(^{159-163}\). Since their first systematic studies over a decade ago, gemini surfactants have been the subject of intensive research. The study of gemini surfactants has generated much interest due to their unusual solution and interfacial properties and their enhanced performance in applications, compared to analogous single chain surfactants. Research has been motivated by the advantages of gemini surfactants over regular ones with respect to various applications, e.g., their increased surface activity, lower critical micelle concentration (cmc), and useful viscoelastic properties such as effective thickness \(^{164-173}\).

![Scheme-1.2](image-url)
In recent years, considerable efforts have been made to design and synthesize new forms of gemini surfactants having the required properties, to elucidate the relationship between the molecular structures of gemini surfactants and their aggregate morphology in aqueous solution and to understand the factors underlying the variation of their thermodynamic properties with the length of the side chains and spacers\textsuperscript{174-176}. They recently have generated much interest in academic circles and among scientists at surfactant-producing companies for the following reasons:

(i) Their cmc is at least one order of magnitude lower than for the corresponding conventional (monomeric) surfactants, on a weight percent basis.

(ii) They are 10–100 times more efficient in reducing the surface tension of water and the interfacial tension at an oil/water interface than conventional surfactants.

(iii) They appear to have better solubilizing, wetting, foaming, and lime-soap dispersing ability than conventional surfactants. Some anionic gemini surfactants have low Krafft temperatures, which make them applicable in cold water. Also, cationic gemini surfactants possess interesting biological properties.

(iv) The aqueous solutions of some gemini surfactants with a short spacer can have special rheological properties (viscoelasticity, shear-thickening) at relatively low concentration.

(v) The micelles present in solutions of some gemini surfactants can have unusual shapes as for instance ring-like or elongated with numerous branches.

(vi) Gemini surfactants can be synthesized with an enormous variety of structures. In principle, it is possible to connect any two identical or different surfactants among the available ones by a spacer group that can be hydrophilic or hydrophobic, flexible or rigid, heteroatomic, aromatic, etc. This is only limited
by the skill of the organic synthetic chemist. Therefore the structures and properties of gemini surfactants can be more finely tuned for a given application than for conventional surfactants.

(vii) The concept of gemini surfactants has been extended to more complex homologues: trimeric surfactants made up of three surfactant-like moieties connected by two spacer groups, tetrameric surfactants, etc. The number of possible structures becomes mind-boggling and some of the gemini and oligomeric surfactants that will be synthesized in the future are likely to show new/unexpected properties.

1.3 MICELLE FORMATION

Gaining a fundamental understanding of the process of micellization bears both academic and practical interest\textsuperscript{177,178}. The association of many classes of surface-active molecules into micellar aggregates is a well-known phenomenon. Surfactants are known to form micelles with polar or ionic groups at the surface in contact with water and have manifold applications, namely in the preparation of surfactant-ion-selective membranes, drug encapsulation and synthesis of nanoparticles.

Upon increasing the concentration of the amphiphilic compound in water, at a certain point the solubility limit will be reached and phase separation will set in. Due to the efficient interactions between the polar headgroups and the surrounding water molecules, a complete phase separation is usually unfavourable. Instead, the process will be arrested in an intermediate stage with concomitant formation of aggregates of amphiphilic material, wherein the nonpolar parts stick together and are shielded from water, whereas the head groups are located in the outer regions of the aggregate. A multitude of different aggregates can be formed in
Surfactants dissolve completely in water at very low concentrations, but above a certain level, the critical micelle concentration (CMC), the molecules form globular aggregates, called micelles. As shown in Figure 1.1, the hydrophobic tails group unite together to create a nonpolar interior with the headgroups located at the surface of the glob in contact with the aqueous environment. Micelles vary in size and shape, but are commonly rough-surfaced spheres with aggregation numbers of the order of 50-100.

Figure 1.1: Schematic representation of formation of micelle.

The interfacial region or Stern Layer (Figure 1.2) having a width about the size of the surfactant head group contains the ionic head groups of the amphiphile, a fraction of the counter ions and water. The Stern layer is extremely anisotropic region with properties intermediate between those of water and hydrocarbon. The reactions at the interfacial region show differential reactivity than the bulk aqueous media. Thermal motion creates a diffuse electrical double layer, called the Gouy Chapman layer, which extends out into the aqueous phase and contains counter ions.
Figure 1.2: Schematic representation of cationic micelle showing counterion electrical double layer.

The presence of micelles can have marked effects on thermodynamic favorability and reaction kinetics as well as on many physical properties. Reaction rates can be either accelerated or decelerated, depending on the chemical system, the type and concentration of the surfactant, and other factors, such as pH, ionic strength, etc. The effect of surfactants on reaction kinetics is often called micellar catalysis.

1.3.1 MICELLAR CATALYSIS

The enormous recent interest in supramolecular chemistry, the chemistry of molecular organized assemblies, reflects the current emphasis on noncovalent intermolecular interactions and molecular recognition\textsuperscript{179}. In this field, chemical research has entered into new dimensions leading to the design and understanding
of hierarchies of physically associated molecules. Surfactant self-organization constitutes a major area of interest. A micelle-bound substrate will experience a reaction environment different from bulk water, leading to a kinetic medium effect. Hence, micelles are able to catalyze or inhibit organic reactions. Research on micellar catalysis has focused on the kinetics of the organic reactions involved. Micellar catalysis of organic reactions has been extensively studied. This type of catalysis is critically determined by the ability of micelles to take up all kinds of molecules. The binding is generally driven by hydrophobic and electrostatic interactions. Catalysis by micelles involves at least three main steps: (i) binding of the substrate(s) to the micelle, (ii) the actual chemical transformation in the micelle (usually at the micellar surface) and (iii) release of product(s).

Micelles can accelerate chemical reactions by virtue of their ability to solubilize both polar and nonpolar reactants from the aqueous phase. The enhancement of the reaction rate results from the following phenomena:
(i) increased local concentration of the reactants at the surface or in the interior of the micelle;
(ii) stabilization of the transition state of the reaction;
(iii) medium effect (polarity, microviscosity and charge effects inside the micelle).

Organic reactions involving ionic, polar and neutral reactants in micellar solution are generally believed to occur in the Stern layer of the micelle of an ionic surfactant. The catalysis and inhibition of ionic micelles is due to ionic micelle incorporation of both the reactants. Due to these facts, a significant amount of systematic kinetic results have been reported on the effect of micelle on various organic reactions during past few decades. Solubilization of solutes from the aqueous medium into the micelle is usually treated in terms of a pseudophase model in which the bulk aqueous phase is regarded as one phase and the micelle.
pseudophase as another. The time-averaged location of different solubilizes in or at the micelle has been a topic of contention. Apart from saturated hydrocarbons, there is usually a preference for binding in the interfacial region, that is, at the surface of the micelle. Such binding locations offer possibilities for hydrophobic interactions and avoid unfavorable disturbance of the interaction between the alkyl groups of the surfactant molecules in the core of the aggregate. Kinetic studies of micellar effects have focused largely on bimolecular reactions of ionic reagents. These effects on rates, and also on equilibria, are treated quantitatively in terms of pseudophase models and rate constants of reaction at micellar surfaces can be estimated and are generally not very different from those in water.

1.4 α-NUCLEOPHILES

It is of paramount importance to design and develop such nucleophile which shows super nucleophilicity. Nucleophiles which bear one or more nonbonding electron pairs at the position α to the nucleophilic center have been termed α-nucleophiles and exhibit enhanced reactivity compared with normal nucleophiles of similar basicity (the α-effect). One of the most comprehensive and conclusive data supporting this hypothesis was presented by Jencks and Carriuolo in the nucleophilic cleavages of 4-nitrophenyl acetate. Although the nucleophilicity of most of nucleophiles monotonously increased with increasing value of $pK_a$ (as expected from Brønsted law), the points for hydroperoxide ion, hydrazine, hydroxylamine and others, which have adjacent unpaired electrons, significantly deviated from this relationship in positive direction. For certain nucleophiles, the deviation was as large as 103- to 104-fold. Similar unusual rate enhancements assignable to α-effect were reported by Bruice et al. for the cleavage of phenyl
acetate. Strong and concrete evidence for "α-effect" was provided. This effect is also significant in biological systems. For example, hydroxylamine and hydrazine attack nucleobases in DNA far more efficiently than does ammonia, resulting in the transformation of DNA to non-natural form\(^{189}\).

Recently research has highlighted the role played by α-nucleophiles in the presence of association colloids\(^ {190-193}\). Current interest in studying the reaction of α-nucleophiles has received major new impetus from the importance of the many applications of these highly reactive species. Several α-nucleophiles, like oximates (X) hydroxamate ions (XI), hydroxylamine (XII), o-iodosobenzoate (XIII), hydroxybenzotriazole (XIV) etc. are characterized by anomalously high reactivity with respect to electron deficient centers of various origins, e.g. carbon, phosphorus and sulfur\(^ {194}\).

\[
\begin{align*}
\text{(X)} & \quad \text{(XI)} & \quad \text{(XII)} & \quad \text{(XIII)} & \quad \text{(XIV)} \\
\begin{array}{c}
\text{R} - \text{C} - \text{C} - \text{R} \\
\text{H-N-O}^- \quad \text{H}_2\text{NOH} \\
\text{O} \quad \text{N} \quad \text{N} \\
\text{O} \quad \text{O} \quad \text{O} \\
\end{array}
\end{align*}
\]

In view of their high nucleophilicity, α-effect compounds appear to be good candidates as nucleophilic catalysts. A large number of research papers in this context have come up recently from our laboratory\(^ {195-203}\). It is now widely accepted that in the presence of cationic surfactants the rate accelerated significantly. Several factors contribute to enhanced reactivity, and the differentiation of the contribution of various factors is extremely difficult.
Among different α-nucleophiles, oximates have featured widely because they represent a class of nucleophilic catalysts which has proved to be very efficient in promoting such important processes as acyl, phosphyl and sulfyl transfers, as well as proton transfers including potential reactivators of acetylcholinesterase (AChE) inhibited by organophosphorus toxics. The mode of action of organophosphorus compounds includes inhibition of neurotransmitter acetylcholine breakdown. Acetylcholine is required for the transmission of nerve impulses in the brain, skeletal muscles and other areas. However, after the transmission of the impulse, the acetylcholine must be hydrolyzed to avoid overstimulating or overwhelming the nervous system. This breakdown of the acetylcholine is catalyzed by an enzyme called acetylcholine esterase. Acetylcholine esterase converts acetylcholine into choline and acetyl CoA by binding the substrate at its active site at serine to form an enzyme substrate complex. Further reactions involve release of choline from the complex and then rapid reaction of acylated enzymes with water to produce acetic acid and the regenerated acetylcholine esterase. It has been estimated that one enzyme can

![Figure 1.3: Schematic representation of action of Acetylcholinesterase.](image-url)
hydrolyze 300000 molecules of acetylcholine every minute. Organophosphorus compounds inhibit the normal activity of the acetylcholine esterase by covalent bonding to the enzyme, thereby changing its structure and function. They bind to the serine 203 amino acid active site of acetylcholine esterase. The leaving group binds to the positive hydrogen of His 447 and breaks off the phosphate, leaving the enzyme phosphorylated. The regeneration of phosphorylated acetylcholine esterase is very slow and may take hours or days, resulting in accumulation of acetylcholine at the synapses. Nerves are then overstimulated and jammed. This inhibition causes convulsion, paralysis and finally death for insects and mammals.

1.5 SOLVENT EFFECT

The influence of solvent on interfacial properties as well as on the reaction rates has been intensively studied in recent years\textsuperscript{209-213}. Addition of polar organic solvents to aqueous micellar solutions will alter the tendency of the amphiphile molecules to avoid contact with the solvent, and therefore, it is expected to affect the value of surfactant concentration at which aggregation occurs (cmc) as well as micelles characteristics such as the micellar ionization degree, aggregation number, and polarity and solvent content in the interfacial region. Solvents that incorporate to some degree into the micelles cause changes in the characteristics of the aggregates not only because of variations in the bulk-phase properties (solvophobic effect) but also because of their incorporation into the micellar aggregates. The contributions of the two effects cannot be separated.

Polar organic cosolvents can be supplemented to increase substrate solubility to achieve higher catalytic efficiencies. Survey of literature shows that considerable effort has been made on the study of the solvent effect on the $\alpha$-effect for esterolytic reactions\textsuperscript{214-218}. 
1.6 NANOTECHNOLOGY AND DETOXIFICATION

Over the past few years, scientists world-wide are continuing to discover unique properties of everyday materials at the sub micrometer scale. This size domain is better known as nano- (a billionth) meter domain. Nanotechnology involves the design, production, characterization and applications of materials (molecules or devices) whose dimensions are less than 100 nm. It has been shown that at nanometric scale, materials acquire new properties that can be exploited in numerous fields, including biotechnology, bioengineering, nanotechnology and nanomedicine.

The synthesis of metal nanoparticles through different routes has become an important area of research and development\textsuperscript{219-228}. It is known that the conventional metals, viz., silver, gold, platinum, etc. become very reactive in the nanosize range; their high surface energy makes them agglomerate. Unfortunately, the synthetic control in making desired size and shape are not yet well established. Due to these facts their synthesis and stabilization has become a very difficult task. Self-organizing assemblies like micelles, microemulsions, reverse micelles and polymers have been used in various ratios to control the particle size, shape and stability\textsuperscript{229}. In the most popular and widely used colloid-chemical synthetic approach the particle size/shape distribution depends on the relative rates of nucleation and growth occurring in the intermediate stages of particle formation. Many workers have been reported novel methods for the preparation of metal nanoparticles\textsuperscript{230-233}. The aim of such investigations can be divided into two main groups. The first group constitutes the preparation and the study of the particles itself. The second group comprises the various experiments aimed at the development of advanced nanostructured materials for catalyst production, semiconductors, supermagnets and ultramodern devices etc. the need for developing
eco-friendly synthesis protocols that do away with the use of toxic chemicals has also fuelled research in this direction and bio-related processes that use bacteria and fungi have been developed to grow nanocrystals.

Now a days there has been an increasing attention of researchers throughout the world to improve the detoxification using nanocatalyst for chemical and biological warfare agents\(^\text{234-238}\)(Chart-3). The development of a new generation of materials is required that can simultaneously act as a barrier, a reporter and a decontaminator for both chemical and biological weapons. Such materials should be active on contact with an agent and retain activity over long periods of time. The merging of biotechnology with materials science offers a wide range of possibilities for the design of advanced materials that are only now being investigated.

### 1.7 REVIEW OF THE EARLIER WORK:

Over the last few years a great deal of work has been done for the development and design of new materials that can irreversibly decompose chemical agents and convert them into a nontoxic form. Specific emphasis has been placed on techniques to provide protection from exposure to chemical warfare agents as well as for the destruction of stockpiles of chemical weapons\(^\text{16-30}\). The significant contribution of Menger\(^\text{170}\), Bunton\(^\text{239-248}\), Moss\(^\text{249-253}\), Buncel\(^\text{254-264}\) and Bhattacharya\(^\text{271-272}\) deserve special mention in this context. Nucleophile-aided hydrolysis is the most preferred reaction to detoxify them\(^\text{190-194}\). In this regard, nucleophiles such as oximates\(^\text{190}\), peroxides\(^\text{191}\), hypochlorites\(^\text{192}\), o-iodosylcarboxylate\(^\text{192}\), hydroxybenzotriazole\(^\text{193}\) and hydroxamate\(^\text{194}\) have been investigated alone or in concert with surfactants.
Bunton et al.\textsuperscript{219-248} studied micellar and solvent effects on geometrical isomerism of hydroxamic acids and their anions which are α-effect nucleophiles. According to them amphiphilic hydroxamate ions form micelles or co-micelles in water, which are effective deacylating and dephosphorylating agents.

Moss et al.\textsuperscript{249-253} examined the influence of the micellar medium on the cleavage of many carboxylic esters and phosphate esters including persistent pesticides using very effective catalysts i.e. o-iodosyl and o-iodylbenzoic acid.

Iodosylcarboxylates appear to promote catalytic hydrolysis of organophosphorus toxicants by nucleophilic substitution at phosphorus, followed by hydrolytic attack at the central iodine to displace the P center from Iodosylcarboxylate (Scheme 1.3)\textsuperscript{1}.

![Scheme-1.3](image-url)
Bunce and Um\textsuperscript{254,270} have published large number of research papers on the effect of surfactants on the \(\alpha\)-effect for the reactions of \(p\)-nitrophenyl acetate (PNPA) and \(p\)-nitrophenyl diphenyl phosphate (PNPDPP) with oximates. The origin of \(\alpha\)-effect and its modulation by solvent have been studied in details.

Recently, Bhattacharya \textit{et al.}\textsuperscript{271-272} published esterolytic properties of different novel nucleophiles such as hydroxybenzotriazoles, tetrazoles and aminopyridines, etc. in cationic micellar media. These nucleophiles enhanced the reaction rates of \(p\)-nitrophenyl diphenyl phosphate (PNPDPP) and \(p\)-nitrophenyl hexanoate (PNPH) tremendously and acted as true catalysts (turn over).

Couderc and Toullec\textsuperscript{190} studied the catalysis of phosphate triester hydrolysis by micelles of hexadecyltrimethylammonium \textit{anti}-pyruvaldehyde 1-oximate. They proposed two competing pathways corresponding in the case of \(p\)-nitrophenyl diphenyl phosphate, to substitution of the 4-nitrophenoxide (path A) or phenoxide ions (path B) in the initial steps (Scheme 1.4).

\begin{equation}
\begin{aligned}
\text{PNP} + \text{Ac}-\mathrm{CH}=\mathrm{N}-\mathrm{O}^+ \xrightarrow{k_B \text{ slow}} \text{PNPO}^- + \text{PhO}^- \\
\text{PNPO}^- + \text{Ac}-\mathrm{CH}=\mathrm{N}-\mathrm{O}^+ \xrightarrow{k_A \text{ fast}} \text{PNPH} + \text{PhO}^- \\
\text{PNP} + \text{PNPO}^- \xrightarrow{k_B \text{ slow}} \text{PNPH} + \text{PhOH} \\
\text{PNP} \xrightarrow{k_A \text{ fast}} \text{PNPH} + \text{PhOH}
\end{aligned}
\end{equation}

\[ \text{PNP} = p\text{-Nitrophenyl}; \text{Ac} = \text{Acetyl} \]

\textbf{Scheme-1.4}
A possible mechanism (Scheme 1.5) for the activity of catalyst substituted iodoxybenzoate, (XV) against organophosphorus esters has been suggested by Hammond et al.\textsuperscript{197}. It involves the nucleophilic attack of the oxyanion (XV) on the central phosphorus atom of substrate to form the phosphorylated intermediate (XVI) with concomitant loss of leaving group X. The proposed intermediate may then hydrolyze by several pathways: (a) attack of OH\textsuperscript{-} (H\textsubscript{2}O) on the carboxylic carbonyl group with subsequent ring opening and loss of \textsuperscript{OP}(O)R\textsubscript{1}R\textsubscript{2} to generate the \textsuperscript{OP}iodosobenzoate form with later recyclization to (XV), or (b) direct attack of OH\textsuperscript{-} (H\textsubscript{2}O) on iodine with subsequent loss of \textsuperscript{OP}(O)R\textsubscript{1}R\textsubscript{2} to generate (XV).

\begin{化学方程式}
\begin{align*}
\text{R}\text{O} & + R_1\text{P-X} & \rightarrow & \text{R}\text{O} + X^- \\
\text{(XV)} & & & \text{(XVI)} \\
\text{R}\text{O} & + \text{OH}^- & \rightarrow & \text{R}\text{O} \text{-H} \\
\text{(XVI)} & & & \text{(XVII)} \\
\text{R}\text{O} & + \text{H}^+ & \rightarrow & \text{R}\text{O} \\
\text{(XVII)} & & & \text{(XV)}
\end{align*}
\end{化学方程式}

\textbf{Scheme-1.5}

Wagner et al.\textsuperscript{237} studied room temperature reactions of VX, GB, GD and HD with nanosize Al\textsubscript{2}O\textsubscript{3} (AP- Al\textsubscript{2}O\textsubscript{3}) by \textsuperscript{31}P, \textsuperscript{13}C and \textsuperscript{27}Al MAS NMR methods. Their reaction proceeds to the particle core. The room temperature reactivity exhibited by these oxides is promising for the use of such a material where CWA
deposited on personnel, equipment, vehicles and perhaps even strategic locations could be quickly removed adsorbed and subsequently detoxified.

Recently Hatton and Bromberg\textsuperscript{238} designed a nanosized particulate carrier with powerful $\alpha$-nucleophiles, an oxime group, immobilized on its surface as a catalytic destruction agent. The carrier comprised iron oxide (Fe$_3$O$_4$) that is superparamagnetic and thus can be separated from an aqueous suspension by high-gradient magnetic separation. Catalytic magnetic particles were synthesized (eq.1.3) with or without a stabilizing compound by the coprecipitation of iron (II) and iron (III) chlorides by ammonia.

\[ 2\text{FeCl}_3 + \text{FeCl}_2 + 8\text{NH}_3 + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4\downarrow + 8\text{NH}_4\text{Cl} \quad 1.3 \]

The hydrolysis of DFP (diisopropyl fluorophosphate) and sarin by metal chelates or oximates proceeds via the formation of complexes that is unstable and easily hydrolysed in water, producing water-soluble phosphoric acids and fluoride ions\textsuperscript{194}. Catalytic hydrolysis of DFP by oxime-modified magnetic particles at neutral pH presented in (Scheme-1.6).

\[ \text{OfPr} \]
\[ \text{C} = \text{N} \backslash \text{O}^- \quad \text{IPrO} \quad \text{PO} \quad \text{F} \quad \text{OfPr} \]
\[ \text{IPrO} \]
\[ \text{C} = \text{N} \backslash \text{OP} \quad \text{O} \quad \text{PO} \quad \text{OfPr} \]
\[ \text{H}_2\text{O} \quad \text{IPrO} \quad \text{PO} \quad \text{OH} \]

Scheme-1.6
From the above discussion it is clear that a great deal of effort has been expended over the past few years. Remediation of decontamination is the ultimate goal. Micellar environment particularly single chain cationic surfactants increase nucleophilic reactivity, solubilize the ester and catalyze the decomposition of the agent. Among the new synthetic surfactants, gemini surfactants appear quite attractive as novel reaction medium, in that the aqueous solutions of such systems display unique properties that can result in improved performance. Therefore, in the present investigation an attempt has been made to study the kinetic advantages in using gemini surfactants for the deacylation and dephosphorylation reaction. The extreme toxicity of actual organophosphorus compounds often mandates that most of University laboratory employ surrogates or simulants instead of the actual chemical agents. Because one surrogate rarely offers all the important features of the agent, multiple surrogates i.e. C, P and S esters have been used in the present investigation.

1.8 PRESENT INVESTIGATION

The works embodied in this thesis are broadly categorized as follows:

(i) Micellization and interfacial properties of some novel surfactants like alkyltriphenylphosphonium bromides, alkanolamine-based and gemini surfactants.

(ii) The kinetics and mechanism of deacylation and dephosphorylation reactions in gemini surfactants.

(iii) The nucleophilic reactivity of oximates with carboxylic esters in alkyltriphenylphosphonium bromide micellar media.
(iv) Synthesis of silver (Ag) nanoparticles by chemical reduction with controlled size, shape with tight shape/size distribution which can be further used for convenient and fast esterolysis of carboxylate and phosphate esters.

(v) Determination of $pK_a$ of the reagents (Bronsted acid) in microorganised media, to enable the work under desired reaction conditions.

(vi) The comparative reactivities of deacylation and dephosphorylation reactions using some $\alpha$-nucleophiles.

Order of Presentation

The entire experimental work has been presented in six chapters. Brief contents of each one of these chapters are discussed below:

CHAPTER-I provides a brief overview on the catalytic methods for the destruction of organophosphorus compounds. Special emphasis has been given on the esterolytic cleavage of carboxylate and phosphate esters using $\alpha$-effect nucleophiles and detoxification chemistry in novel microorganised media. Different self-organizing systems like micelles and microemulsions have been discussed. The background of the present work, order of presentation and importance of the work has also been included in this chapter.

CHAPTER-II comprises two important aspects of micellization beaviour of gemini and alkyltriphenylphosphonium bromide surfactants and can be divided into following sections:
[A] Micellization behaviour of $[C_{16}-12-C_{16}]_{2}Br$ gemini surfactant in binary aqueous-solvent mixtures.


In Section A, the micellization behaviour of a bis cationic gemini surfactant, $C_{16}H_{33}N^+(CH_3)\text{CH}_2(N^+(CH_3)_{12}C_{16}H_{33})_{2}Br$ (XVIII) has been studied in binary aqueous mixtures of dimethyl sulfoxide, methanol, 1,4-dioxane, glycerol and ethylene glycol by conductivity and surface tension measurements at 300 K.

$$\begin{align*}
\text{CH}_3 & \quad 2 \text{Br} \\
\text{N} & \quad \text{CH}_3 \\
\text{C}_{16}H_{33} & \quad \text{C}_{16}H_{33}
\end{align*}$$

(XVIII)

The critical micellar concentration, degree of counterion dissociation ($\alpha$), surface excess concentration ($\Gamma_{\text{max}}$), minimum surface area per molecule of surfactant ($A_{\text{min}}$), Gibbs free energy of micellization ($\Delta G_m$), the surface pressure at $cmc$ ($\pi_{\text{cmc}}$), and the Gibbs energy of adsorption ($\Delta G_{\text{ad}}$) of the gemini surfactant have also been determined. The interfacial properties of the gemini surfactant, solute-solute, solvent-solute interactions and the effectiveness of a surface-active molecule in binary solvent systems have been discussed.

In Section B, the thermodynamics of micellization and other micellar properties of alkyl ($C_{10}$, $C_{12}$, $C_{14}$ and $C_{16}$) triphenylphosphonium bromide in
presence of water-ethylene glycol (EG) (0 to 30% v/v) over a temperature range of (298- 318K) and cetyltriphenylphosphonium bromide in presence of water-diethylene glycol (DEG) (0 to 30% v/v) at 298 K have been studied conductometrically. On the basis of the results, the thermodynamic parameters, Gibbs free energy ($\Delta G_m^0$), enthalpy ($\Delta H_m^0$) and entropy ($\Delta S_m^0$) of micellization have been evaluated. In addition to conductivity measurements, kinetic experiments have also been done to determine the dependence of observed rate constant for the nucleophilic substitution reaction of p-nitrophenyl acetate and benzohydroxamate ion in the presence of cetyltriphenylphosphonium bromide surfactant with varying volume percent of EG and DEG from 0 to 50%(v/v) at pH 7.9 and 300 K. The kinetic micellar effects have been explained by using the pseudophase model.

**CHAPTER-III** of the thesis deals with the study of kinetics of the hydrolysis of p-nitrophenyl acetate (PNPA) and p-nitrophenyl diphenyl phosphate (PNPDPP) using hydroxamate ions mediated by gemini surfactants with quaternary ammonium bromide ($16-n-16,2Br^-$, $n = 3, 4, 6, 12$) (XIX) and pyridinium chloride ($12py-n-py12, 2Cl^-$, $n = 3, 4$) (XX) head group have been investigated at 27°C.

\[
\begin{align*}
\text{CH}_3 & \quad 2\text{Br}^- \\
\text{H}_3\text{C} & \quad \text{N}^- (\text{CH}_2)_n \quad \text{N}^- \text{CH}_3 \\
\text{C}_{16}\text{H}_{33} & \quad \text{C}_{16}\text{H}_{33}
\end{align*}
\]

16-3-16,2Br$^-$ ($n = 3$),
16-4-16,2Br$^-$ ($n = 4$),
16-6-16,2Br$^-$ ($n = 6$),
16-12-16,2Br$^-$ ($n = 12$)

\[
\begin{align*}
\text{N}^+ & \quad (\text{CH}_2)_n \\
\text{C}_{12}\text{H}_{25} & \quad \text{C}_{12}\text{H}_{25}
\end{align*}
\]

12py-3-12py,2Cl$^-$ ($n = 3$),
12py-4-12py,2Cl$^-$ ($n = 4$)

(XIX) (XX)
The gemini surfactant with pyridinium head group, 12-py-4-py12,2Cl (tetramethylene-1,4 bis dodecylypyridinium chloride) shows large rate acceleration effect, than that with ammonium head group, 16-12-16,2Br\(^-\), relative to those in water. The apparent pK\(_a\) of the hydroxamic acids have been determined in the presence of gemini surfactants. The second order rate constant and binding constants for reactions were determined employing pseudophase model for micellar catalysis.

**CHAPTER-IV** describes the study of kinetics of reaction of hydrolysis of \(p\)-nitrophenyl acetate and \(p\)-nitrophenyl diphenyl phosphinate using Butane 2, 3-dione monoximate ion at pH 7.9 and 27\(^\circ\)C in alkyltriphenylphosphonium (C\(_{12}^-, C_{14}^-, C_{16}^-\)) bromide micellar media (Scheme-1.7).

\[
\begin{align*}
\text{\(p\)-nitrophenyl acetate} & \quad \text{\(p\)-nitrophenyl diphenyl phosphinate} \\
\begin{array}{c}
\text{H}_3\text{C} \quad \text{O} \\
\text{O} \quad \text{H}_3\text{C} \quad \text{O} \\
\text{O} \quad \text{O} \\
\end{array}
& \quad \begin{array}{c}
\text{C}_6\text{H}_5 \quad \text{O} \\
\text{C}_6\text{H}_5 \quad \text{O} \\
\text{O} \quad \text{O} \\
\end{array}

\text{\(\text{Nu}^- = CH_3-C-C-CH_3\)}

\text{Butane 2, 3-dione monoximate}

\text{Scheme-1.7}
\]
The rate-surfactant profiles are fitted quantitatively in terms of pseudo phase model (eq. 1.4),

$$
k_{\text{obs}} = \frac{k_2^w + \frac{k_2^m}{V}K_{m}^{\text{ESTER}}K_{m}^{\text{Ox}}[D_n]}{1 + K_{m}^{\text{ESTER}}[D_n]} \left(1 + K_{m}^{\text{Ox}}[D_n] \right)^{-1} \tag{1.4}
$$

where $k_2^w$ and $k_2^m$ is the second order rate constant in aqueous and micellar media respectively. The distribution of ester between the aqueous and micellar pseudophases is given by $K_{m}^{\text{ESTER}}$ and of oximate ion is $K_{m}^{\text{Ox}}$. Molar volume of the reaction media is denoted by $V$ and $D_n$ considered as micellized surfactant ($[D_n] = [D_T] - \text{cmc}$).

**Chapter V** deals with the study and synthesis of physicochemical properties of silver (Ag) nanoparticles by the nature of the used chemical reductors. The reported procedures describe the reduction of metal ions using hydroxamic acid and ascorbic acid individually. The influencing factors including cationic, anionic, zwitterionic and non-ionic surfactants and pH have also been investigated in detail. The nanoparticles were characterized by UV-visible absorption spectroscopy and transmission electron microscopy (TEM). The particle size depends on the pH of the reaction mixture.

**Chapter VI** is divided into two sections:

[A] Determination of $pK_a$ of different $\alpha$-nucleophiles in the presence of novel cationic surfactant and nonionic surfactant.

[B] Comparative nucleophilic reactivities in carboxylate and phosphate esters cleavage with different $\alpha$-nucleophiles.
In Section-A, the determination of acid dissociation constant \( (pK_a) \) have been determined spectrophotometrically by nucleophilic substitution reactions of \( p \)-nitrophenyl acetate with different \( \alpha \)-nucleophiles i.e. \( N \)-phenylbenzohydroxamic acid, butane 2,3-dione monoxide, 1-hydroxybenzotriazole and \( \alpha \)-iodosobenzoic acid at \( 27 \pm 0.1^\circ C \) in different pH ranging from 6 - 12 in aqueous and in the presence of novel cationic surfactant (cetyltriphenylphosphonium bromide) and nonionic surfactant (Triton X-100).

In Section-B, the study of kinetics of nucleophilic deacylation of \( p \)-nitrophenyl acetate and dephosphorylation of paraoxon, with these \( \alpha \)-nucleophiles have been determined spectrophotometrically at \( 27^\circ C \) in the presence of \([C_{16}-12-C_{16}],2Br^-\) gemini surfactants. Finally the nucleophilic reactivity of hydroxamate ions has been compared with other \( \alpha \)-nucleophiles, like oxime, 2-iodosobenzoic acid and hydroxybenzotriazole. The order of reactivity at different electrophilic centers i.e. \( C=O \) and \( P=O \) have also been discussed.

1.9 NEW TRENDS & FUTURE PERSPECTIVES

Fission of the phosphoester and carboxylic ester is involved in numerous chemical and biochemical reactions. The novelty of the work is to find out rapid method capable of deacylating the carboxylate and dephosphorylating the toxic organophosphorus esters. Novel catalysts that hydrolyze phosphoesters and carboxylic esters under mild conditions could have very broad applications across many fields such as organic synthesis, industrial process, environmental treatment and national defence. In particular, agents that promote the hydrolysis of
phosphoesters could be utilized for decontamination of environmental organophosphate pollutants. The catalytic cleavage of toxic esters using \( \alpha \)-nucleophiles in novel micellar medium shows enhanced reactivity. Despite the tremendous progress achieved in the area of gemini surfactants, there still remain significant limitations to develop and design novel gemini surfactants as a reaction media for kinetics of hydrolysis reactions. The study of micellization and interfacial properties of novel surfactants are expected to shed more light on the interpretation and quantification of the phenomena in the field of physicochemistry and thermodynamics. From the viewpoint of usability, stability and spontaneity of micelle formation, this type of investigation is essential. These make an ample scope for synthesizing new surfactants as well as modifying head group/tail/counter ions of existing surfactants and studying their solution properties with reference to applications. The investigation on the formation of silver nanoparticles using UV-vis spectroscopy shows that the silver colloids formed are nanosized, uniformly distributed and stable at least for two weeks. The reproducible preparation of small and stable nanoparticles with tight size distribution using a simple route is of immense importance and still remains a challenging task. With future advances in biotechnology and material science, we can expect a better system, which will not only play an integral role in defence industry, but in the agricultural, biomedical, food and chemical industries as well.
REFERENCES


Introduction


457.


